Three-dimensional optical beam lithography for functional photonic devices

A thesis submitted for the degree of

Doctor of Philosophy

by

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Melbourne, Australia

2013
Abstract

Three-dimensional (3D) optical beam lithography (OBL) based on far field focusing of light through a high numerical aperture (NA) objective lens is an ultimate approach to 3D nanofabrication. This laser direct writing based technique has become a widely implemented enabling technology to fabricate 3D structures in the micro or nano scale for a variety of applications. The ability of fabricating structures with an arbitrary 3D geometry in the micro or nano scale is the most important advantage of 3D OBL compared with other nanofabrication techniques such as electron-beam lithography (EBL), ion-beam lithography and maskless plasmonic lithography. This advantage makes 3D OBL a most promising fabrication technology to fabricate photonic devices with tuneable functions for different photonic applications. In this thesis, the investigation of 3D OBL is conducted as an advanced nanofabrication technology to fabricate functional photonic devices. Though it has been widely used to fabricate photonic devices such as photonic crystals (PCs) and metamaterials, there are still critical challenges for 3D OBL to become a fully competent technique for fabricating photonic devices with versatile photonic applications.

For photonic applications that rely on the local photonic environment such as spontaneous emission (SE) manipulation, 3D OBL should be able to support local structure designing induced photonic functions. To demonstrate this point, SE from emitters inside PCs fabricated by two-photon OBL is investigated experimentally and theoretically. To enable quantitative and accurate investigation of SE manipulation, a molecular linking method is developed to put SE emitters into the 3D PCs with controllable emitter quantity. The SE modification for emitters inside the PCs is measured and the experimental result is consistent with the theoretical expectation of the SE change determined by the photonic local density of states (LDOS). With 3D OBL, photonic devices with locally designed structures such as defects can be easily fabricated. After inducing a simple plane defect in the centre of a woodpile PC
fabricated by two-photon OBL, the photonic LDOS at the local position of the defect is found to be changed significantly. Significant SE enhancement is observed which is otherwise not available at the wavelength of the photonic band edge of a low refractive-index PC due to its pseudo-gap property. These results indicate the great potential of 3D OBL to fabricated functional photonic devices for photonic applications and particularly for SE manipulation applications.

The working wavelength range of the functional photonic devices fabricated by 3D OBL is limited by the fabrication resolution because of light diffraction. To remove the resolution limitation, a 3D diffraction-unlimited OBL technique based on the super-resolution photoinduced-inhibition nanolithography (SPIN) is developed with two-photon polymerisation and single-photon inhibition. To facilitate the development, simulation work based on a kinetic model is first carried out, which shows the great potential of two-beam photo-inhibition assisted OBL to break the diffraction limit for getting nanometre resolution. With the enlightenment from the simulation, a new photo-resin with two-photon initiator and single-photon inhibitor is developed with high photosensitivity, high structure mechanical strength and effective photo-inhibition effect. Three-dimensional diffraction-unlimited OBL with 9 nm feature size and 52 nm two-line resolution is realised based on this photo-resin. For this 3D diffraction-unlimited OBL, the linewidth and resolution, which decrease with the increasing of the photo-inhibition beam intensity satisfy the formula of \( \alpha_1 / \sqrt{1+\beta_1 \times I_{\text{inhibition}} / I_S} \) and \( \alpha_2 / \sqrt{1+\beta_2 \times I_{\text{inhibition}}^2 / I_S} \) respectively, at the nanometre scale and show the diffraction-unlimited property of this technique. It is the first time to show that OBL can break the diffraction limit to realise 3D fabrication with nanometre resolution, which can support the nanoscience and nanotechnology in three dimensions as well as fabricating functional photonic devices with shorter working wavelengths.

Although 3D OBL based on the top-down strategy is widely used to fabricate 3D photonic devices, it has requirements to the fabricated material. Longer excitation
wavelength and refractive-index mismatch hinder the achieving of high resolution and depth uniform structures for the fabrication of structures made by materials with a narrow electronic bandgap and a high refractive-index by 3D OBL. To enable 3D OBL to fabricate photonic devices made by materials with a narrow electronic bandgap and a high refractive-index and avoid the current problems, a bottom-up strategy based method is proposed. To demonstrate its feasibility, the fabrication of 3D structures made by PbSe as a typical example of narrow electronic bandgap and high refractive-index materials with two-photon OBL is shown. By dissolving Pb and Se elements in a photo-resin beforehand, laser irradiation of the photo-resin at the laser focal spot can instantly form PbSe and thus fabricate 3D PbSe structures. As the photo-resin can be excited by a wavelength of 580 nm via a two-photon process and has a refractive-index about 1.5, this bottom-up strategy based 3D OBL avoids the problems of single-photon absorption and refractive-index mismatch.

The work done in this thesis demonstrates the unique fabrication advantage of 3D OBL to fabricate arbitrary 3D structures which can induce local photonic functions effectively and overcome the most concerned challenges for 3D OBL to fabricated photonic devices for versatile photonic applications. The whole work is focused on 3D OBL as an advanced nanofabrication technology and contributes to a powerful platform to fabricate functional photonic devices and to support the investigation and application of photon manipulation.
Acknowledgements

In the September of 2008, after my graduation as a bachelor student in physics, I was searching for a Ph. D. position in photonics with an interest in the control of fluorescence emission. I actually found the Centre for Micro-Photonics (CMP) with the Google searching and send an email to Prof. Min Gu to have a try. It was this email that has profoundly and lastingly changed my academic career. To my surprise, Prof. Min Gu offered me a wonderful opportunity to undertake a Ph. D study at here. I would like to first give my sincerest gratitude to Prof. Min Gu for giving me the precious opportunity to conduct my Ph. D. project as I wished in this world-leading facility. During the past four years, I have truly enjoyed working in the CMP at the research directions of spontaneous emission (SE) control and optical beam lithography (OBL). The enthusiastic supervising from Prof. Min Gu with profound inspiration, far-reaching insights and patient guidance has greatly contributed to each of the step I have made during my Ph. D. This will continually contribute to any achievement I might make in my future career.

I would like to thank my co-supervisor, Dr. Baohua Jia. She helped me with her precious experimental skills and experience, useful suggestions and discussions. These help benefited the quick growing of me from a bachelor student to a Ph. D. candidate. I also would like to thank Dr. Yaoyu Cao. We have collaborated to develop the diffraction-unlimited OBL technique, which has become a most important part of this thesis. His essential contributions make this powerful technology become a reality. My thanks go to our collaborators Dr. Jingfeng Liu and Prof. Xuehua Wang from the Sun Yat-sen University in China for their essential contributions on the theoretical investigation of local density of states in photonic crystals. I would like to thank Dr. Xiaosong Gan, Dr. Dru Morish and Dr. Michal James Ventura for the Ph. D. organizing, equipment trainings, laboratory managements and laboratory establishment. Thanks very much to Dr. Joel van Embden for his training and help in
quantum dots synthesis. Thanks to Dr. Betty Kouskousis and Dr. Ye Chen for their help in operation and training of the fluorescence imaging measurement system. I also want to thank Dr. Xiangping Li for his help in the fluorescence spectrum measurement and his beneficial discussion on the stimulated emission depletion microscopy technology. Thank Mr. Mark Kivinen as he made many custom required opto-mechanical components for me. Thank James Wang from the Centre for Atom Optics and Ultrafast Spectroscopy in the Swinburne University of Technology for his help in the scanning electron microscopy measurement with experience and patient.

Thank all the members in the Centre for Ultrahigh-bandwidth Devices for Optical Systems (CUDOS) group in the CMP for the discussions and help during my PhD study. Thanks especially go to the former CMP Ph. D. student, Dr. Jiafang Li, for his help on equipment training of the laser fabrication system and lifetime measurement system. To other CUDOS students (Dr. Mark D. Tuner, Dr. MD Muntasir Hossain, Dr. Elisa Nicoletti, Mr. Han Lin, Mr. Benjamin Cumming and Mr. John He), I thank them for sharing their valuable experience and knowledge.

I would like to thank the administrative staff members Ms. Johanna Lamborn, Ms. Barbara Gillespie and Ms. Jia Lou for their contribution with the general student work during my PhD study. To other CMP members, Dr. Hongchun Bao, Dr. Jing Li, Dr. Xingyu Gao, Mr. Adam Taylor, Dr. Qiming Zhang, Dr. Jingzhi Wu and Dr. Guangyong Zhou, I thank them for their help and discussion in academic with varieties of topics. I would also like to express my acknowledgement to the Swinburne University of Technology and the CMP for providing me a scholarship to support my Ph.D. study.

Finally, I would like to acknowledge the encouragement from my family to finish my Ph.D. To my extraordinary wife, Qi, I give my deepest gratitude to her for the great support and understanding of my work.

Zongsong Gan

Melbourne, Australia, On June 17th, 2013
Declaration

I, Zongsong Gan, declare that this thesis entitled:

“Three-dimensional optical beam lithography for functional photonic devices”

is my own work and has not been submitted previously, in whole or in part, in respect of any other academic award.

The original data of figure 3.14 has been provided by Dr. Jingfeng Liu and Prof. Xuehua Wang.

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Dated this day, 17 June 2013
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<tr>
<td>PC</td>
<td>photonic crystal</td>
</tr>
<tr>
<td>3D</td>
<td>three-dimensional</td>
</tr>
<tr>
<td>OBL</td>
<td>optical beam lithography</td>
</tr>
<tr>
<td>2D</td>
<td>two-dimensional</td>
</tr>
<tr>
<td>SE</td>
<td>spontaneous emission</td>
</tr>
<tr>
<td>2PP</td>
<td>two-photon polymerisation</td>
</tr>
<tr>
<td>fs</td>
<td>femtosecond</td>
</tr>
<tr>
<td>NA</td>
<td>numerical aperture</td>
</tr>
<tr>
<td>LDOS</td>
<td>local density of states</td>
</tr>
<tr>
<td>QD</td>
<td>quantum dot</td>
</tr>
<tr>
<td>SPIN</td>
<td>super-resolution photoinduced-inhibition nanolithography</td>
</tr>
<tr>
<td>1BZ</td>
<td>the first Brillouin zone</td>
</tr>
<tr>
<td>UV</td>
<td>ultra-violet</td>
</tr>
<tr>
<td>EBL</td>
<td>electron beam lithography</td>
</tr>
<tr>
<td>CPU</td>
<td>centre processing unit</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>CCD</td>
<td>charge-coupled device</td>
</tr>
<tr>
<td>STED</td>
<td>stimulated emission depletion</td>
</tr>
<tr>
<td>DLW</td>
<td>direct laser writing</td>
</tr>
<tr>
<td>OPO</td>
<td>optical parametric oscillator</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-transform infrared</td>
</tr>
<tr>
<td>ODE</td>
<td>1-octadecene</td>
</tr>
<tr>
<td>NIR</td>
<td>near infrared</td>
</tr>
<tr>
<td>APTES</td>
<td>3-aminopropyltriethoxysilane</td>
</tr>
<tr>
<td>TCSPC</td>
<td>time-correlated single photon counting</td>
</tr>
<tr>
<td>PMT</td>
<td>photomultiplier</td>
</tr>
<tr>
<td>TED</td>
<td>tetraethylthiuram disulfide</td>
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CW: continuous wave
BDEP: bis(4-(dimethylamino) phenyl)methanone
BDMA: 2,5-bis-[4-(dimethylamino)benzylidene]cyclopentanone
BDCC: 2,5-bis(p-dimethylamino cinnamylidene) cyclopentanone
EDAB: ethyl 4-(dimethylamino)benzoate
CQ: camphorquinone
DM: dichroic mirror
FWHM: full width at the half maximum
PbOA: lead oleate
TOPSe: Se dissolves in trioctylphosphine
TOP: trioctylphosphine
EDS: energy dispersive spectrum
HRTEM: high resolution transmission electron microscopy
Chapter 1

Introduction

The ability for human beings to manipulate electrons is one of the most important prerequisites for the development of science and technology in the past few decades. Now the manipulation of photons is highly pursued by human beings as photons are thought to have advantages and greater potential than electrons to perform various functions as information carrier. Different from an electron, a photon is massless, has no electrical charge and can move as fast as the speed of light. Because of these intrinsic properties, photons are delicate to be manipulated.

With an aim to manipulate photons including their emission, propagation and interaction with materials, different photonic devices have been developed and used to realise different functions. These functional photonic devices provide the essential powerful tools and platforms to manipulate photons according to the wishes of the people. The unique functions of the photonic devices generally come from two aspects. One is the unique intrinsic properties of the material that the devices are made of. Different intrinsic properties of the material correspond to different functions of the photonic devices. For example, the material of the photonic device which has a higher third-order nonlinear refractive-index can enable the device having stronger third-order nonlinear effect [1]. The other aspect is the material geometrical configuration of the photonic devices. For example, a photonic crystal (PC) can be used to control photon propagation when photons go through it [2]. For photons with different energies, their propagation in different directions inside a PC can be tuned
by the PC structure parameters. Functional photonic devices can be built with a PC based on its ability to control photon propagation such as a super-prism [3].

An efficient way to fabricate photonic devices with different materials and material geometrical configurations for different functions is obviously important for the purse of manipulating photons effectively. The development of advanced fabrication technologies to fabricated versatile functional photonic devices supports the studying, understanding and manipulating of photons with essential tools and directly contributes to a range of applications from fundamental optical science to everyday-used technologies.

For the fabrication of functional photonic devices, though it has been a challenge for a long time, a fabrication technique with the following advantages is highly favoured: a high fabrication resolution, a three-dimensional (3D) arbitrary fabrication ability, suitable for different materials and avoiding complex and high cost fabrication systems.. As 3D optical beam lithography (OBL) such as two-photon polymerisation (2PP) [4, 5] has the distinguished advantage for fabricating 3D photonic devices of arbitrary geometry with a resolution higher than the wavelength of the used laser, functional photonic devices fabricated by 3D OBL shows a promising potential as powerful tools and platforms for photon manipulation [6, 7, 8]. For the wide and profound impact of photon manipulation in optical science and technology, we have enough reasons to believe that these functional photonic devices fabricated by 3D OBL can become an essential part for a life supported by photonic technologies in the coming future.

In this chapter, a basic introduction to 3D OBL for fabricating functional photonic devices is given. The main challenges of 3D OBL for the fabrication of functional photonic devices are described. The objectives of this thesis are presented and the arrangement of this thesis is summarised.
1.1 Functional photonic device fabrication with three-dimensional optical beam lithography

Three-dimensional photonic devices such as PCs [6, 8] and metamaterials [7, 9] have their unique advantage to manipulate photons because of their ability to tame light in three dimensions [10, 11]. Two-dimensional (2D) ones can also be used to manipulate photons; however, the effect of the manipulation is limited due to the unutilised third dimension. For example, when 2D PCs are used to manipulate photon emission, it is impossible to realise complete spontaneous (photon) emission (SE) suppression due to the unblocked SE in the third dimension [12]. Complete SE suppression is thought to have potentially important applications. For example, to enable two-entangled-photon emission [13] between two energy levels, the one-photon emission needs to be suppressed as much as possible to avoid depopulation by one-photon emission as two-entangled-photon emission is normally a weak phenomenon. Although there are many good methods to fabricate 2D functional photonic devices, for better photon manipulation performance, only those methods having the feature to fabricate 3D functional photonic devices are of the interest of this thesis.

Three-dimensional OBL is an advanced 3D fabrication technology based on laser direct writing to fabricate 3D micro or nano scale structures. For this technology, light is focused into an optical transparent material by an objective lens and the light focal spot is used to write the wanted structure. A selective etching process is required to remove the unexposed material to reveal the fabricated structure. The focusing of light into a transparent material enables the possibility of 3D writing. The used material should have no single-photon absorption of the light beam. The high intensity light in the laser focal spot can induce the material property difference in the focal volume via a multi-photon process and create the 3D lithography process. As the
lithography process is confined in the focal volume due to the multi-photon process, 3D OBL has its unique advantage of fabrication flexibility that provides the convenience to fabricate 3D functional photonic devices with arbitrary geometry. The manipulation of photons with functions coming from the structure geometry can be well supported by 3D OBL.

**Figure 1.1** (a) Schematic of 3D OBL via 2PP. (b) Polymer freestanding structures fabricated by the two-photon OBL with 2PP. The scale bar is 200 nm.

Two-photon polymerisation [4, 5, 6] is a commonly used 3D OBL technique to fabricate 3D low refractive-index polymer photonic devices with sub-micron resolution. For 2PP (Fig. 1.1a), a femtosecond (fs) pulsed laser beam is focused into the photo-resin by a high numerical aperture (NA) objective lens. The photo-resin absorbs the photo-energy and initiates the polymerisation. As light absorption of the photo-resin at the focal spot is a two-photon absorption process, the polymerisation occurs only within the focal volume of the laser beam [4, 5, 6]. By moving the focal spot in a 3D space, arbitrary 3D structures can be fabricated. As two-photon process rather than single-photon process is used, 2PP provides the ability of fabricating 3D arbitrary structures (Fig. 1.1b) with a resolution higher than that of single-photon polymerisation with light at the same wavelength and size down to tens of nanometres.
(Fig. 1.1b). When this 3D OBL technology is used to fabricate functional photonic devices, the fabricated functional photonic devices can have the working wavelength at the infrared or near infrared wavelength range [6]. Figure 1.1b shows two suspended X-shape structures at different layers fabricated by 2PP that demonstrates the 3D fabrication ability with high resolution of 2PP.

1.2 Challenges of three-dimensional optical beam lithography for functional photonic devices

For a fabrication technology that can support the fabrication of different 3D photonic devices having versatile functions for a variety of photonic applications with full competency, the following abilities are precious:

- It can fabricate 3D structures with designed geometries to enable the fabricated photonic devices to fully exhibit photonic functions originated from the structure geometry.

- It can fabricate structures with a high spatial resolution to enable the fabricated photonic devices working at a wide wavelength range.

- It can fabricate structures made by different kinds of materials with different intrinsic properties.

With the state-of-the-art 3D OBL method, 3D functional photonic devices made by materials with different refractive-indices and with working wavelengths ranging from the microwave to the near infrared wavelength range [6] have been realised. However, to serve as a solid and powerful platform for the fabrication of functional photonic devices, there are several critical challenges for 3D OBL.
First, for some of the photonic applications, for example, by utilising the photonic stopgap of a PC to control the photon propagation inside the PC, the fabrication technique is required to have the convenience to fabricate periodic structures. These periodic structures have been widely fabricated by 3D OBL as it allows easy fabrication with a resolution comparable to the wavelength of the used light [4, 5, 6]. However, for a number of photonic applications that rely on the local photonic environment such as the spontaneous emission (SE) manipulation, the fabrication technique is required to have the convenience to design the local structure geometry flexibly. Spontaneous emission from emitters inside a photonic device is highly dependent on the photonic local density of states (LDOS) at the position where an emitter is located [14, 15]. Because of this, the manipulation of SE requires the functional photonic device having designed photonic LDOS. Three-dimensional OBL has the unparalleled ability to fabricate photonic devices with arbitrary geometrical configuration and thus can tune the photonic LDOS with different structure configurations. When a photonic device, i.e. a PC, is used to manipulate the SE, a local structure such as a defect is a key component as it is thought to be able to change the LDOS significantly. A defect as a typical example of local structures can be easily induced into a photonic device fabricated by 3D OBL such as 2PP. However, it is yet to be demonstrated that the defect induced by 3D OBL can be used to control the SE effectively.

Then, functional photonic devices fabricated by 3D OBL have the limitation of the working wavelength range. As 3D OBL uses light to do the fabrication, the fabrication resolution is limited due to the diffraction nature of light [16-19]. Though the multi-photon process in OBL has been used to achieve sub-diffraction resolution [4-6], it is challenged to get resolution below 200 nm because the resolution is still limited by diffraction. For the fabrication of PCs with a woodpile geometry, this means that the line centre-to-centre distance is limited by the diffraction of the used light. As a result, it is challenging to fabricate a PC with a photonic stopgap at a
wavelength, such as green and blue light wavelength for a light source with commercially available wavelengths suitable for 3D OBL. Working wavelengths at the visible and UV ranges are important for a plenty of photon manipulation applications. A lot of the light involved technologies work at the visible wavelength range. Thus, how to improve the fabrication resolution to extend the working wavelength range of the fabricated functional photonic devices is an important problem need to be solved for functional photonic devices fabricated by 3D OBL.

Finally, the fabrication of depth uniformity unaffected 3D photonic devices made by materials having a narrow electronic bandgap [20] and a high refractive-index by 3D OBL is a challenge. Materials with a narrow electronic bandgap and a high refractive-index can enable the functional photonic devices with unique functions which are unavailable for materials with a wide electronic bandgap and a low refractive-index. The development of 3D OBL to fabricate 3D photonic devices made by narrow electronic bandgap and high refractive-index materials with high resolution and depth unaffected uniformity is of great meaningful for functional photonic devices with better and new effects.

1.3 Thesis objective and thesis preview

The objective of this thesis is to study 3D OBL as an advanced fabrication technology to fabricate functional photonic devices. To support the objective, this thesis consists from three main pillars. First, a demonstration of 3D OBL with fabricated 3D photonic devices which support local structure designing induced functions, i.e. SE manipulation, can indicate the great promising of 3D OBL for functional photonic devices. Then, to extend the working wavelength range of the fabricated functional photonic devices, 3D diffraction-unlimited OBL needs to be developed. The third, to
enable functional photonic devices with better performance and to facilitate diverse property requirements for device applications, 3D OBL of photonic devices made by materials with a narrow electronic bandgap and a high refractive-index which is challenged for the currently developed 3D OBL is pursued. The whole work is done to provide photonic applications with a fabrication technique having an unparalleled fabrication ability. For these aims, the studies have been conducted in the following aspects.

Chapter 2 reviews the current progress of 3D OBL to fabricate functional photonic devices for photonic applications, which serves as an introduction to the foundation of this thesis. Sec. 2.2 introduces the photonic LDOS theory for the understanding of the SE control in Chapter 3. Several general used techniques to fabricate 3D photonic structures are compared in Sec. 2.2.2. Sec. 2.3 reviews the current research status of OBL to break the diffraction barrier. The progress of 3D OBL to fabricate structures made by materials with different electronic bandgaps and high refractive-index is given in Sec. 2.4.

To indicate the great promising of 3D OBL to fabricate functional photonic devices for photonic applications and particularly for the SE manipulation applications, SE control with PCs as a functional photonic device fabricated by two-photon OBL is selected as the studying objective in Chapter 3. By fabricating PCs with a designed local geometrical configuration such as a locally induced defect by 2PP, the SE is expected to be manipulated according to the structure designing. Sec. 3.2 presents the preparation of samples including the fabrication of PCs by two-photon OBL, synthesising of semiconductor quantum dots (QDs) as a SE source and integration of the QDs into the PCs to transform the PCs to SE controlled devices. Sec. 3.3 investigates the photonic LDOS property of SE manipulation by PCs in experiment as well as in theory. Sec. 3.4 demonstrates the changing of photonic LDOS due to a locally induced plane defect, which can significantly enhancing the SE of the locally
located emitters. The ability of the fabricated photonic structures to both suppress and enhance the SE shows the great promising of 3D OBL as an essential tool for functional photonic device fabrication.

As the resolution of 3D OBL is limited by the diffraction nature of light, the working wavelength range of the fabricated photonic devices that is available to manipulate photons is hence limited. To solve this problem, a 3D diffraction-unlimited OBL technique needs to be developed in order to break the diffraction barrier. Super-resolution photoinduced-inhibition nanolithography (SPIN) [21, 22] is adopted with two-photon polymerisation and single-photon inhibition to realise the 3D diffraction-unlimited OBL. This 3D OBL technique is called diffraction-unlimited because the fabrication resolution is no longer constrained by the diffraction limit of the far field optical system though it is limited by the properties of the material. Chapter 4 introduces the theoretical work done on SPIN. A theoretical model to simulate SPIN is established in this chapter to provide the important information needed for the development of a suitable photo-resin. Chapter 5 presents the experimental work done with SPIN with two-photon polymerisation and single-photon inhibition to achieve 3D diffraction-unlimited OBL. With the knowledge obtained from chapter 4, a new photo-resin is developed. The development of a new photo-resin is introduced in Sec. 5.2. Feature size reduction and resolution improvement of SPIN with the new photo-resin are stated in Sec. 5.3 and Sec. 5.4, with the achievement of 9 nm minimum feature size and 52 nm best two line resolution respectively. The currently achieved smallest feature size and highest resolution for 3D OBL can well support the extension of the working wavelength range and the integration of more compact components for functional photonic devices.

To fabricate 3D photonic devices made by narrow electronic bandgap and high refractive-index materials with 3D OBL, a method based on the bottom-up strategy is
developed in this thesis. This bottom-up strategy method enables the fabrication of narrow electronic bandgap and high refractive-index material structures in a solution rather than in a bulk solid. Chapter 6 present the fabrication of 3D structures made by PbSe as a typical material with a narrow electronic bandgap and a high refractive-index by 3D OBL with the bottom-up strategy. Sec. 6.2 describes the challenges for 3D OBL to fabricate 3D structures made by PbSe with the top-down strategy. Sec. 6.3 introduces the preparation of a new photo-resin for the fabrication of 3D PbSe structures with 3D OBL based on the bottom-up strategy. Sec. 6.4 presents the fabrication results. The extension of 3D OBL to the fabrication of photonic structures made by narrow electronic bandgap and high refractive-index materials confirms the importance of 3D OBL as an essential tool for functional photonic device fabrication.

In Chapter 7, a summary of this thesis is given and the future work is discussed. Sec. 7.2.1 proposes the study of SE manipulation at the visible wavelength range with photonic devices fabricated by the 3D diffraction-unlimited OBL. Sec. 7.2.2 suggests the possible methods to achieve super-resolution 3D OBL for the fabrication of 3D structures made by high refractive-index materials with different electronic bandgaps.
Chapter 2

Review

2.1 Introduction

Before the discussion of what has been done in this thesis to demonstrate the arbitrary three-dimensional (3D) fabrication ability to fabricate functional photonic devices with local structure geometry supported functions by 3D optical beam lithography (OBL) and to remove the fabrication limitations of 3D OBL to device applications, a review of the-state-of-the-art is necessary for better understanding the background, motivation and novelty of this thesis. In Sec. 2.2, the progress of spontaneous emission (SE) manipulation with functional photonic devices, i.e. photonic crystals (PCs), is reviewed including its physical foundation and device requirements. As the SE manipulation with a photonic device is depended on the photonic local density of states (LDOS) [14, 15], the theoretical calculation of the LDOS is introduced. Different fabrication methods to fabricate 3D photonic devices are outlined. Sec. 2.3 and Sec. 2.4 review two of the most important aspects to improve the 3D OBL fabrication ability. One is super-resolution OBL to extend the working wavelength range of the functional photonic devices fabricated by diffraction-limited OBL (Sec. 2.3) and the other is 3D OBL to fabricated 3D functional photonic devices made by materials with a narrow electronic bandgap and a high refractive-index (Sec. 2.4).
2.2 Spontaneous emission manipulation by local density of states in photonic devices

2.2.1 Local density of states in photonic devices

Since the pioneering work of Yablonovitch [23] and John [24], people have recognised that SE is the result of the interacting of an emitter with its radiation field, and thus SE can be controlled by controlling the surrounding photonic environment of the emitter. The rate for the emitter to emit photons is determined by the LDOS of the electromagnetic field at the position where the emitter is located [14, 15]. The photonic LDOS is used to characterise the density of the local electromagnetic field mode, which corresponds to the local density of the virtual photon generated by the radiation field. Consequently, it is feasible to manipulate the interaction between emitters and the radiation field by enhancing or decreasing the corresponding photonic LDOS and hence manipulate the SE.

Before an accurate theoretical investigation of the SE in photonic devices, dispersion models considering the isotropic or anisotropic property of light propagation in photonic devices were used to interpret the vacuum fluctuation modification induced SE modification phenomenon [25-27]. Wang et al. [14, 15] and Li et al. [28] proposed a full vector model within the framework of quantum electrodynamics between 2000 and 2003. This model considers the basic interaction of an emitter with the electromagnetic field and thus gives a good explanation of the SE control in the experiments. The theory of this model is now known as the “LDOS theory” [29, 30].
Consider the SE of a two energy level emitter transiting from its up energy level to its down energy level with a transition frequency $\omega$ and locating at the position of $r$ in a photonic device, i.e. a PC, the SE decay lifetime of the emitter at the position $r$ is the reciprocal of the SE decay rate $\Gamma(d, r, \omega)$, where $\Gamma(d, r, \omega)$ can be written as [29, 30]

$$\Gamma(d, r, \omega) = \frac{\pi \omega d^2}{\varepsilon_0 \hbar} \sum_{nk} \left| \vec{d} \cdot \vec{E}_{nk}(r) \right|^2 \delta(\omega - \omega_{nk}),$$

(2.1)

where $\vec{d}$ is the unit vector of the emitter’s transition dipole moment between the two energy levels and $d$ is the magnitude of the transition dipole moment. $\{\omega_{nk}, \vec{E}_{nk}(r)\}$ are the frequency and the electric field of the radiation electromagnetic eigenmodes in the photonic device which can generally be mathematically solved by the plane-wave expansion method for a PC. The subscript $n$ is the band index; $k$ is the wave vector; $\hbar$ is the reduced Plank constant; and $\varepsilon_0$ is the vacuum permittivity. The dot symbol of $\vec{d} \cdot \vec{E}_{nk}(r)$ presents the dot product of two vectors.

Define the general projected photonic LDOS as [29, 30]

$$\rho(d, r, \omega) = \frac{\omega d^2}{2\hbar \varepsilon_0} \sum_{nk} \left| \vec{d} \cdot \vec{E}_{nk}(r) \right|^2 \delta(\omega - \omega_{nk}),$$

(2.2)

then

$$\Gamma(d, r, \omega) = 2\pi \rho(d, r, \omega) = 1/\tau.$$  

(2.3)

When the emitter has a random orientation of the transition dipole moment, the SE decay rate can be obtained as [29, 30]

$$\Gamma(r, \omega) = \frac{\pi \omega d^2}{3\hbar \varepsilon_0} \sum_{nk} \left| E_{nk}(r) \right|^2 \delta(\omega - \omega_{nk}) = I(\omega)\rho(r, \omega).$$

(2.4)
Here, $\Gamma(r, \omega)$ has been separated into two parts: factor $I(\omega) = d^2 \omega / (6\hbar \varepsilon_0)$, which is the contribution of the transition dipole moment of the emitter and the LDOS [29, 30]

$$\rho(r, \omega) = \sum_{nk} |E_{nk}(r)|^2 \delta(\omega - \omega_{nk}) = \frac{1}{(2\pi)^3} \sum_n \int_{1BZ} d^3 k \delta(\omega - \omega_{nk}) |E_{nk}(r)|^2,$$  

which reflects the special properties of the PC. 1BZ is the first Brillouin zone which is the integral region of the wave vector $k$.

From the equations (2.1) to (2.5), we know that the SE decay rate of a two-level emitter in a PC is dependent on the transition dipole moment, the transition frequency of the emitter itself and the photonic LDOS of the PC at the position where the emitter is located. From equations (2.3) and (2.5), the numerical calculation of the SE decay rate of an emitter in a PC is challenging due to its complexity. The 3D integration of the electric field in the 1BZ is required to be calculated accurately to show the position dependent property of the LDOS. This means that the calculation is time consuming for accurate results. Finding an appropriate method to simplify the numerical calculation is an important issue for the theoretical investigation of SE manipulation with a PC.

In 2003, Wang et al. used a transform method to simplify the LDOS calculation [29]. The transform method applies the transformation of the electric fields in the PC between real-space position points and reciprocal wave vector points based on the lattice-point group operation. Therefore, this method avoids the integration over the full 1BZ zone. Based on this method, Liu et al. investigated the SE decay lifetime of emitters in a woodpile PC [31] and show the property of position, emission frequency and dipole orientation dependence of SE decay lifetime for emitters in the PC. In this work [31], for a woodpile PC with a refractive-index contrast as low as 1.55, the lifetime of emitters inside the PC has a wide distribution. The SE decay lifetime distribution of emitters inside the PC has the same symmetry as that of the unit cell.
[31]. It is found in the work of Liu et al. [31] that the SE lifetime of emitters in a PC is determined by all the electromagnetic field modes in all directions but not by the electromagnetic field modes along a certain direction.

As the transition dipole moment orientation of an emitter is not randomly distributed in many cases, the investigation of orientation dependent LDOS has the real meaning for SE manipulation applications. However, the orientation dependent LDOS breaks the symmetry of the SE decay lifetime distribution in a unit cell and makes the integration can be reduced to only half of the unit cell. Liu et al. developed a point group transform method, which can significantly simplify the orientation dependent LDOS calculation [32]. With this method, the orientation dependent LDOS in PCs has been investigated and shows an up to 15.4 folds of the orientation dependent LDOS difference for an emitter inside a PC with different polarisation orientation directions [32]. These solid theoretical works done on the LDOS build up the fundamental theoretical frame for SE manipulation with photonic devices.

2.2.2 Spontaneous emission manipulation with photonic devices

From Sec. 2.1.1, for a given emitter with a defined transition dipole moment and transition frequency, the core concept of SE manipulation with a photonic device is to control the photonic LDOS of the device at the position where the emitter is located. The photonic LDOS in a photonic device such as a PC is determined by the material properties of the structure such as the refractive-index and the structure geometrical parameters. For a given material of the structure, different structure geometrical parameters can give out different photonic LDOS. Thus, by changing the structure geometry, the SE inside the photonic devices can be changed, which gives the basic way to manipulate SE. For photonic devices to manipulate the SE of an emitter, the
used method to fabricate the photonic devices should have the ability to fabricate arbitrary structure geometries to allow the photonic devices have designed structure geometry. With a designed structure geometrical configuration to obtain a designed photonic LDOS, versatile functions for SE manipulation can be realised. Because of this, SE manipulation with photonic devices fabricated by 3D OBL is selected as the studying objective to demonstrate the arbitrary structure geometry designing ability of 3D OBL for designable photonic functions.

Figure 2.1 (a) Schematic of a 3D woodpile PC. (b) The 1BZ of the wood PC with a face-centred-cubic lattice in the reciprocal space. (c) The calculated band diagram of the woodpile PC, the vector points correspond to the labelled high symmetry points in (b). The grey area indicates the existence of a photonic bandgap when the refractive-index of the PC material is 3.17. (d) Schematic of SE control with PCs.

For a PC, for example a woodpile PC (Fig. 2.1 a), light with a specific frequency is forbidden to propagate along certain directions and the forbidden frequency range in a
certain direction is called the stopgap. The photonic LDOS can be decreased for wavelengths within the photonic stopgap [8] and be enhanced at some other wavelengths such as the photonic band edge [33, 34]. A longer SE decay lifetime is expected for a decreased photonic LDOS and conversely a shorter SE decay lifetime corresponds to an increased photonic LDOS. When the material of the PC has a high enough refractive-index contrast, light could not propagate along any direction of the PC and the frequency range in this situation is called a photonic bandgap [35, 36] (as shown in Fig. 2.1b and Fig. 2.1c). For this situation, if the emission wavelength of the emitter is coupled to the photonic bandgap, the emission of the emitter is completely forbidden (Fig. 2.1d) as the photonic LDOS of the PC is zero. When the material of the photonic device is given, by tuning the structure geometrical parameters such as inducing defects, the photonic LDOS of a PC can also be tuned. For example, if the emission wavelength of the emitter is coupled to a defect mode of a PC (Fig. 2.1d), as the defect mode can significantly increase the photonic LDOS at the emitter’s local position, the photon emission of the emitter can be greatly enhanced [37].

Since the first observation of inhibited SE of dye molecules in an ordered suspension of polystyrene sphere beads by Martorell [38], even though the reliability of this experiment is doubted because of unequally designed references, there has been a variety of experimental reports on the influence of PCs to the SE of internal emitters. These include the spectral redistribution [39, 40], the SE decay lifetime change [41] and the detection angle dependent of the SE decay [42]. In 2004, Lodahl et al. [43] demonstrated both the inhibition and enhancement of the SE from CdSe/ZnSe core-shell quantum dots (QDs) in 3D inverse opal PCs. A 30% longer and 40% shorter SE decay lifetime were observed in this demonstration from these CdSe/ZnSe QDs imbedded in the PCs with different lattice parameters. This experiment result indicates the full possibility and feasibility of SE control with PCs by modifying the structure geometrical parameters such as lattice constants.
Although there are varieties of experimental reports on the inhibition or enhancement of SE for internal emitters in colloidal PCs and polystyrene opals [43-46], these PC structures are intrinsically challenged for controllable structure design, flexible structure geometry and potential functionality, which prevents them from device and chip based device applications with designed LDOS by designed local structure geometries. To fabricate 3D functional photonic devices such as 3D PCs with the working wavelength ranging from the microwave [57] to the visible [48] or even to the ultra-violet (UV) wavelength ranges [49], different techniques have been developed by scientists and engineers from various disciplines. To judge whether a fabrication method is suitable for 3D functional photonic device fabrication for versatile photon manipulation applications, mostly the following issues are important. The method should be easily used to fabricate arbitrary 3D photonic structures. The method is supposed to have the ability to realise high fabrication resolution and the method can be easily used to fabricate photonic structures with different kinds of materials having different intrinsic properties. Based on these considerations, in Table 1.1, four commonly used 3D fabrication methods are listed with their advantages and disadvantages.

The layer-by-layer lithography [35, 50] method takes all the advantages of 2D photonic structure fabrication techniques. Using this method, a 2D layer is firstly fabricated. Then another 2D layer is fabricated and stacked to the first layer in a certain direction. This process is repeated to form the layer-by-layer 3D photonic structure. As the 2D fabrication method can be used to fabricate each layer of the layer-by-layer 3D structure, the 2D layer made with different kinds of materials can be fabricated by the high-resolution fabrication methods such as electron beam lithography (EBL) with resolution smaller than 100 nm. In addition, different kinds of materials can be fabricated with this method. However, the accurate stacking process makes this method complicated to operate and the cost of this method becomes an important issue for its application.
Table 2.1 A comparison of four commonly used 3D fabrication techniques.

<table>
<thead>
<tr>
<th>Method</th>
<th>3D designable fabrication ability</th>
<th>Fabrication resolution</th>
<th>Suitable material diversity</th>
<th>System comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer-by-layer lithography</td>
<td>Yes, but not arbitrary structure</td>
<td>Below 100 nm</td>
<td>Excellent</td>
<td>High cost and high complexity</td>
</tr>
<tr>
<td>Self-assembly of colloid spheres</td>
<td>Yes, but not arbitrary structure</td>
<td>Down to several nanometers</td>
<td>Good</td>
<td>Low cost for large scale easy fabrication</td>
</tr>
<tr>
<td>Interference lithography</td>
<td>Yes, but not arbitrary structure</td>
<td>Diffraction-limited</td>
<td>Limited</td>
<td>Low cost and easy fabrication</td>
</tr>
<tr>
<td>Two-photon OBL via laser direct writing</td>
<td>Yes, capable of 3D arbitrary fabrication</td>
<td>Diffraction-limited</td>
<td>Limited</td>
<td>Low cost and easy fabrication</td>
</tr>
</tbody>
</table>

Self-assembly of colloidal suspended micron or nano scale spheres can also be used to fabricate 3D functional photonic devices [48, 51]. This self-assembly method is based on the local interactions of the assembly components. The local interactions of the colloidal micron or nano scale spheres suspended in a solution organise the spheres to form an ordered structure or pattern. This method can fabricate 3D functional photonic devices with periodic geometrical configuration at a scale of centimetres. The resolution of this method is defined by the self-assembly building component and thus has theoretically nanometre resolution. In addition, the self-assembly building component can be made by different kinds of materials. However, this method does not have the convenience for arbitrary 3D photonic structure fabrication and does not allow easy structure design, such as defect design.

The interference lithography [52, 53] method also has the ability to fabricate large scale 3D PCs. The basic principle of this method is to use two or more coherent light beams to generate an interference pattern and record this pattern into a material. As light is used to fabricate, the resolution of this method is limited by light diffraction.
Chapter 2

The interference pattern designing to fabricate an arbitrary 3D structure is much more complex than that of regularly geometrical structure. This disadvantage makes this interference lithography method not suitable for fabricating of 3D PCs with designed defects.

Three-dimensional OBL offers an unparalleled flexibility to fabricate high quality and sophisticated 3D photonic devices with controllable structure geometrical configurations [4-6]. It provides the fabricated photonic device with the ability of designable local optical properties including the photonic LDOS and thus supports the photonic applications with a most powerful tool. More importantly, the photonic devices fabricated by 3D OBL can be easily incorporated with functional materials, such as QDs [8, 54, 55], transforming the fabricated PC into a unique active platform for diverse photonic applications.

2.3 Diffraction-unlimited optical beam lithography

Light with the wavelength of several hundreds of nanometres provides human beings with a tool of sub-micron precision. Photolithography has been long-term developed since the beginning of using light as a tool to do fabrication and manufacturing. It has broad applications in nanoscience and nanotechnology and becomes one of the leading manufacturing technologies in micro and nano-electronics, which supports the blooming of the information technology.

Since the emerging of the laser devices in the last century, a laser has been used as a high precision tool in different scientific and technological fields due to its unique property as a powerful light source. In the current age of nanometre, the pursuing of tools with precision targeting the nanometre range (1-100 nm) boosts quickly.
However, because of the precision limitation of light, technologies which have been developed to achieve nanometre resolution base on light are rare compared with technologies based on electron, x-ray and so on.

The awareness of the precision limitation of light for human beings arises at the time as early as the 19th century. When Ernst Abbe investigated the imaging resolution of a microscope, he found the resolution of the microscope for distinguishing two objectives was basically limited by a simple formula: $\frac{\lambda}{2NA}$, where $\lambda$ is the wavelength of the used light and NA is the numerical aperture of the objective lens used in the microscope system. This limitation comes from the fundamental property of light as an electromagnetic wave. This fundamental property of light is described as diffraction which is a universal property for waves (Fig. 2.2). It is disappointed for people to understand that the physical principle behind the diffraction limit is the well-known wave-particle duality which is the foundation of quantum physics (Fig. 2.2). This means any attempt to break the diffraction limit at the physical principle level would not work at the current framework of quantum physics. However, the knowledge we know from the diffraction limit sheds light on the development of high resolution optical technologies.

![Light single slit diffraction](image)

**Figure 2.2** Light single slit diffraction as an example for the demonstration of uncertainty principle. $L$ is the slit width and $n$ is the refractive-index.
A simple way in theory to improve the resolution is to use short De Broglie wavelength sources such as UV light, x-ray and electron. For example, using extreme UV light to do lithography, Intel can manufacture a centre processing unit (CPU) with 22 nm resolution [56] which has already become the goods on the shelf of an e-shop. However, the huge cost for Inte to develop its 22 nm technology for CPU fabrication suggests the great difficulty of resolution improving by decreasing wavelength. Also, as materials normally absorb high energy photons via a single-photon process or response to high energy lithography sources such as electrons or ions via a single-particle process, nanometre resolution fabrication techniques based on short De Broglie wavelength source do not have the intrinsic 3D fabrication ability at this situation.

Near field optics is thought to be promising to overcome the diffraction limit. It provides people the opportunity of high precision optical manipulation at the near field. For imaging application with near field optics, an image with a resolution far beyond the diffraction limit shows people the fine details of the measured sample. It has also been used to do lithography recently. The work done by L. Pan et al. demonstrates a 22 nm resolution (actually the centre-to-centre distance is about 50 nm) maskless lithography method at the near field region with the help of surface plasmons [57]. However, the lithography technology with near field optics as the basement is still limited in two-dimensional (2D) applications.

In 2001, photo-polymerisation based on two-photon absorption [4] demonstrated the 3D fabrication ability based on far field optics with an optimized resolution better than the size of the diffraction limit set by the light used to do the lithography. Though a single feature with size smaller than the diffraction limit can be fabricated by single-beam 3D OBL, the fabrication resolution is still limited to above the nanometre range and the diffraction limit can make the fabricated two features with centre-to-centre distance smaller than the diffraction limit merged together (Fig. 2.3a).
This has been experimentally shown with the two-photon OBL in polymer. In Fig. 2.3b, Fig. 2.3c and Fig. 2.3d, when the line centre-to-centre distance was decreased from 600 nm to 500 nm and 400 nm, the separated lines became closer and closer and eventually merged together. As a consequence, the attempt to fabricate structures with high density feature arrays is failed.

![Figure 2.3](image)

**Figure 2.3** The resolution limitation in general OBL system due to light diffraction. (a) Schematic of the fabricated features merging together with resolution smaller than the diffraction limit. (b), (c) and (d) show scanning electron microscopy (SEM) images of structures fabricated by two-photon OBL in polymer with line centre-to-centre distance varying from 600 nm, 500 nm to 400 nm, respectively. The scale bar is 1000 nm.

Although a lot of efforts have been done to extend the working wavelength range of the PCs fabricated by 3D OBL with post treatment, the extension is also limited. For example, post-thermal treatment has been used to engineer the 3D inorganic-organic PCs fabricated by two-photon OBL for smaller feature size by removing the organic compositions in the inorganic-organic backbones with thermal [58]. The width of the freestanding lines can be reduced to about 33 nm by post-thermal treatment after the two-photon OBL fabrication. However, almost all of these post-treatment methods
have little effect on efficiently reducing the line centre-to-centre distance which defines the lattice constant of the PCs and thus limits the final extension performance. This is because the fabricated lines with centre-to-centre distance smaller than the diffraction limit have already merged together before the fabricated structure was washed out.

\[\text{Figure 2.4} \] Far field imaging resolution improving based on doughnut-shaped beam suppression. (a) The focus profile of the excitation beam. (b) The focus profile of the doughnut-shaped beam. (c) and (d) Two emitters with distance much smaller than the focal spot size emit with roughly the same emission intensity (c) and with significantly different emission intensities (d). (e) and (f) Schematic of the signal profile detected by a plane detector without suppression (e) and with suppression (f).
For real application, closer line centre-to-centre distance is much more important than smaller linewidth for structures requiring high density feature arrays. For this reason, the fabrication of structures with resolution (defined as the closest feature centre-to-centre distance) beyond the diffraction limit to nanometre range is highly pursued in the laser fabrication community. The development of 3D OBL with nanometre resolution is the direction for fabricating next generation nano-devices for wide application disciplines and it has promising important applications for the miniaturization of devices.

In a work done as early as about 18 years ago [59], S. Hell proposed a method to technically overcome the diffraction limit in the far field by using the old principles of spectroscopy to suppress the diffraction induced signals from emitters at the outer ring of the focal zone (Fig. 2.4) [59]. The basic ideas are as follows [60]: Two emitters with distance much smaller than the focal spot size emit roughly with the same emission intensity (Fig. 2.4c). These two emitters contribute equally to the final signals and this leads to the undistinguishing of them (Fig. 2.4e). However, when the emission of one emitter is suppressed while the other emitter contributes almost the entire final signals (Fig. 2.4d), the emitter without suppression can be accurately positioned (Fig. 2.4f). The suppression of the emission was achieved by depleting the population of the emitter with stimulated emission via a doughnut-shaped beam (Fig. 2.4b) which is overlapped with the excitation beam at the Gaussian mode (Fig. 2.4a). His method is now well known by people with a name of STED (stimulated emission depletion) microscopy with an imaging resolution down to several nanometres.

The pioneering work done by S. Hell et al. [59, 60] aspired the development of 3D OBL beyond the diffraction limit. The basic idea of these lithography technologies to break the diffraction limit is to use another beam to suppress the lithography process at the outside ring of the diffraction region of the beam which induces the lithography process. As the seconded beam is designed to form a doughnut shape with zero
intensity at the focal centre, the lithography process is then confined at the centre position of the diffraction region and this can lead to features with smaller size and higher resolution. Because of this, these lithography technologies is thought to be able to break the diffraction limit. In 2009, three groups demonstrated the reducing of photolithography feature size by with the help of a second beam [61-63]. Thought they did not demonstrated resolution improvement, it is thought to be highly promising to improve fabrication resolution to break the diffraction limit with the advantages of low cost and 3D fabrication ability. Table 2.2 shows the details of the work done by five research groups to develop OBL beyond the diffraction limit.

<table>
<thead>
<tr>
<th>Research group</th>
<th>Suppression mechanism</th>
<th>λ write/suppression (nm)</th>
<th>dot size (nm)</th>
<th>Resolution (nm)</th>
<th>Show 3D?</th>
<th>Suppression beam power</th>
<th>Simultaneous suppression</th>
</tr>
</thead>
<tbody>
<tr>
<td>R. Menon [63, 65]</td>
<td>Absorption modulation</td>
<td>325/633</td>
<td>30</td>
<td>153</td>
<td>No</td>
<td>Low</td>
<td>No</td>
</tr>
<tr>
<td>M. Wegener [66-68]</td>
<td>STED</td>
<td>810/532</td>
<td>65</td>
<td>150</td>
<td>Yes</td>
<td>High</td>
<td>Yes</td>
</tr>
<tr>
<td>J. Fourkas [61]</td>
<td>STED</td>
<td>800/800</td>
<td>40</td>
<td>-</td>
<td>Yes</td>
<td>High</td>
<td>Yes</td>
</tr>
<tr>
<td>R. McLeod [62]</td>
<td>Photo-inhibitor</td>
<td>364/473</td>
<td>65</td>
<td>-</td>
<td>No</td>
<td>Low</td>
<td>Yes</td>
</tr>
<tr>
<td>M. Gu [22]</td>
<td>Photo-inhibitor</td>
<td>488/375</td>
<td>40</td>
<td>-</td>
<td>No</td>
<td>Low</td>
<td>Yes</td>
</tr>
</tbody>
</table>

“-“ means no resolution data was shown in their publications.

Table 2.2 The general information for the current development of OBL to break the diffraction limit.

R. Menon’s group uses the concept of absorption modulation to suppress the lithography process [63, 64]. The photo-resin at the doughnut-shaped ring is modulated to be not response to the beam which induces the lithography process by absorbing light of another wavelength. When light with diffraction-limited focal spot is used to irradiate the photo-resin, as the photo-sensitive component at the doughnut-shaped ring has been modulated to a meta-stable state, the lithography
process only occurs at the doughnut-shaped centre due to the absorption modulation. After the exposure, the photo-sensitive component in the meta-stable state is tuned back by irradiating it with light at a specific wavelength. About 30 nm line width is achieved by using this absorption modulation method [63]. Because the absorption modulation is based on the light absorption of molecules, low modulation beam power can be used to avoid high intensity light induced side effect in the focal region. However, this method highly relies on the anti-fatigue property of the photo-resin under the repeated excitation of two laser beams for high resolution (defined as the closest line centre-to-centre distance) structure fabrication. Because of this, though the achieved smallest line width is 30 nm, the achieved best resolution is 153 nm which is about 5 times the value of smallest line width [65]. In addition, as a reversing process is required to make the material ready for the fabrication of structures at the close region of a fabricated structure, the fabrication speed is slowed down.

M. Wegener’s group uses the concept of stimulated emission depletion to suppress the formation of photo-initiator radicals which results to the suppression of photo-polymerisation at the doughnut-shaped ring [66-68]. This was first demonstrated by J. Fourkas et al. in 2009 [61]. The photo-initiator molecules at the excited state are depleted to their ground state rather than generate photo-initiator radicals by the stimulated emission. The line width and line resolution achieved in his group is 65 nm [66] and 150 nm [68]. As the stimulated emission process is required to depopulate the excited state initiator, this is happened simultaneous with the lithography process. So the whole fabrication process is continuous which contribute to fast fabrication. To further improve the resolution with this method, depletion beam with higher intensity is required for the stimulated emission process to compete with the photo-initiator radical generation process. However, higher intensity depletion beam can lead to significant side effects such as photo-damage and uncontrolled thermal effect [66]. For the achieving of 65 nm line size, the power of the doughnut beam is about 70 mW which is more than 5 times of the value of the writing beam.
Although both size reduction and resolution improvement has been demonstrated in this group, these high intensity depletion beam induced side effects hinder the obtaining of resolution deep beyond the diffraction limit.

In this thesis, we use the concept of photo-inhibitor to suppress the photo-polymerisation for the realising of fabrication resolution beyond the diffraction limit [22, 62, 69]. A doughnut-shaped beam at the focal centre is used to generate photo-inhibitor radicals which can react with the photo-initiator radicals to form inert molecules. By reducing the local concentration of the photo-initiator radicals, the polymerisation at the doughnut-shaped ring is thus suppressed. This method to achieve nanometre resolution lithography is given the name of super-resolution photoinduced-inhibition nanolithography (SPIN) [22]. Compared with the above two methods, SPIN has combined their advantages of both a low exposure power of the second beam and the simultaneous photo-suppression with the photolithography process. It is expected for SPIN to achieve a smaller feature size and a higher resolution than the above two methods. Utilising photo-inhibitor to reduce the fabricated feature size has been proposed by McLeod et al. [62]. However, due to the lack of suitable photo-resin, they could not produce features with size below 50 nm nor demonstrate resolution improvement. By improving the property of the photo-resin, M. Gu’s group achieved the fabrication of dot with 40 nm size based on the photo-inhibition strategy [22]. This minimum dot size of 40 nm was achieved by developing a photo-resin with high photosensitivity which promotes a fast curing speed and enhances the photo-polymerisation efficiency. But this work was based on single-photon polymerisation which does not have the 3D fabrication capability. Compared with other 2D nanometre resolution fabrication techniques such as EBL, this work do not have significant advantages. For this aim, based on the single-photon polymerisation and single-photon inhibition strategy, two-photon polymerisation and single-photon inhibition is proposed to be a solution in this thesis.
Chapter 2

For the SPIN, although a lot of theoretical model has been established to investigate the photo-polymerisation under the irradiation of single-beam, a model which can effectively consider the photo-inhibition process under the irradiation of two beams is yet to be set up. The development of 3D OBL with nanometre resolution based on SPIN with two-photon polymerisation and single-photon photo-inhibition is presented in this thesis. Chapter 4 introduces the theoretical work done on this topic and Chapter 5 presents the experimental details and achievement.

2.4 Three-dimensional optical beam lithography of high refractive-index and narrow electronic bandgap material

The ability for high refractive-index material to confine light better makes high refractive-index material highly favored for photonic applications. For 3D OBL to fabricate photonic devices made by high refractive-index material with the top-down strategy, light focusing into a high refractive-index material encounters a problem of refractive-index mismatch. To solve this problem, refractive-index mismatch induced aberration can be compensated, which makes the fabrication of depth uniform structures in a high refractive-index material feasible [20]. In 2006, chalcogenide glass As$_2$S$_3$ as a high refractive-index material has been successfully developed for 3D OBL [70]. Laser exposure initiates the topotactic ring-opening polymerisation back into the glassy As$_2$S$_3$. By selective etching, the unexposed part can be removed to reveal the fabricated structure. As the semiconductor absorption edge of glass As$_2$S$_3$ is 530 nm, two-photon process at the excitation of light with a 800 nm wavelength enables 3D OBL in this material. As has been expected, strong aberration was observed during the fabrication.

Generally, there are two basic strategies to fabricate nanostructures. One is
top-down and the other is bottom-up. When OBL is used to fabricate photonic devices, these two strategies can both be adopted. The using of a concrete strategy is decided by the consideration of the feasibility and convenience of the OBL fabrication. The fabrication of structures by 3D OBL with these two strategies has different requirements to the fabrication system, fabrication process and post-fabrication processing.

Until now, almost all of the materials used for 3D OBL based on the top-down strategy have no single-photon absorption to the used light. The satisfying of multi-photon response makes the materials with a certain electronic bandgap not suitable for 3D OBL with a give laser wavelength. To make these materials suitable for 3D OBL, a simple way is to use longer laser wavelength. However, this is not good for system operation and not suitable for high resolution fabrication. If the material has an electronic bandgap smaller than 0.5 eV, then an appropriate laser wavelength should be longer than 2400 nm. It is disappointed to use such long or even longer wavelength to fabricate in a material for 3D OBL. An extreme situation for 3D OBL is to fabricate in a material with a zero electronic bandgap such as metal.

The problems for 3D OBL in a narrow electronic bandgap material with the top-down strategy can be fixed by adopting the bottom-up strategy. The fabrication of silver structures by 3D OBL via photo-reduction is a good example [71]. Different from the top-down strategy, silver is dissolved in a solution possessing a moderate refractive-index with the form of silver ions and the whole solution can absorb the excitation photons via a multi-photon process. When silver ions absorb light, they can be reduced to silver elements. The silver structures are then made by the reduced silver elements.

Semiconductor materials with a narrow electronic bandgap and a high refractive-index such as PbSe have unique optical and electrical properties. These materials are promising for different applications including photonics and electronics.
However, the fabrication of photonic structures made by these materials is challenged for 3D OBL with the top-down strategy. The bottom-up strategy opens a window for 3D OBL to enlarge its suitable material range. To solve the problems of narrow electronic bandgap and refractive-index mismatch, a method for 3D OBL to fabricated 3D structures made by materials with a narrow bandgap and a high refractive-index based on the bottom-up strategy is proposed. To demonstrate the feasibility of this method, the 3D OBL of structures made by PbSe is shown in chapter 6.

2.5 Chapter summary

This chapter presents all the necessary background for understanding the content and novelty of this thesis. The theory for photonic devices to manipulation photon emission and the requirement of 3D OBL for photon emission manipulation with photonic devices are reviewed which serves as a background and benchmark for investigating 3D OBL of functional photonic devices for photon manipulation applications including SE manipulation in this thesis. Methodologies and technologies regarding removing the current limitations of 3D OBL to fabricate 3D photonic devices for photon manipulation applications are introduced for better understanding of the work in this thesis.
Chapter 3

Spontaneous emission manipulation with three-dimensional photonic devices fabricated by optical beam lithography

3.1 Introduction

Three-dimensional (3D) optical beam lithography (OBL) has the distinct ability to fabricate 3D arbitrary structures and thus supports the fabricated devices to photonic applications with a designed local photonic environment. When spontaneous emission (SE) is manipulated with a photonic device, i.e. a photonic crystal (PC), the photonic local density of states (LDOS) property of the PC determines the manipulation performance for a given emitter inside the PC [14, 15]. A 3D PC can be fabricated by different methods including 3D OBL. When the fabricated material is given, 3D OBL can fabricate a PC with designed structures such as a defect that can greatly change the photonic LDOS.

In this chapter, by measuring the SE decay rate change for emitters imbedded in PCs compared with that in a reference system, the SE control property of the 3D PCs fabricated by 3D OBL based on two-photon polymerisation (2PP) was investigated. In Sec. 3.2, the sample preparation to measure the SE modification with PCs fabricated by two-photon OBL is presented. By a simple integration of semiconductor quantum dots (QDs) into the PCs, the PCs are transformed to photonic devices with unique


Chapter 3

photon emission manipulation functions. Then, the photonic LDOS dependent SE manipulation property of PCs is experimentally and theoretically studied in Sec. 3.3. The demonstration of local structure induced photonic LDOS tuning is stated in Sec. 3.4.

3.2 Sample preparation

To measure the photonic LDOS change induced SE modification, the sample preparation can be separated into three important parts: quality requirement satisfied PCs, quality requirement satisfied SE probes and SE related measurement of the SE probes embedded in the PCs to reveal the photonic LDOS change.

3.2.1 Photonic crystal fabrication

Figure 3.1 (a) Schematic of a woodpile PC with elliptical rods that can be fabricated by two-photon OBL. (b) The band diagram of the woodpile PC. Two grey labels indicate the stopgaps in the Γ-X and Γ-L directions.
The first part is the fabrication of 3D PCs. The geometry of the PC structure is an issue need to be considered for a given fabrication material as the geometry of the structure determines the photonic LDOS inside the PC. Except for easy fabrication, woodpile geometry proposed by Ho et al. in 1994 [72] was selected for the demonstration because of two main reasons. First, 3D woodpile PCs fabricated by two-photon OBL such as 2PP are robust and repeatable. The layer-by-layer geometry (Fig. 3.1a) makes the fabricated structure stable. This guarantees high quality structure without unwanted defect due to structure deforming and reliable data obtained from the structure. Then, a woodpile PC fabricated by OBL with 2PP has an obvious stopgap along a certain direction such as the Γ-X direction even the refractive-index of the material is low (Fig. 3.1b) and this has already been experimentally demonstrated [3, 6]. As OBL with 2PP can easily fabricate woodpile PCs with lattice constant around 1000 nm and line lateral width about 150 nm, the fabricated PC can have a stopgap with wavelength at the near infrared range, for example the Γ-X direction stopgap [73, 74]. With an appropriate post-treatment method, the fabricated PC can even have Γ-X direction stopgap wavelength at the red edge of the visible range [58]. This greatly facilitates the SE decay lifetime measurement of the SE probes with detectors operating at the sensitive wavelength such as the near infrared or even the visible range.

Three-dimensional woodpile PC was fabricated by two-photon OBL in Ormocer (photo-sensitive resin, Micro Resist Technology). A femtosecond (fs) pulsed laser beam of wavelength 800 nm, generated from a Ti:sapphire laser (Spectra Physics Mai Tai), was set to go through an optical parametric oscillator (Coherent Mira OPO). The output beam with a wavelength of 580 nm, a repetition rate of 76 MHz and a pulse duration of 200 fs was first beam expanded and then focused into the Ormocer with a high numerical-aperture (NA) oil immersed objective lens (Olympus, NA=1.4, 100×) to induce photo-polymerisation. The Ormocer was sandwiched by two cover slips and affixed to a 200×200×200 μm³ x-y-z piezoelectric scanning stage (P562, Physik
Instrumente) for fabrication. A mechanical shutter which is synchronized with the scanning stage was used to control the on and off status of the laser exposure. Both the mechanical shutter and the scanning stage were controlled by a computer programming with the designed structure. The fabrication process is monitored at real time by a charge-coupled device (CCD) camera. The structure was fabricated on the up surface of the down cover slip. With the position of the laser beam focal spot fixed, 3D arbitrary structures were fabricated by controlling the moving of the scanning stage in 3D space. Figure 3.2 shows the schematic of the two-photon OBL system.

![Schematic of the 3D two-photon OBL system](image)

**Figure 3.2** Schematic of the 3D two-photon OBL system used to fabricate PCs in Ormocer.

After the fabrication, the cover slip without the stick of the fabricated structure was mechanically taken off with care. Then the whole down cover slip was immersed into a washing solution (4-methyl-2-pentanone: isopropanol =1:2 in volume) for 90 secs to remove the un-solidified photo-resin and to reveal the fabricated structure. The fabricated structure was finally dried in air at the room temperature. To make the fabricated structure more solid, the cover slip with the structure attached on was irradiated under ultra-violate (UV) light for more than 3 hours.
Figure 3.3 Polymer 3D woodpile PCs fabricated by the two-photon OBL. (a) Woodpile PCs with different layers. (b) A 60 × 60 μm² woodpile PC with 24 layers supported by a frame with a thickness of 10 μm. The detailed view shows a lattice constant of 1250 nm. The scale bar is 10 μm. (c) The Γ-X direction transmission spectrum of the PC in (b). (d) Woodpile PCs with different lattice constants.

For the fabrication of woodpile PCs, the PCs were fabricated layer by layer by moving the sample away from the objective lens, which is controlled accurately by a computer program according to the geometrical designing of the woodpile structure (Fig. 3.3a). A frame was designed to support the woodpile PC to avoid structure deforming (Fig. 3.3b). With this method, woodpile PCs with lattice constant down to 500 nm can be fabricated (Fig. 3.3d). To characterise the photonic stopgap of the fabricated PC, a Fourier-transform infrared (FTIR) microscope (Thermo Nicolet) was used to measure the transmission spectra. The measurement with the FTIR was modified by tilting the sample with an angle and by putting a small pinhole in front of the objective lens for accurate measurement with flexible angles [75, 76]. Figure 3.3c
shows the transmission spectrum of a woodpile PC with a lattice constant of 1250 nm at the Γ-X direction (Fig. 3.3b).

3.2.2 Synthesis of PbSe/CdSe core-shell quantum dots

The emitters selected to use in this thesis are semiconductor QDs. A QD (Fig. 3.4) is a quasi-two-level system with high quantum efficiency [77, 78]. Compared with fluorescence dye molecules, QDs have moderate SE decay lifetime with excellent anti-photo-bleaching property [77-79] that is highly desired for SE decay lifetime measurement. As the PC fabricated by two-photon OBL has a photonic bandgap with centre wavelength at the near infrared range, Lead selenide (PbSe) QDs are used to match this wavelength range.

Figure 3.4 A Semiconductor QD as a quasi-two-level system.

The chemical materials used for PbSe/CdSe core-shell QD synthesis include: lead oxide (PbO, 99.999%), cadmium oxide (CdO, 99.999%), oleic acid (90%), selenium
(99.5%, 100 mesh), trioctylphosphine (90%), 1-octadecene (90%) and tetrachloroethylene (99%) were purchased from Aldrich. Chloroform, methanol and toluene were obtained from Fisher.

The synthesising of PbSe QDs with emission at the wavelength region from 1000 nm to 2000 nm is as follows [80]: A mixture of PbO (0.252 g), oleic acid (0.960 g) and technological grade 1-octadecene (ODE, 3.500 g) was stirred and heated to 120 °C for 1 hour under the vacuum. After that, the mixture was switched to nitrogen gas and the temperature of the mixture was allowed to increase to 170 °C. The mixture turned colourless upon heating to around 150 °C in a three-neck flask under the nitrogen gas. A second solution was prepared by dissolving selenium (0.358 g) in trioctylphosphine (3.220 g) and ODE (5.000 g). The second solution was kept at the room temperature and was swiftly injected into the first solution when the temperature of the first solution hit 170 °C for the nucleation of the PbSe nano particles. After the injection, the temperature of the whole solution could drop down to about 120 °C. The nanoparticles were allowed to grow for 3 to 6 mins under 120 °C. The system was then quickly cooled down to the room temperature. The synthesised QDs were purified by washing with chloroform/methanol solution repeatedly and finally dissolved in chloroform or toluene after filtered by a 0.2-μm mesh filter. The PbSe QDs prepared by such a method were reported to have quantum efficiency more than 85% in a solution [80].

To improve the quality of the PbSe QDs for higher quantum efficiency and better anti-photo-bleaching property, CdSe shell was coated to the surface of the PbSe QDs by a cation-exchange method [81]. The precursor for the cation exchange was prepared as follows: A mixture of CdO (0.200 g), oleic acid (10.000 g), and ODE (10.000 g) was stirred and heated to 120 °C for 1 hour under the vacuum. After that the mixture was switched to nitrogen gas and the mixture was allowed to heat to around 250 °C to turn colourless in a three neck flask under the nitrogen gas. The
mixture was quickly cooled down to the room temperature under the nitrogen gas. At the room temperature, excessive cation-exchange precursor was mixed with the synthesised PbSe QDs in chloroform and the mixture was put under stirring for 20 hours. After washing with chloroform/methanol solution repeatedly, the final product, PbSe/CdSe core-shell QDs, was dissolved in toluene.

![Absorption spectra of the PbSe QDs and the same PbSe core QDs after CdSe shelling and the emission spectrum of the PbSe/CdSe core-shell QDs.](image)

**Figure 3.5** Absorption spectra of the PbSe QDs and the same PbSe core QDs after CdSe shelling and the emission spectrum of the PbSe/CdSe core-shell QDs.

The absorption spectra of the PbSe/CdSe core-shell QDs in toluene or tetrachloroethylene were measured by the FTIR spectroscopy (Thermo Nicolet). Compared with that of the core PbSe QDs, the first exciton absorption peak of the core-shell PbSe/CdSe QDs is blue shift for about 50 nm (Fig. 3.5) which indicates the successful coating of the CdSe shell.

The emission spectra of the synthesised QDs were measured with a homemade spectroscopy. To measure the emission spectra, continues wave mode laser beam with a wavelength of 800 nm chopped by a mechanical chopper (maximum 800 Hz) was focused into the QDs with an objective lens (NA=0.8) for excitation. The emission signal was collected with the same objective lens and detected by a fast near infrared
(NIR) photomultiplier (Hamamatsu, H10330-75) after dispersing by a spectrograph (Acton Spectropro 300i). A lock-in amplifier (Stanford Research Systems SR850) connected with the mechanical chopper was employed in the system to enhance the signal-to-noise ratio for weak signal detection.

3.2.3 Put PbSe/CdSe quantum dots into PCs

Putting the synthesised PbSe/CdSe core-shell QDs into the PCs and the reference system is an important issue for the measurement of SE decay lifetime modification with PCs and for the functionalising of PCs into photon emission control devices. Spontaneous emission from nano emitters such as QDs is sensitive to their surrounding environment. It is important to make sure QDs in PCs and in the reference system have the same surrounding radiation and non-radiation environment except the modified LDOS of the PC as a background to refer the LDOS change.

![Figure 3.6](image)

**Figure 3.6** The infiltration of QDs into the PCs by physical adsorbing. (a) Schematic of the physical adsorbing infiltration process. (b) The Γ-X direction transmission spectra of a PC before and after the infiltration of the QDs by physical adsorbing.

Previous experiments of putting QDs into the PCs fabricated by two-photon OBL adopted a simple infiltration method (Fig. 3.6a) [55, 76]. As this method is based on
the physical adsorbing of nanoparticles, it is difficult to control the quantity of the QDs adsorbed on the surface of the woodpile PC rods. The QD infiltration uniformity is losing control for this method. The infiltrated QDs can change the local refractive-index of a PC and hence change the PC’s stopgap. The easy clogging up of the QDs inside the PC can even destroy the PC’s stopgap (Fig. 3.6b). These drawbacks could result in distorted experimental results. Figure 3.6b shows the transmission spectrum of a PC before and after the QD infiltration with this physical adsorbing method. After the QD infiltration, the stopgap along the Γ-X direction was disappeared due to the clogging up of the QDs inside the PC.

Figure 3.7 The SE decay lifetime of the QDs in the PC with the stopgap disappeared and in the reference. (a) A SEM image of the woodpile PC used in Fig. 3.6. The scale bar is 10 μm. (b) Schematic of the thickness of the QDs inside the PC and on the surface of the frame. (c) Typical decay curves from the QDs in the PC and in the reference fitted with a single exponential decay function. (d) and (e) Histogram of lifetime value for the QDs measured inside the PC (e) and on the surface of the frame as a reference (f).
Figure 3.7a shows a scanning electron microscopy (SEM) image of the PC used in Fig. 3.6. The QDs on the surface of the PC frame was used as a reference system. The average SE decay lifetime of the QDs inside the PC is 14% longer than that in reference system (Fig. 3.7). This can be explained as a thicker QD layer thickness in the reference system than in the PC while the thicker QD layer thickness leads to a quicker SE decay rate and a shorter SE decay lifetime (Figs. 3.7a and 3.7b). So this 14% lifetime longer does not come from the effect of the PC but from a shorter reference lifetime value. This 14% lifetime longer result indicates the importance of appropriate reference designing which should rule out any other influence to the QD lifetime change except the photonic LDOS of the PC. Reference system designing is crucial for a quantitative investigation to accurately reflect the SE manipulation capability of the PCs. It is also crucial to compare the experiment result with the theory.

To solve the problem of the unequal background environment in the PC and in reference system and to develop a QD placing method with controllable QD quantity, a molecular linking method was developed in this thesis (Fig. 3.8) [82]. Using this molecular linking method, PbSe/CdSe core-shell QDs with a desired emission wavelength were deposited with controlled layer numbers on the surface of the polymerised rods of an Ormocer woodpile PC. The polymerised Ormocer structure was first functionalised with amino group by immersing the structure into a 3-aminopropyltriethoxysilane (APTES) in toluene solution with 5% (weight/weight) concentration for 45 mins. The structure was then washed with a solution with pure toluene to remove unattached APTES molecules. After that, the structure was immersed into the PbSe/CdSe core-shell QD solution for 12 hours for QD attaching. Then the structure was washed again with toluene to remove unattached QDs. By this method, one layer of QDs can be statistical uniformly attached on the surface of the woodpile PC rods (Fig. 3.8a). Repeat this process for several times, multi-layer of QDs can be deposited (Fig 3.8c).
**Figure 3.8** The attaching of the QDs via the molecule linking method. (a) Schematic illustration of one layer of QDs attached to the polymer structure. (b) Schematic diagram of the fabricated PC before and after the QD attachment. (c) Schematic of multi-layer QD attachment. (d) The SEM images of the 3D PC and the reference block which shows the X-Y plane of the structure with the top view.

The reference system is the same QDs distributed on the top surface of a square block which is fabricated at the near side of the PC with the same material and the same fabrication condition on the same cover slip (Fig. 3.8d). The QDs distributed statistical uniformly inside the PC and on the surface of the square block with the same layer number via the same molecular linking process. The SE measurement of the QDs inside the PC and in the reference system was kept as the same for reliable experimental result as much as can be done. To get enough fluorescence signals for the SE decay lifetime measurement and to avoid significant influence of the attached QDs to the PC stopgap, the QD attaching process was repeated 3 times and 4 layers of the QDs are attached to the surface of the PC structure in the experiment. The Γ-X direction transmission spectra of the same PC before, during and after
the QD attachment were shown as Fig. 3.9. The almost unchanged transmission spectra in the Γ-X direction indicate that the QD attaching method is good to avoid significant change to the property of the PC.

![Graph showing transmission spectra](image)

**Figure 3.9** The Γ-X direction transmission spectra of a same PC before, during and after the molecular linking of the QDs.

### 3.2.4 Measurement of quantum dot spontaneous emission lifetime

The measurement of the LDOS modification by a PC can be done by measuring the SE decay lifetime change of the QDs in the PC compared with that in a reference system with a same non-radiative decay environment. The SE decay lifetime of the attached PbSe/CdSe core-shell QDs in a PC and in the reference was measured by the time-correlated single photon counting (TCSPC) system conjunct with a home-made confocal detection system (Fig. 3.10a) [82]. Laser excitation was provided by a diode laser with a wavelength of 1064 nm, a pulse duration of 49 ps and a repetition rate of 5 MHz. The signals were collected by an objective lens (Olympus, NA=0.8) and detected by a fast NIR photomultiplier (PMT) (Hamamatsu, H10330-75) after dispersing by a spectrograph (Acton Spectropro 300i). The time signals from the PMT
and the reference diode trigger were collected by the TCSPC module (PicoHarp 300, PicoQuant GmbH).

![Figure 3.10](image)

**Figure 3.10** Measurement of QD SE lifetime. (a) Schematic of the SE decay lifetime measurement setup. (b) Typical SE decay curves of PbSe core and PbSe/CdSe core-shell QDs.

Histograms of the photon arrival time compared with the reference trigger time were recorded by the PMT as SE decay curves. To monitor the position of the focal spot of the excitation beam, a CCD camera is used with a position precision of ±2 μm. To measure the SE decay lifetime of QDs inside the PC, the CCD was used to ensure that the excitation focal spot was located in the geometrical centre of the PC in the plane parallel to supporting cover slip. By moving a scanning stage, 3D SE decay lifetime measurement can be performed. The measured decay curve was fitted with a single exponential decay function (Fig 3.10b) as the excitation intensity was kept as low as possible to avoid fast Aüger recombination and no significant exciton-exciton interaction was observed due to the CdSe shelling of the PbSe/CdSe core-shell QDs [83]. Compared with the core QDs, core-shell QDs exhibit a slower decay trend,
which can be well fitted with a single exponential decay function (Fig 3.10b). This also shows the quality improvement of the PbSe QDs after the CdSe shelling.

3.3 Spontaneous emission manipulation with a photonic crystal

A 3D woodpile PC with 24 layers (60×60×10 (X-Y-Z) μm³ with 10 μm frame, standard woodpile geometry with a lattice constant of 1150 nm, a refractive-index n=1.52) was fabricated by the two-photon OBL. The PbSe/CdSe core-shell QDs were attached to the surface of this PC as SE emitters via the molecular linking method. The PbSe/CdSe core-shell QDs have an emission peak wavelength at 1480 nm that matches the centre wavelength of the Γ-X stopgap of the PC (Fig. 3.11). The emission of the QDs as embedded emitters inside the PC, was expected to be inhibited compared with that in the reference.

Figure 3.11 Transmission spectra of the PC in the Γ-X direction before and after the QD attachment and the emission spectrum of the attached QDs with an emission peak wavelength matching the stopgap of the PC in the Γ-X direction. The shadow zone indicates the calculated wavelength range of the Γ-X direction stopgap.
In theoretical calculation of the photonic LDOS in a PC, the PC size is infinite. However, this is never the real situation in the experiment. The finite size induced surface defect can influence the SE manipulation performance for emitters at a position near the geometric edge of the PC. This has to be considered for the comparison of experimental result with theoretical calculation. For this reason, the influence of the finite size structure to the SE decay was first measured.

The excitation focal spot was moved to the X-Y plane (the plane parallel to the PC attached cover slip) geometrical centre of the PC with the help of the CCD camera. In the Z direction, the focal spot was moved to the up surface edge by the help of the CCD camera and fluorescence signal detection. The relative position of the excitation focal spot to the PC has the precision of ±2 μm. Then, the moving of the relative excitation focal spot position to the PC was controlled by a scanning stage (the same as the one used to do the two-photon OBL fabrication) with nanometre precision. Beginning from the initial excitation focal spot position, the focal spot was move deeper into the PC with two microns a step until it reached the PC surface at the other side. At each position of the Z direction, three different X-Y positions near the X-Y plane centre were picked. Each position gave out a SE decay curve. An average SE decay lifetime for each Z position can be obtained and is showed in Fig. 3.12.

**Figure 3.12** Averaged SE decay lifetime value changing with the Z direction position.
The SE decay lifetime has the largest value when the excitation focal spot was moved to the geometrical centre of the PC (z=8 μm). This is due to the finite size of the 3D woodpile PC structure. Photonic stopgap effect at the geometrical centre of the PC is the strongest, and thus induces the strongest SE inhibition. To make experiment more consistent with the theory, the following SE decay lifetime measurement was done at the geometrical centre of the PC if without specific note.

To compare the SE decay lifetime of the QDs in the PC with that in the reference system, 64 positions at the z=8 μm plane and 64 positions at the z=7 μm plane of the excitation focal spot were picked for the SE decay lifetime measurement. Consider the size of the focal spot and measurement error, the measurement were not fixed at the z=8 μm plane. The X-Y position of these 128 times measurements was kept at the X-Y plane centre within a 7 μm × 7 μm square zone at the step of 1 μm × 1 μm. In the reference system, 121 times measurements within a 10 μm × 10 μm square zone at the step of 1 μm × 1 μm were done as a comparison. Lifetime distributions obtained for these measurements both in the PC and in the reference is shown in Fig 3.13. Typical decay curves for the QDs in the PC and in the reference shows a significant SE decay lifetime longer (Fig 3.13a).

Figure 3.13 (a) Typical decay curves fitted with single exponential decay function for QDs in the PC and in the reference. (b) Distribution of SE decay lifetime for QDs inside the PC and in the reference.
The lifetime distribution of the QDs inside the PC is broader than that in the reference. This is expected as QDs in the PC experience position dependent LDOS. The LDOS in the PC is increased at some positions and decreased at some other positions compared with that in the reference. If the LDOS in the PC are fluctuated more significantly, the lifetime distribution of QDs is broader compared with that in the reference. The relative broader value (the full width at the half maximum of the lifetime distribution divided by the average lifetime value) is 3.2%. The lifetime distribution of QDs inside the PC is long shift compared with that in the reference. The average lifetime is increased by 20.5%. This indicates a SE suppression with 20.5% decay lifetime longer. The SE decay rate was decreased by about 20% by the effect of the photonic stopgap. As the average SE decay lifetime of the QDs in the reference is about 40 ns, the decreased SE decay rate was speculated to be about the magnitude of $5 \times 10^6$/s.

![Figure 3.14](image)

**Figure 3.14** Calculated lifetime distribution of emitters at 22,300 positions in a unit cell of a PC with the same parameters as the one in Fig. 3.11. The lifetime of the emitters in the PC is compared with that in the reference.

The experimental result with a 20.5% average lifetime longer is consistent with the theoretical calculation. Figure 3.14 shows the calculated lifetime distribution of emitters inside the PC compared with that in the reference. The calculation is based on the LDOS theory, which is introduced in Sec. 2.1. The parameters used in the
calculation are based on the experiment (woodpile PC material refractive-index: 1.526, nearest PC rods centre distance: 1150 nm; PC elliptical rod short axis: 175 nm, long axis: 350 nm). The calculation calculated the LDOS of 22,300 local positions in a basic unit of the PC.

The arithmetic average lifetime change based on the LDOS of 22,300 local positions is 19.9% longer than that of the reference. The SE in some particular position is suppressed with a 60% lifetime longer. Compared with this, the SE in some other particular position is enhanced with a 10% lifetime shorter. As these local positions only occupy less than 1% of the total positions inside the unit cell, this information is totally lost in the measured lifetime distribution. A higher spatial resolution measurement can get a lifetime distribution with details more similar to the calculated one. The consistency of the theory with the experiment indicates that the sample preparation method support the quantitative investigation of SE manipulation with PCs and the SE manipulation for emitters inside a PC is defined by the photonic LDOS of the.

3.4 Enhancing spontaneous emission with a designed defect in a photonic crystal

A general viewpoint for realising SE enhancement with a PC without a defect or cavity is using the band edge enhancement [33, 34, 84]. A reduced light group velocity was expected due to the nearly flat photonic bands near the band edge [85, 86]. The SE could be enhanced as LDOS is inversely proportional to the group velocity. However, a low refractive-index pseudo-gap PC has different properties from a high refractive-index complete bandgap PC.
Different directions exhibiting different stopgaps make the band edge phenomenon for low refractive-index 3D pseudo-gap PCs not as clear as the complete band gap PCs.

**Figure 3.15** (a) Experimental and calculation results of emission lifetime versus the emission wavelength for QDs inside the PCs compared with that in the reference. (b) Calculated photonic band diagram of the 3D pseudo-gap PC with a refractive-index of 1.526. The shadow zone indicates the calculated wavelength range of the Γ-X direction stopgap.

A low refractive-index pseudo-gap PC does not have complete band gap. Stopgaps of different directions have different stopgap wavelength ranges and thus the SE decay behavior at the band edge of one direction stopgap is greatly influenced by other direction stopgaps. To measure the band edge enhancement of QDs in low refractive-index PCs and to better understand the band edge phenomenon for low refractive-index PCs, the wavelength response of the photonic LDOS in the PC was studied. First, five PCs with the same parameters as the one in Fig. 3.11 were fabricated. Then, five PbSe/CdSe QDs with emission peaks at 1350 nm, 1400 nm, 1450 nm, 1500 nm and 1550 nm were synthesized according to the same method as the one used in Fig. 3.11 but with different growth time. The QDs were attached to the structure surface of the PCs and the reference square blocks with one kind of QDs to one PC and one reference block via the molecular linking method. As the Γ-X direction stopgap is one of the most interested stopgaps [8, 55, 58, 87] for the woodpile PCs, the emission wavelengths of the QDs were selected to lie in the wavelength range of the Γ-X direction stopgap.
For each of the five samples, SE decay curves of 60 excitation focal spot positions inside a PC were measured and each position gives out a lifetime value. As a comparison, SE decay curves of 60 excitation focal spot positions on the surface of the reference block were measured and fitted to give out lifetime values. By comparing the average SE decay lifetime value of QDs in the PC and in the reference, the lifetime change for QDs inside the PC can be obtained. For each sample, the emission wavelength for the SE decay measurement is the emission peak wavelength of the QDs attached to that sample. Combine the data of the five samples and the one has been shown in Fig. 3.13, the wavelength response of the SE decay lifetime change for emitters in the PC compared with that in the reference can be plotted. As shown in Fig. 3.15a, SE inhibition was achieved at the wavelength of the Γ-X direction stopgap centre with an average of 20.5% lifetime increasing. However, for QD emission wavelengths at the band edge of the Γ-X direction stopgap, the emission of the QDs is still inhibited; no band edge enhancement was observed. This can be explained as follows: In a pseudo-gap PC, different direction stopgaps have different stop wavelength ranges which make the band edge of a certain direction stopgap not necessary the band edge of another direction stopgap (as shown in Fig.3.15b). This is different from high refractive-index PCs with complete bandgap. Spontaneous emission decay lifetime reflects the influence of all direction stopgaps. The band edge behavior of a certain direction stopgap was blurred by different direction stopgaps for a pseudo-gap PC. This weakens the band edge enhancement of SE or even makes it not possible. The theoretical calculation supports this explanation. The principle of the calculation and the parameters used about the PC and the QDs except the emission wavelength of the QDs are the same as the one done to get Fig. 3.14. As shown in Fig. 3.15a, the calculation fits the experiment well. This result in a further step demonstrates the photonic LDOS defined SE manipulation.

Inducing a defect is a good method to enhance the SE as a defect can effectively change the LDOS in a PC [88-90]. Defects such as nano-cavity in two-dimensional (2D) PC slabs or in 3D PCs show the capability of enhancing emission tuned by the defects [88-90]. Plane defect can be easily introduced into 3D low refractive-index pseudo-gap PC fabricated by
two-photon OBL. With plane defect properly designed, the observed pronounced defect mode with wavelength peak within the photonic stopgap in a 3D low refractive-index pseudo-gap PC [91] indicates the potential of realising SE enhancement control. Important applications, for example, integrated micro-lasers or micro-fluidic sensing [92], aspired to enhance SE with a plane defect in 3D pseudo-gap PCs.

Figure 3.16 (a) The Γ-X direction transmission spectra of the PCs with and without the plane defect. (b) The Z direction lifetime response of the QDs in the PCs with and without the plane defect compared with that in the reference.

In experiment, a 24 layer woodpile PC was fabricated. Another 24 layer woodpile PC was fabricated with the same fabrication parameters except 10% longer of the 12th and the 13th layer distance than the normal woodpile PC layer space. This means a plane defect has been introduced into this PC. These two structures and the square block were fabricated on the same cover slip. Quantum dots with emission wavelength of 1450 nm which matches the Γ-X direction stopgap centre wavelength of the PC without the plane defect were attached to the surface of the two PCs’ rods and the reference square block surface. The defect mode appears within the wavelength range of the Γ-X direction stopgap shows the successful inducing of a plane defect (Fig. 3.16a). The same lifetime measurement method was used to measure the SE decay lifetime of the attached QDs. SE decay curve of QDs in the PC with and without the plane defect was measured for different Z direction positions (perpendicular to the woodpile layer, Z direction zero point plane is roughly the up first layer plane which is
positioned by the CCD camera). For each Z direction position, 40 different excitation focal spot positions were measured.

Figure 3.16b shows the Z direction lifetime response of the QDs in the PC with and without the plane defect compared with that in the reference. From this data, for the PC without the plane defect, a maximum lifetime value was observed at the Z direction centre position of the PC. Due to the finite structure size of the fabricated PC, emission of QDs in the PC structure geometric centre experiences a most effective interaction with the PC while emission of QDs in the PC close to the first or the 24th layer of the structure is influenced by the boundary of the structure. For the PC with the plane defect, as SE determined by the LDOS of the position where the emitter is \([14, 15]\), the position closer to the defect experiences stronger defect influence. Fifteen percent average decrease of QD SE decay lifetime was observed in the Z direction centre position for the PC with the plane defect. Compared with PC without the defect, the plane defect significantly changes the LDOS and changes the lifetime from about 20% average increase without the defect to 15% average decrease with the defect compared with the reference.

3.5 Chapter conclusion

The SE manipulation property of the PCs fabricated by two-photon OBL was experimentally and theoretically investigated in this chapter. A controllable and reliable method to integrate semiconductor QDs into PCs has been developed for quantitatively investigating purpose and for accurate design of the reference system. The integration of QDs into PCs transforms the PCs into photonic devices with unique SE manipulation functions. The SE modification with a PC was measured with a result which is consistent with the calculation based on the photonic LDOS theory. Limited by the low refractive-index of the PC material, the overlapping of different
direction stopgaps prohibits the observation of SE enhancement at the wavelength of the \( \Gamma \)-X direction stopgap band edge. This is predicted by the theoretical calculation and proofed by the experimental results. These results demonstrate the property of photonic LDOS defined SE manipulation. A defect can effectively change the LDOS in a PC. By inducing a plane defect, an average of 15\% emission lifetime decrease was obtained from a 20\% emission lifetime increasing without the plane defect. This result suggests that 3D OBL can design the structure geometry of the photonic devices flexibly which can well support SE manipulation with a tuned photonic LDOS.
Chapter 4

Theoretical study of diffraction-unlimited optical beam lithography

4.1 Introduction

To develop a three-dimensional (3D) optical beam lithography (OBL) technology by breaking the diffraction limit to achieve nanometre resolution, in this chapter, a theoretical framework suitable for different local lithography suppression mechanisms is developed. As a concrete mechanism and real mechanism adopted in the experiment in this thesis, diffraction-unlimited OBL based on the super-resolution photoinduced-inhibition lithography (SPIN) is studied. As polymer based photo-resin is the mostly used material for the fabrication of 3D artificial photonic structure with a laser, the object of theoretical investigation in this chapter is the polymer material based SPIN. Sec. 4.2 presents the theoretical framework. A kinetic model on SPIN is established in Sec. 4.3. Sec. 4.5 shows the numerical results of the kinetic model.

4.2 Theoretical framework

The diffraction-unlimited OBL in polymer based on the suppression of local polymerisation with a second doughnut-shaped beam such as SPIN involves laser
induced photo-polymerisation and anti-photo-polymerisation in the focal region of the fabrication system. The main concept for theoretical investigation of this technique is as follows [93]: In each local position of the focal region, the time dependent photo-physical and photo-chemical reactions of the photo-resin with two laser beams can be described as a set of differential equations which dominate the polymerisation process of the photo-resin in the focal volume. Due to the laser intensity difference in the focal region for both the fabrication beam and the confinement beam, each local position has a final conversion degree of the polymerised monomer, which indicates the percentage of the polymerised monomer in the local position. For the whole focal region, a conversion degree map of the polymerised monomer can be obtained. During the washing out process to remove the insufficiently polymerised photo-resin, partially polymerised photo-resin at the local positions with a conversion degree of the polymerised monomer below the conversion threshold was washed away. The remaining sufficiently polymerised part forms the structures designed to be fabricated.

The above concept builds up the framework for theoretical investigation of the diffraction-unlimited OBL in polymer with different mechanisms to suppress the local polymerisation [93]. First, kinetic processes rather than static processes are used to describe the photo-physical and photo-chemical reactions involved during the fabrication. In the focal region, the intensities of both the fabrication laser beam and the confinement laser beam vary with the local positions. In addition, the laser exposure time in a volume about the size of the fabrication laser beam focal spot is normally less than 1 second. A dynamic description can provide the details of different photo-physical and photo-chemical processes under the pumping of light with local position dependent intensities at a short period. This eventually leads to a conversion degree map of the polymerised monomer at the focal region. With the final conversion degree map calculated, the size of the formed structure after fabrication and after the removing of insufficient polymerised photo-resin can be
obtained which provides the necessary information for the evaluation of the fabrication feature size and resolution.

Generally, partially polymerised photo-resin with the polymerisation conversion degree of the monomer lower than the polymerisation threshold value is washed away during the washing out process [22]. Considering the percolation property of typical polymer materials, the threshold value of the polymerisation conversion degree of the monomer should be the gelation critical point of the polymer percolation system [94]. This threshold value of the polymerisation degree varies for photo-resins with different properties such as viscosity and the form of monomer linking. For the same conversion degree map of the polymerised monomer, the higher the polymerisation threshold value is, the smaller the structure size can be obtained. In this work, the used threshold value is 0.33 [95]. Then, the final conversion degree map of the polymerised monomer is determined by the real photo-physical and photo-chemical processes in each local position of the focal region. Different mechanisms to realise the lithography confinement to the centre of the focal volume can be described as different forms of differential equation set. Thus, different mechanisms can be investigated under this framework with different presentation forms of the differential equations. Though only photo-inhibition mechanism is investigated in this thesis, this framework provides the possibility of comparing the advantages and disadvantages of different mechanisms to realise diffraction-unlimited OBL based on the two-beam strategy.
4.3 Kinetic model of photo-inhibition assisted diffraction-unlimited optical beam lithography

The mechanism of the SPIN is to use a Gaussian-mode laser beam to do lithography and the other doughnut-shaped laser beam in the focal region to confine the lithography at the focal volume centre when these two beams are overlapped [94]. The Gaussian-mode beam is used to generate the initiator radicals to initiate the photo-polymerisation while the doughnut-shaped beam is used to produce the inhibitor radicals that react with the initiator radicals to form an inert molecule and to stop the photo-polymerisation at the doughnut ring of the inhibition beam (Fig. 4.1). As a result, the photo-polymerisation is confined at the centre of the focal spot, which can lead to smaller feature size and finer resolution beyond the diffraction limit. Figure 4.1 shows the related reaction processes.

![Figure 4.1 Schematic of the photo-physical and photo-chemical processes in the SPIN system.](image)

For each local position in the focal region, the fabrication beam and the inhibition beam can independently drive the photo-polymerisation and the photo-inhibition processes. The kinetic model presented here for photo-inhibition assisted
diffraction-unlimited OBL is based on the reaction processes involving photo-initiation, chain-propagation, chain-termination and photo-inhibition [96]. The following differential equations were used to describe the related photo-physical and photo-chemical processes for the photo-resin under the irradiation of the two laser beams in the focal region:

\[
\frac{dP_0}{dt} = -\sigma E E (P_0 - P_1) + \tau_1 P_1 + \tau_2 I_1 \\
\frac{dP_1}{dt} = \sigma E E (P_0 - P_1) - \tau_1 P_1 - \tau_2 I_1 - k_d P_1 + k_r P_2^2 \\
\frac{dP_2}{dt} = 2k_d P_1 - 2k_r P_2^2 - k_i P_2 M - k_i P_3 P_2 - r_l I_2 P_2 - r_k I_2 I_2 \\
\frac{dP_3}{dt} = k_i P_2 M + r_l I_2 M - k_i (P_3 + P_2) P_3 - r_l I_2 P_3 - r_k I_2 P_3 \\
\frac{dI_0}{dt} = -\sigma S S (I_0 - I_1) + \tau_2 I_1 + \tau_2 I_1 \\
\frac{dI_1}{dt} = \sigma S S (I_0 - I_1) - \tau_2 I_1 - \tau_2 I_1 - r_a I_1 + r_i I_2^2 \\
\frac{dI_2}{dt} = 2r_a I_1 - 2r_i I_2^2 - r_i I_2 M - r_i (P_3 + P_2) I_2 - r_k (P_3 + P_2) I_2 \\
\frac{dM}{dt} = -k_p P_3 M
\]

In these equations, the following conditions have been used:

a. \(P_0\) and \(I_0\) are the local concentrations of the photo-initiator and photo-inhibitor at the ground state; \(P_1\) and \(I_1\) are the local concentrations of the photo-initiator and photo-inhibitor at the excited state; \(P_2\) and \(I_2\) are the local concentrations of the photo-initiator and photo-inhibitor formed primary radicals, respectively; \(P_3\) is the local concentration of the initiator propagating radicals generated from the primary radicals and from the inhibitor radicals as a side effect. \(M\) is the local concentration of the monomers.
b. For the photo-initiator considered, when it is excited (one-photon excitation or two-photon excitation, with the absorption cross-section \( \sigma_E \)), the molecule is pumped to the excited state. The excited state molecule can form two initiator primary radicals (\( 2k_d P_1 \), Norrish type one initiator) [97] with the rate constant of the initiator primary radicals generation, \( k_d \) (for Norrish type two initiator, one initiator generates two primary radicals, but one of the generated radicals is weak. So its contribution can be omitted and only the term \( k_d P_1 \) [98] is used for this situation). As the primary radical recombination rate is slow, the recombination term in Eq. (4.2) is not considered. Recombination of the initiator radicals caused by the caging effect is considered (\( k_r P_2 P_2 \)) with a recombination reaction constant of photo-initiator radicals, \( k_r \). These initiator radicals can react with monomers to form propagating radicals with the kinetic constant rate of the initiation, \( k_i \). The propagating radicals lead to the propagation of the chain at the rate constant, \( k_p \), which contributes to the monomer polymerisation conversion. The termination of the propagating radicals and initiator radicals is also included with the constant rate of \( k_t \). \( \tau_1 P_1 \) and \( \tau n \) describe the radiation and non-radiation decay from \( P_1 \) to \( P_0 \), respectively.

c. For the photo-inhibitor, when it is excited (one-photon excitation or two-photon excitation, with the absorption cross-section \( \sigma_S \)), the molecule can be pumped to the excited state. Then the molecule in the excited state dissociates to generate inhibitor radicals (\( 2r_d I_2 \)) with the rate constant of the inhibitor radical generation, \( r_d \). Recombination of the inhibitor radicals caused by the caging effect is considered (\( r_r I_2 I_2 \)) with a recombination reaction constant of photo-inhibitor radicals, \( r_r \). Inhibitor radicals can react with the initiator radicals (\( r_k I_2 P_2 \)) and the chain radicals (\( r_k I_2 P_3 \)), which inhibits the polymerisation with the kinetic constant \( r_k \). As a side effect, inhibitor radicals can react with the monomers and form propagating radicals (\( r_i I_2 M \)) with the kinetic constant \( r_i \), which can also initiate the chain propagation with the kinetic constant of \( k_p \), and contribute to the monomer
polymerisation conversion. The terminations of the inhibitor radicals with initiator primary radicals and propagating radicals generated from the initiator radicals are also involved with the kinetic constant $r$, $\tau_2 I_1$ and $\tau n_2 I_1$ describe the radiation and non-radiation decay from $I_1$ to $I_0$, respectively.

d. The diffusion of the photo-initiator radicals, the photo-inhibitor radicals and chain radicals are also included and synchronized with the kinetic differential equations. The following simplifications are made in the model: first, the complex inhibition processes are simplified as the reactions of inhibitor radicals with the initiator primary radicals and the propagating radicals with the kinetic constant of $r_{kt}$, which forms inactive molecules. Other inhibition reaction processes are not considered. Second, all of the reaction kinetic parameters, which may vary during the reaction processes, are set as averaged constant values [96].

e. The initial conditions are: concentrations of initiators, inhibitors and monomers (molar percentage): $P_0$, $I_0$ and $M=1-P_0-I_0$, while $P_0$ and $I_0$ can be tuned. For example, if no photo-inhibitor is used, $I_0$ is zero. The monomer conversion-rate is defined as $1-M$. Initially, $P_1$, $P_2$, $P_3$, $I_1$, $I_2$ and $I_3$ are zeros.

### 4.4 Laser intensity distribution in the focal region

The equations in Sec. 4.2 determine the final polymerisation conversion degree of monomers for each local position. Under the irradiation of the fabrication beam and the inhibition beam, the photo-resin in the focal region is driven to form polymer according to the kinetic equation set. Under the same initial conditions with the same laser exposure time, the fabrication laser intensity and the inhibition laser intensity at a local position determine the local positional conversion degree of the polymerised
monomer. The degree map of the polymerisation monomer conversion in the focal region is the function of the local laser intensities of the fabrication and the inhibition beams in this situation. If the local laser intensities of the fabrication and the inhibition beams were known, the final conversion degree map of the polymerised monomer can be calculated. Consequently, the size and resolution of the formed features can be obtained. As a theoretical work to facilitate material development, size reduction and resolution improvement in two dimensions are considered here.

The focal profiles of the focused laser beam are calculated according to the references [99-101]. For the excitation beam, a completely coherent and linearly polarised beam (x direction polarised) was focused by a high numerical-aperture (NA) objective lens. The electric field of the focal region is expressed as [99-101]:

\[
E(r, \theta_p, \phi) = \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} = \frac{iK}{2\pi} \int_0^\alpha \int_0^{2\pi} A(\theta) \exp(i\phi) \sin \theta \sqrt{\cos \theta} \\
\times \exp\left[ikrn(\cos \theta \cos \theta_p + \sin \theta \sin \theta_p \cos(\phi - \varphi))\right] \\
\times \begin{bmatrix} (\cos \theta + 1) + \sin 2\phi(\cos \theta - 1) \\
(\cos \theta - 1) \\
-2 \sin \theta \cos \phi \end{bmatrix} d\theta d\phi
\]

(4.9)

here \( r, \theta_p, \phi \) are the spherical polar coordinates of an observation point, \( \phi \) is the azimuthal angle of the incident beam, \( \theta \) is the NA angle that varies from 0 to \( \alpha \) and the maximum angle \( \alpha \) is expressed as \( \alpha = \arcsin(NA/n) \) where \( n \) is the refractive-index of the material in the focal region. \( A(\theta) \) is the pupil apodization function at the objective aperture surface; \( \exp(i\phi) \) is the vortex phase factor of the incident beam. Here let \( m=0 \).

The inhibition beam is generated with circular polarized beam going through a \( 2\pi \) vortex phase plate with helical phase retardation from zero to \( 2\pi \) to focus with a
high NA objective. The $2\pi$ phase plate is used for lateral resolution improvement. For this $2\pi$ phase plate situation, the electric field of the focal region is expressed as [99-101]:

$$E(r, \varphi, z) = \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} = -\frac{ikf}{2\pi} \int_0^\alpha \int_0^{2\pi} A(\theta) \exp(i\phi) \sin \theta \sqrt{\cos \theta}$$

$$\times \exp[ik(z \cos \theta + r \sin \theta \cos(\varphi - \phi))]$$

$$\times (\cos^2 \phi \cos \theta + \sin^2 \phi) \pm i \cos \phi \sin \phi(\cos \theta - 1)$$

$$\times \cos \phi \sin \phi(\cos \theta - 1) \pm i(\cos^2 \phi + \sin^2 \phi \cos \theta) \sin \theta \exp(\pm i\phi)$$

\[ (4.10) \]

Here $r$, $\varphi$, $z$ are the cylindrical coordinates of an observation point, $\phi$ is the azimuthal angle of the incident beam, $\theta$ is the NA angle that varies from 0 to $\alpha$ and the maximum angle $\alpha$ is expressed as $\alpha = \arcsin(NA/n)$ where $n$ is the refractive-index of the material in the focal region. $A(\theta)$ is the pupil apodization function at the objective aperture surface; $\exp(i\phi)$ is the vortex phase factor of the incident beam; for $2\pi$ phase plate, let $m=1$; $k = 2\pi/\lambda$ is the wave vector and $f$ is the focal length of the high NA objective; The symbol $\pm$ comes from left hand and right hand circular polarised beam and in this calculation, plus is used.

**Figure 4.2** Focal spot profiles of the fabrication laser beam with wavelengths of 488 nm (a) and 800 nm (b) for the single and two-photon excitation respectively, and inhibition laser beam with the wavelength of 375 nm (c) in the focal region. The calculated area is $2 \mu m \times 2 \mu m$.  

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For all the above focal spot calculation, the NA of the objective lens is 1.4. The wavelengths for the fabrication laser beams are 488 nm for single-photon fabrication and 800 nm for two-photon fabrication, respectively. For the inhibition laser beam, the wavelength is 375 nm. Fig. 4.2 shows the focal spot profiles of these beams in the lateral plane of the focal region.

4.5 Photo-inhibition induced size reduction and resolution improvement in diffraction-unlimited optical beam lithography

4.5.1 Model validation

The model in Sec. 4.2 involves 18 parameters to specify the material properties. For a given material [22], the reaction constants can be fixed leaving only the laser powers of the fabrication and inhibition beams and the exposure time for the dot fabrication variable. To validate the model, a material used in our experiment is simulated. Figure 4.3 shows the simulation results (the initiator used here is a Norrish type two initiator) and the experiment data (details about the material, the fabrication and the washing-out process can be found in reference [22]). The sizes of the dots in the experiment were measured with a scanning electron microscope (SEM).

The power of the excitation laser beam is 200 nW. The corresponding exposure time is 700 ms. The parameters used in the calculation are as follows: The absorption cross-sections of initiators and inhibitors are 2.1×10^{-21} cm^{2} and 5.9×10^{-21} cm^{2}, respectively. $k_d=5×10^{-5}$ s^{-1}, $r_d=5×10^{-5}$ s^{-1}; $k_i=3×10^7$ cm^{3}mol^{-1}s^{-1}, $r_i=3.6×10^5$ cm^{3}mol^{-1}s^{-1}; $k_f=1×10^7$ cm^{3}mol^{-1}s^{-1}, $r_f=1×10^7$ cm^{3}mol^{-1}s^{-1}; $k_p=2×10^6$ cm^{3}mol^{-1}s^{-1}, $r_k=1.2×10^8$ cm^{3}mol^{-1}s^{-1}; $k_l=2.4×10^7$ cm^{3}mol^{-1}s^{-1}, $r_l=1.6×10^7$ cm^{3}mol^{-1}s^{-1}; $\tau_1$, $\tau_2$, $\tau_n$. 

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and \( n_2 \) are set as \( 1 \times 10^2 \text{ cm}^3\text{mol}^{-1}\text{s}^{-1} \). The diffusion constant of the initiator and the inhibitor radicals is \( 0.25 \ \mu \text{m}^2\text{s}^{-1} \) and the diffusion constant of the chain-initiating radicals is \( 0.05 \mu \text{m}^2\text{s}^{-1} \). These values were obtained from the literatures [97, 102, 101, 103, 104, 105] and estimated from the fits to the experimental data.

![Figure 4.3](image)

**Figure 4.3** (a) Dot sizes plotted as a function of the power of the inhibition laser beam. (b) The conversion degree map of the polymerised monomer in the focal region at the lateral plane for different levels of the inhibition beam power. The laser beam power corresponds to that used in the Fig. 4.3a. Each of the calculated pattern area is \( 2 \ \mu \text{m} \times 2 \ \mu \text{m} \).

As shown in Fig. 4.3, the model implies that the dot size decreases with the increasing of the inhibition beam power. This prediction is confirmed by the experiment, which indicates that the model is effective and the values of the 18 parameters from the references are reliable for the material used in this Fig. 4.3a. By increasing the inhibition beam power to 5 \( \mu \text{W} \), the dot size is significantly reduced from 1.23 \( \mu \text{m} \) to 0.38 \( \mu \text{m} \), which means a reduction of size by 2/3. However, further increase of the inhibition beam power does not reduce the dot size significantly, which indicates the saturation of the inhibition effect when the inhibition beam power is high. This feature is in line with the previously reported experimental results [62].
4.5.2 Photo-inhibitor induced polymerisation

The function of the inhibitor radicals in the material is to inhibit the initiator-triggered polymerisation. With the polymerisation at the ring region of the doughnut-shaped inhibition beam inhibited, the fabrication feature size can be tuned by changing the inhibition beam powers. It is expected that the fabrication feature size can be infinitely reduced to approach to zero under the ideal situation. However, the inhibitor radicals have the probability to react with the monomers and initiate the polymerisation. To make a comparison of $r_i$ with $k_i$, where $k_i$ is the reaction constant for the initiation induced by the initiator radicals, $r_i$ is normalized by $k_i$ ($r_i/k_i$, where $k_i$ is kept as a constant).

![Figure 4.4](image)

**Figure 4.4** (a) Dot size plotted as a function of the inhibition laser power with different reaction constants of the inhibitor radicals with monomers. (b) Calculated achievable dot minimum size for different $r_i/k_i$ values. The other parameters are the same as those used in Fig. 4.3.

As shown in Fig. 4.4a, the inhibitor induced polymerisation has a significant side effect on the size reduction. Dot size is increased and this phenomenon becomes more significant at high inhibition beam powers, when $r_i/k_i$ value increases. In particular, when an inhibition laser power is higher than 20 μW with $r_i/k_i =0.84\%$, significant photo-inhibitor induced polymerisation can be observed. Under such a circumstance, there exists a minimum achievable dot size with moderate inhibition laser power.
Figure 4.4b shows the minimum achievable dot size for different \( r/k_i \) values with the inhibition laser power ranging from 0 to 121 μW. For the situation of \( r/k_i < 0.5\% \), the dot minimum size is zero, which means all the polymerisation monomer conversion degree can be tuned below the threshold and the infinitely reduced feature size can be achieved with the photo-inhibition assisted diffraction-unlimited OBL in principle. For the situation of \( r/k_i > 0.5\% \), a minimum non-zero dot size is expected. This indicates that even when the photo-inhibitor induced polymerisation reaction rate is slow; there exists a limitation for the minimum achievable dot size, which is determined by the material and the fabrication parameters.

For the material used in the experiment, with the same fabrication parameters as those in Sec. 4.4.1, there exists a smallest dot size for different values of the inhibition beam power. However, this conclusion does not mean that the smaller dot size could not be achieved with different fabrication parameters, such as a shorter exposure time. Actually, dot size infinitely approaching zero is possible in theory if the maximum conversion degree of the polymerisation monomer after laser irradiation infinitely approaches to the threshold. However, during the washing out process, these infinitely small structures may be washed away due to the reasons such as surface tension or weak mechanical strength. To realise infinitely small structures fabricated by the photo-inhibition assisted diffraction-unlimited OBL, the material is required to have small \( r_i \) value and the fabricated structures are mechanically strong enough to survive during the washing out process.

### 4.5.3 Multi-dot fabrication simulation

As a candidate material for the photo-inhibition assisted diffraction-unlimited OBL, the minimum feature size is not the only valuable data to achieve lithography with
nanometre resolution. The minimum resolvable distance between two separated features is also valuable for the applications such as high-density data storage and photonic crystals (PCs). For the PC application, for example a woodpile structure, the smallest distance between two separated lines determines the minimum achievable lattice constants and thus determines the stopgap wavelength range. With a defined lattice constant, the smallest line size only determines the filling ratio of the woodpile PC. The stopgap wavelength range is limited by both the lattice constant and the filling ratio, but lattice constant is more important than the filling ratio as lattice constant determines the minimum achievable stopgap centre wavelength. For high-density feature arrays, the density is determined by the minimum resolvable feature distance. Smaller feature size does not necessary mean higher feature density. Here, the smallest distance between two separated dots (lines) is defined as the dot (line) resolution.

![Figure 4.5 Dot size and resolution plotted as a function of the inhibition laser power.](image)

For the single-photon case (a), all the parameters used are the same as those in Fig. 4.3. For the two-photon fabrication case (b), all the parameters related to photo-inhibitor are the same as those used in Fig. 4.3.

For the same parameters used in Sec. 4.4.1, the dot size and the resolution data are plotted as a function of the inhibition laser power in Fig. 4.5. As is known from Sec. 4.4.2, with \( r/k_i = 0.36\% \) for the material, the fabricated dot size can be reduced to zero by increasing the inhibition beam power. However, the dot resolution does not follow
the same trend as that of the dot size, which is greatly different from the single or two-photon OBL with a single beam exposure where dot size and dot resolution always follow the same trend. From Fig. 4.5, the dot resolution can be improved by increasing the inhibition beam power. A further increasing of the inhibition beam power does not improve the dot resolution, but on the contrary deteriorate the dot resolution. For single-photon fabrication situation, the inhibition laser power to achieve the best resolution is 14 μW. However, the dot size can be further reduced by increasing the inhibition beam power. In the photo-inhibition assisted diffraction-unlimited OBL with fixed fabrication beam power, the dot minimum size and best resolution occur under different inhibition beam powers. Compared with the dot resolution calculation with $r_i/k_i = 0$ (Fig. 4.5a, blue curve), this feature can be attributed to the photo-inhibitor induced polymerisation. Similar phenomenon can also be observed in the two-photon fabrication case (Fig. 4.5b).

Experiment work conducted on two-photon excitation and single-photon inhibition with the same inhibitor molecules also shows this different behaviour of dot size and two-dot resolution. As shown in Fig. 4.6, the inhibition beam power to achieve best resolution is 4 μW while the inhibition beam power to achieve smallest dot size is 7 μW. This result indicates a balance between the fabrication minimum size and best resolution in the photo-inhibition assisted diffraction-unlimited OBL for complex structure fabrication in the experiment. In addition, materials with a low $r_i/k_i$ value are vital for realising the fabrication feature size and resolution beyond the diffraction limit with the photo-inhibition assisted diffraction-unlimited OBL. As the photo-inhibition exhibits the ability to reduce fabricated feature size and resolution both in theory and in experiment, it is of great potential of the photo-inhibition assisted diffraction-unlimited OBL to break the diffraction limit to achieve nanometre resolution if a material with sufficient mechanical strength and low $r_i/k_i$ value can be developed.
Figure 4.6 shows dot size and resolution for different inhibition laser powers. The dot sizes were measured from the scanning electron microscopy (SEM) images of the separated dots. The dot resolution was determined from the shortest distance between two separated dots. From up to down, each line is eleven dot pairs fabricated with distance changing from 300 nm to 1300 nm (from right to left with 100 nm increment in each step). The dot pairs fabricated with small separation distance connect to each other and form a large dot, while the dot pairs fabricated with a distance larger than the dot resolution can be separated and remains as two dots. The smallest distance for two dots to keep separated is used as the experimental dot resolution value. The plot in Fig. 4.6 shows the different dependences of the dot size and resolution on the inhibition beam power. The data shows a fabrication window to fabricate structures with moderate feature size and feature resolution. With the photo-inhibition assisted diffraction-unlimited OBL to fabricate complex structures, it is important to consider both the fabrication feature size and feature resolution requirement.

![Figure 4.6](image)
The formulation of the photo-resin was composed of 0.02 wt% 2,5-bis(p-dimethylamino cinnamylidene) cyclopentanone, 0.5 wt% camphorquinone and 0.5 wt% ethyl4-(dimethylamino)benzoate as photo-initiator components, and 2.5 wt% tetraethylthiuram disulphide (TED) as the photo-inhibitor, and 96.48 wt% SR 349 (Sartomer Inc.). The dots were fabricated with the fabrication beam power of 20 mW at the wavelength of 800 nm. The inhibition beam wavelength was 375 nm and the exposure time was 50 ms. The fabrication beam laser operates at repetition rate of 80 MHz with a 140-femtosencond pulse width. The inhibition beam laser works at the continuous wave (CW) mode. These two beams are overlapped and introduced to an objective lens with a NA of 1.4. The dot fabrication exposure time is 50 ms. After fabrication, the gelated structure was washed out by rinsing the structure in pure isopropanol for 5 mins, then in pure acetone for 2 secs and then in pure ethanol for 2 secs. This photo-resin is designed to show the different behaviour of dot size and two-dot resolution because of not perfect \( r_i/k_i \) value. Though fabrication dot size reduction and resolution improvement is realised, the photo-resin has a monomer that is not benefit for the surviving of features with nanometre size and shows significant photo-inhibitor induced polymerisation phenomenon as prediction. The development of a more powerful photo-resin aiming for 3D OBL with feature size below 10 nm and resolution smaller than 100 nm is introduced in Chapter 5.

**Figure 4.7** Simulation of four sequentially fabricated dots for different values of the inhibition beam laser power (from a to e). All the parameters are the same as those used in Fig. 4.3. Each of the calculated pattern area is 2 \( \mu \text{m} \times 2 \, \mu \text{m} \).
Finally, the effect of the photo-inhibitor concentration on the fabrication of complex structures was investigated. Figure 4.7 shows the simulation of the sequential fabrication of four dots with a time interval of 3 folds of the dot exposure time for different levels of the inhibition laser power. The first fabricated dot is plotted in the up position, the second down, the third left and the forth right. With the increasing of the inhibition laser power, the dot size and the resolution can be both improved. However, at the high level of the inhibition laser power, the four dots after the fabrication are not uniform. This is because after the fabrication of the first and second dots, the photo-inhibitor molecules near the third and the forth dots have been partially consumed. When the third and fourth dots are fabricated adjacent to the first and the second dots, the reduced concentration of the photo-inhibitor molecules leads to the weak confinement of the polymerisation and consequently a larger dot size. In experiment, this problem can be solved by adding sufficient amount of the inhibition molecules in to the photo-resin. The fabrication of the first and the second dots consumes part of the inhibitor molecules, however, there are still enough inhibitor molecules to provide strong enough inhibition effect for the third and the forth dots fabrication.

4.6 Chapter conclusion

To theoretically investigate the OBL with the aim of fabricating features with size and resolution beyond the diffraction limit, a kinetic model based on the photo-physics and the photo-chemistry processes for the SPIN has been established. With this model, SPIN with the fabrication dot size and resolution beyond the diffraction limit has been studied. Numerical simulation results indicate that this technique can effectively reduce the dot size and improve the resolution to the nanometre range, which shows
the diffraction-unlimited potential of this technique. The reasons limiting the reduction of the feature size and the improvement of the resolution include the caging effect of the initiator and inhibitor radicals and the photo-inhibitor induced polymerisation. As one of the most interested and important issues for SPIN, the photo-inhibitor induced polymerisation has been investigated with details and the results indicate it has a significant side effect to the size reduction and resolution improvement according to the simulation. It has been discovered theoretically that the dot minimum size and best resolution occur under different inhibition beam powers with this technique. It has been also found that the dot size and dots uniformity in the sequential fabrication can be affected by the variation of the concentration of the photo-inhibitor molecules. With sufficient quantities of inhibition molecules, this problem can be solved.

The investigation in this chapter shows that SPIN has the ability to fabricate structures with a smaller feature size and a better resolution than the single-beam diffraction-limited OBL. This can be used to develop diffraction-unlimited OBL with a resolution down to the nanometre range. The investigation about the material hints the development of suitable materials for 3D diffraction-unlimited with resolution at the nanometre range.
Chapter 5

Three-dimensional diffraction-unlimited optical beam lithography

5.1 Introduction

Optical beam lithography (OBL) based on far field focusing through a high numerical aperture (NA) objective lens [4] is a most powerful approach to three-dimensional (3D) nanofabrication (Fig. 5.1b). This is the most important advantage of far field OBL compared with other nanofabrication method such as electron-beam lithography (EBL) (Fig. 5.1a), ion-beam lithography and maskless plasmonic lithography. Although the diffraction nature of light is the basic physical barrier preventing the achieving of sub-diffraction or nanometre resolution with the diffraction-limited far field OBL system [6], this physical barrier can be overcome technically by utilising the properties of the material. Two-beam OBL based on the polymerisation and photo-inhibition strategy [22, 61-63, 106] is thought to be promising for 3D fabrication to break the diffraction limit to achieve nanometre resolution (Fig. 5.1c). In principle, this technique based on diffraction-limited optical system can infinitely reduce the fabrication feature size and improve the fabrication resolution beyond the diffraction limit if a photo-resin with large two-photon absorption cross-section, sufficiently high mechanical strength and significant photo-inhibition effect can be developed. But it has been impossible to realise the fabrication with resolution comparable to that achievable by EBL due to the lack of appropriate photo-resins. In
this chapter, the experimental details done to develop the 3D diffraction-unlimited OBL with feature size and resolution down to the nanometre range is presented. Sec. 5.2 introduces the development of a new photo-resin for 3D diffraction-unlimited OBL with the polymerisation and photo-inhibition strategy. Sec. 5.3 and Sec. 5.4 shows the experiment work on size reduction and resolution improvement with this 3D diffraction-unlimited OBL technique based on the new photo-resin.

**Figure 5.1** Comparison of EBL (a), diffraction-limited (b) and diffraction-unlimited (c) OBL. (a) EBL can achieve high resolution about 50 nm; however, EBL is incapability of 3D fabrication. (b) Diffraction-limited OBL can fabricate 3D arbitrary geometry; however, the diffraction nature of light limits fabrication resolution. (c) 3D Diffraction-unlimited OBL has the advantage of fabricating 3D arbitrary geometry with nanometre feature size and resolution comparable to EBL by the photo-inhibiting strategy. The image in the inset shows the focal spot of the fabrication beam and the inhibition beam.
5.2 New photo-resin development for three-dimensional diffraction-unlimited optical beam lithography

The key to develop 3D OBL by utilizing the polymerisation and photo-inhibition strategy with feature size and resolution beyond the diffraction limit is the development of a unique material with two different chemical activation channels. One is for two-photon polymerisation (2PP) and the other is for photo-inhibition. For this aim, the material should be designed to satisfy the following requirements. First, it should include an initiator that is highly photo-sensitive to two-photon absorption which is induced by the fabrication beam. This allows the near threshold fabrication to fabricate small sized features. Accordingly, it is possible to achieve a minimum degree of photo-polymerisation monomer conversion, which is required for building solidified structures with a feature size smaller than the focal spot of the fabrication beam. This is the basis to get resolution beyond the diffraction limit. Second, it should exhibit an effective inhibition of the 2PP process that corresponds to a doughnut-shaped inhibition beam in a wavelength region different from the fabrication beam wavelength. This serves as the critical component for size reduction and resolution improvement based on two-photon OBL. The cross excitation between the fabrication and the inhibition beams, which means the excitation of the inhibitor by the fabrication beam or the excitation of the initiator by the inhibition beam, should be avoided. Third, the threshold intensity $I_{th}$ for the fabrication beam to generate 2PP should be as low as possible to avoid photo-damage and uncontrolled thermal process. The photo-damage and uncontrolled thermal process can not only influence the 2PP process but influence the performance of the photo-inhibition. This also requires that the monomer has low polymerisation gelation threshold. Fourth, it should exhibit sufficient mechanical strength so that the structures fabricated at the
near threshold condition can survive during the washing out process and withstand the unavoidable stress for 3D structures. Structures with a conversion degree of the polymerised monomer higher than the polymerisation threshold could be disintegrated and thus could not survive during the washing out process if the mechanical strength is not good enough.

A critical development of the new photo-resin was the appropriate selection of a photo-initiator that satisfies the conditions 1, 2 and 3. For the realisation of 3D diffraction-unlimited OBL with nanometre feature size and resolution, three two-photon photo-initiators, bis(4-(dimethylamino) phenyl)methanone (BDEP), 2,5-bis-[4-(dimethylamino)benzylidene]cyclopentanone (BDMA), and 2,5-bis(p-dimethylamino cinnamylidene) cyclopentanone (BDCC) were introduced into the formulation [71].

The BDEP, known as Michler’s ketone, was purchased from Sigma-Aldrich and used as supplied. The synthesis of the BDMA and BDCC were performed using a general method as outlined in the literature [22, 107]. The synthesis of the BDCC is as follows [22]: Lithium hydroxide monohydrate (0.1 ME, 28 mg, 0.671 mmoles) was added to cyclopentanone (1 ME, 0.564 g, 6.71 mmoles) in ethanol (12 ml) and stirred for 10 minutes. Then N,N-dimethylamino -p-benzaldehyde (2 ME, 2 g, 13.4 mmoles) was added and the reaction was stirred overnight. The reaction was worked up by dilution with ethanol and collection by filtration. The material was recrystallised from chloroform (ca. 150 ml for 3 grams) to give 0.65 g. The mother liquor was evaporated to half the initial amount and another 0.85 g was harvested. Both batches were of the same high purity. $^1$H NMR (CDCl$_3$, 400 MHz) δ 3.03 (s, 6H, CH$_3$), 3.07 (s, 4H, CH$_2$), 6.73 (d, 2H, aromatic J 8.7 Hz), 7.52 (s, 2H, =CH-), 7.55 (d, 2H, aromatic, J 8.7 Hz) ppm.

The synthesis of the BDMA is as follows [107]: Lithium hydroxide monohydrate (0.1 ME, 28 mg, 0.671 mmoles) was added to cyclopentanone (1 ME, 0.564 g, 6.71
mmoles) in ethanol (12 ml) and stirred for 10 minutes. Then N,N-dimethylamino-p-benzaldehyde (2 ME, 2 g, 13.4 mmoles) was added and the reaction was stirred overnight. The reaction was worked up by dilution with ethanol and collection by filtration. The material was recrystallised from chloroform (ca. 150 ml for 3 grams) to give 0.65 g. The mother liquor was evaporated to half the initial amount and another 0.85 g was harvested. Both batches were of the same high purity. 

$^1$H NMR (CDCl$_3$, 400 MHz) δ 3.03 (s, 6H, CH$_3$), 3.07 (s, 4H, CH$_2$), 6.73 (d, 2H, aromatic J 8.7 Hz), 7.52 (s, 2H, =CH-), 7.55 (d, 2H, aromatic, J 8.7 Hz) ppm.

**Figure 5.2** Single-photon absorption spectra and two-photon absorption cross-section of three two-photon initiators. (a) BDCC. (b) The molecule structure of BDCC. (c) BDEP. (d) BDMA. The inserts show the structures of the initiator molecules.

The BDCC was selected as the used initiator (Fig. 5.2a and 5.2b) which is an example of the D-π-A-π-D class of non-linear dyes. The π-conjugated ketone
derivatives of this class [108-110] were examined to be capable of two-photon excitation. They have electron donating diakylamino groups and carbonyl groups as the electron withdrawing (acceptor) group that can also allow hydrogen abstraction for subsequent initiation of free radical polymerisation. Moreover, the length of π-conjugated chain in between donor and acceptor parts allowed tuning the position of the absorption band into the visible region (Fig. 5.2a) and led to the enhancement of the two-photon cross-section (Fig. 5.2a) compared with that of BDEP (Fig. 5.2c) and BDMA (Fig. 5.2d). The red shifted absorption band of BDCC facilitated the inhibition process when tetraethylthiuram disulfide (TED) was adopted as an ultra-violate (UV) inhibitor. It was evident that the absorption peak of BDCC was shifted to 511 nm from 360 nm of BDEP or from 480 nm of BDMA which both had shorter lengths of π-conjugation (Fig. 5.2).

To measure the two-photon cross-section of the two-photon initiators, the Z-scan method was used [111]. A femtosecond (fs) pulsed laser beam (Spitfire, Spectra-Physics, USA) with a repetition rate of 1 KHz, a pulse width of 110 fs and a wavelength of 800 nm was used as the light source. A convex lens with the focal length of 250 mm was used to focus the laser beam into the sample. The sample solution was sandwiched in a quartz cell with a thickness of 1 mm. It was prepared by dissolving the BDEP, BDMA and BDCC in chloroform, respectively, with a concentration of $2 \times 10^{-4}$ M.

The two-photon cross-section of BDCC at 800 nm wavelength was enhanced to 293 GM from 128 GM of BDEP or from 225 GM of BDMA (Fig. 5.2). In the meantime, the laser intensity threshold $I_{th}$ for 2PP with BDCC was reduced to 75.75 mW/cm$^2$ from 303.03 mW/cm$^2$ (BDEP) or from 189.39 mW/cm$^2$ (BDMA) at the scanning speed of 160 μm/s. Among these initiators, BDCC exhibited the highest two-photon cross-section and low absorption potential under the exposure of the inhibiting beam operating at a wavelength of 375 nm. Based on these considerations,
BDCC was selected to use in the formulation for the 3D diffraction-unlimited OBL based on the photo-inhibited polymerisation method. As a photo-initiator, BDCC also facilitates the easy inhibition of polymerisation with photo-inhibitor, which provides the possibility for photo-inhibition assisted OBL.

For the photo-inhibitor, TED was introduced to the formulation, which can generate inhibitor radicals to scavenge propagating and initiator radicals to inhibit the polymerisation. The photo-inhibitor was excited by a laser beam with a wavelength of 375 nm working at the continuous wave (CW) mode. To avoid the excitation of the photo-inhibitor by the fabrication beam, the photo-inhibitor has no single-photon absorption and two-photon absorption under the exposure of the fabrication beam with the wavelength of 800 nm and this was shown in Fig. 5.3.

![Figure 5.3](image)

**Figure 5.3** Single-photon absorption spectrum and two-photon absorption cross-section of the photo-inhibitor. The insert show the structure of the inhibitor molecule.

For the selection of monomers, a five-functional monomer, SR399 (Dipentaerythritol pentaacrylate, Fig. 5.4a), was used to improve the chemical reactivity for high photosensitivity and mechanical strength against the shrinkage and damage during the developing process. Compared with other less-functional
monomers, this five-functional monomer supports a lower gelation threshold of the monomer conversion degree. It is also thought to be helpful for more uniform structure fabrication at the near threshold. Structure uniformity plays a critical role for small size freestanding features to withstand the tension as not to be pulled off. Another tri-functional monomer, SR 444 (Pentaerythritol triacrylate, Fig. 5.4b), was introduced to keep the viscosity from decreasing the photo-inhibition efficiency. These two multi-functional monomers contribute sufficient photo-polymerisation at low excitation power of the fabrication beam to avoid photo-damage and unwanted thermal process.

![Molecule structure of monomers](image)

**Figure 5.4** The molecule structure of the monomers used in the photo-resin. (a) SR399. (b) SR444.

With a standard initiation system of camphorquinone (CQ) and ethyl 4-(dimethylamino)benzoate (EDAB) as co-initiator, the photosensitivity of the final photo-resin was confirmed to be at 0.18 g/J, implying at least two orders of magnitude higher than that of the formulation used in the single-photon fabrication [22].

To prepare the photo-resin, the photo-initiator (BDCC), co-initiators (CQ and EDAB) and the photo-inhibitor TED were firstly dissolved in chloroform and then mixed with the monomers. The mixture was kept in the oven at the temperature of 50 °C for 24 hrs to remove the chloroform. The final formulation of the photo-resin was composed of 0.02 wt% BDCC, 0.5 wt% CQ and 0.75 wt% EDAB as
photo-initiator components, and 2.5 wt% TED as the photo-inhibitor, and 96.23 wt% monomer blends of SR399 and SR444 (40:60 wt%) (Sartomer Inc.). The photo-resin was baked at 60 °C for 10 mins before fabrication. Samples used for the fabrication were prepared by sandwiching a drop of the photo-resin between two coverslips separated by 60 μm with thick sticky-tapes.

5.3 Experimental setup and fabrication characterisation

Figure 5.5 Schematic of the setup for 3D diffraction-unlimited OBL.

Figure 5.5 shows the setup of the 3D diffraction-unlimited OBL system. A fs pulsed laser (Coherent, chameleon, USA) with a wavelength of 800 nm was used as the fabrication beam which is operated at a repetition rate of 80 MHz with a
140-femtosecond pulse width. After beam expansion, the fabrication beam was introduced into a high NA objective lens (NA=1.4, Olympus). A CW mode laser (Coherent-cube, USA) with a wavelength of 375 nm was adopted as the inhibition beam. The inhibition beam was expanded after going through a half wave plate. It was then modulated by a phase plate (RPC Photonics Inc. USA) to generate a doughnut-shaped focus profile with zero intensity at the centre of its focal region for spatially confined photo-polymerisation. Then, the inhibition beam was overlapped with the fabrication beam at a dichroic mirror (DM) and focused by the objective lens. A $\lambda/4$ wave plate was used to modulate the inhibition beam to a circular polarised beam. Confocal detector photomultiplier (PMT) were used for the alignment of the system and the overlapping of the two beams. The intensity of the two beams was measured exactly before their entering the objective with a fabrication beam size of 26.4 mm$^2$ and an inhibition beam size of 86.6 mm$^2$. A charge-coupled device (CCD) camera was used to monitor the fabrication. The applying of the fabrication beam and the inhibition beam to the photo-resin for diffraction-unlimited OBL was simultaneously.

For all the fabricated freestanding structures, they are suspended by a frame with a height of about 3 microns above the cover slip. The fabricated freestanding lines are about 900 nm lower than the up surface of the frame. The frame is adhered with the cover slip. After fabrication, the cover slip without the sticking of the fabricated structure was mechanically taken off with care then the structures were rinsed with isopropanol for 5 mins, then acetone for 2 secs and then ethanol for 2 secs. The structure was dried in air at the room temperature.

The fabricated structures were measured with a ZEISS Supra 40 VP Field Emission scanning electron microscopy (SEM). Before the measurement, the sample was coated with a gold layer with the thickness of 5-6 nm for the case without inhibition beam and 1-2 nm for the case with inhibition beam. The size of the fabricated feature
is obtained based on the cross sectional profile of the feature in the SEM image. Figure 5.6 shows the measurement of linewidth of a freestanding nanowire based on the SEM images. The full width at the two thirds maximum was used for conservative estimation.

![Figure 5.6](image)

**Figure 5.6** The measurement of the linewidth based on the SEM image. (a) A SEM image shows the measurement of a line. The yellow straight line indicates the position selected for cross sectional view. (b) The plot of the cross sectional profile of the yellow line in (a).

5.4 Feature size reduction with three-dimensional diffraction-unlimited optical beam lithography

With our new two-photon absorption photo-resin which facilitates an immediate polymerisation degree threshold operation (Fig. 5.7a), the 800 nm wavelength laser beam can produce not only a dot size of 95 nm (not shown here) but also the freestanding nanowires of linewidth beyond the diffraction limit. Without the inhibition beam, the feature size, i.e. the linewidth of the nanowire could be reduced from 150 nm (Point A in Fig. 5.7b) to 42 nm (point B in Fig. 5.7b), if the energy dose
was decreased from 8 times of $E_{\text{min}}$ to $E_{\text{min}}$. The energy dose was tuned in the experiment by changing the scanning speed of the fabrication beam by increasing from 20 $\mu$m/s to its near threshold of 160 $\mu$m/s with 20 $\mu$m/s increasing each step when the fabrication beam intensity is 75.75 mW/cm$^2$. There exists a minimum energy dose $E_{\text{min}}$ for the fabricated polymer feature to survive against destructive forces. The maximum polymerisation monomer conversion degree corresponding to $E_{\text{min}}$ is higher than the polymerisation monomer conversion degree threshold but only structures with strong enough mechanical strength can survive.

This result confirms that the monomers in the photo-resin allow the fabricated structures with feature size down to 42 nm to have enough mechanical strength to survive during the post-irradiation developing process and to become freestanding structures. Though the nanowire linewidth of 42 nm which is much smaller than the full width at the half maximum (FWHM) of the focal spot (point B in Fig. 5.7a) was achieved in the new photo-resin, the focal spot of the fabrication beam was still formulated by the diffraction nature of light. A further decrease of the energy dose of the fabrication beam decreased the degree of photo-polymerisation monomer conversion at the focal centre, leading to the disintegration of the fabricated structures after the developing process. This result indicates a critical limitation in the diffraction-limited OBL for features with size far beyond the diffraction limit due to the existence of the material threshold for structure surviving in the focal centre, resulting from the minimum degree of photo-polymerisation monomer conversion required to compete with deconstructive forces, such as the surface tensions.
Figure 5.7 Feature size (the linewidth) decreasing with the 3D diffraction-limited OBL and the 3D diffraction-unlimited OBL. (a) Schematic demonstration of the linewidth decreasing by decreasing the energy of the fabrication laser beam close to the polymerisation degree threshold of the photo-resin. (b) Feature size versus the fabrication laser beam dosed energy into the new photo-resin. (c) Schematic illustration of reduced feature size by increasing the inhibition beam intensity. The yellow arrow indicates the direction of increasing the laser intensity of the inhibition beam. (d) Nanowire Feature size versus the inhibition beam intensity. The scatter dots with error bars represent the experimental results. Curves guide the scatter dots with error bar are the fitting with the empirical formula. The insert pictures show the SEM images of B, C, D, E and F with a scale bar of 100 nm.

The inhibition beam is introduced to confine the photo-polymerisation at the centre of the focal spot. This photo-induced inhibition of polymerisation was happened by the chemical reaction of the inhibitor generated radicals with the initiator generated radicals and thus failed the polymerisation initiated by the initiator. Tetraethylthiuram disulfide was introduced for this exact purpose of photo-inhibition. Since the inhibition process is achieved immediately near the threshold at the doughnut-shaped
ring of the inhibition focal spot in the new photo-resin, the photo-polymerisation monomer conversion degree profile becomes sharper (Fig. 5.7c) and thus the photo-polymerised feature size can be further reduced (Fig. 5.7d). As this method only inhibits the photo-polymerisation in the ring of the doughnut-shaped inhibition beam, the degree of photo-polymerisation monomer conversion at the focal centre does not change and remains above the threshold, allowing the photo-polymerised structure to survive during the developing process. With the inhibition beam of intensity levels of 0.69 μW/cm², 1.15 μW/cm², 1.62 μW/cm², 2.31 μW/cm² and 2.42 μW/cm², the feature size, i.e. the linewidth of the freestanding nanowires, is experimentally reduced from 42 nm (point B in Fig. 5.7d) to 34 nm (point C in Fig. 5.7d), 25 nm (point D in Fig. 5.7d), 18 nm (point E in Fig. 5.7d), 11 nm (point F in Fig. 5.7d) and 9 nm (point G in Fig. 5.7d), respectively. This result agrees with the prediction by the theoretical numerical simulation, which is shown in Fig. 5.8b.

**Figure 5.8** (a) Cross sectional profiles of the fabrication and the inhibition beam focal spots. (b) Feature size variation with the inhibition beam intensity for experimental data (blue squares) and the fitted curve (red) overlapped by the simulation curve (black).

A theoretical model was used to simulate the two-photon excited 3D diffraction-unlimited OBL based on 2PP and single-photon inhibition. The concrete model was based on the framework established in Chapter 4 and modified from that
for two-photon fabrication and single-photon inhibition. The parameters used in the simulation were the same as in the experiment for the concrete initiator, inhibitor and monomer used. The focus profiles of the fabrication and the doughnut-shaped inhibition beam were calculated according to the formula listed in Chapter 4 and their cross sectional were shown in Fig. 5.8a. Reaction processes involving photo-initiation, chain-propagation, chain-termination and photo-inhibition were also considered. All the photo-physical and photo-chemical processes were expressed as a set of differential equations for two-photon fabrication and single-photon inhibition. A final conversion degree map of the polymerisation monomer at the fabrication focal region could be obtained after the irradiation of the fabrication beam and the doughnut-shaped inhibition beam. The partially polymerised photo-resin with a polymerisation monomer conversion degree lower than the threshold value 0.33 [95] was washed away during the developing process. The feature size of the final fabricated structures was calculated based on the remained polymerised photo-resin after the developing process. The numerical simulation data was shown in Fig. 5.8b. The experimental and numerical simulation data of linewidth for single line fabrication with the help of the inhibition beam can be fitted with an empirical formula (Fig. 5.8b. Consider the resolution formula of STED imaging [59, 60], an empirical formula with a similar form is used here.): \[
\text{linewidth (nm)} = \frac{\alpha_1 \sqrt{1 + \beta_1 \times \frac{I_{\text{inhibition}}}{I_S}}}{}
\] with \(\beta_1 = 0.44 \text{ (\mu W/cm}^2\text{)}^3\) and \(I_S\) is defined as the inhibition beam saturation intensity which is related to the properties of the fabricated photo-resin. The \(\alpha_1\) is a parameter related to the inhibition beam conditions. This formula stands with different \(\alpha_1\) values when the inhibition beam applied at different scanning speed conditions to give different energy doses into the photo-resin as can be seen in Fig. 5.7d. When the inhibition beam scanning speed is 100 \(\mu\text{m/s}\), 120 \(\mu\text{m/s}\), 140 \(\mu\text{m/s}\) and 160 \(\mu\text{m/s}\) respectively, the corresponding \(\alpha_1\) value is 34.48 (nm), 53.80 (nm), 82.10 (nm), 109.00 (nm). The fabrication of lines with width below 50 nm with higher energy dose of the fabrication beam and higher inhibition beam intensity means the
possibility of fabrication small sized features with high exposure latitude of both the fabrication beam dose and the inhibition beam intensity, which is highly meaningful for industry application. It is clear that the size dependence determined by
\[ \frac{\alpha_\lambda}{\sqrt{1 + \beta_\lambda I_{\text{inhibition}}^{1/4} I_\lambda}} \]
reveals the diffraction-unlimited size reduction ability with the help of the inhibition beam in the far field optical components based OBL system.

*Figure 5.9* Axial direction linewidth of nanowires fabricated by the 3D diffraction-unlimited OBL. The insert shows two examples of the SEM measured data and a schematic of angle tilt SEM measurement. The scale bar is 100 nm.

This amazing size decreasing feature holds in the axial direction as shown in Fig. 5.9. According to the 45 degree tilted SEM measurement image of a freestanding nanowire fabricated by the 3D diffraction-unlimited OBL with 2PP and single-photon inhibition, the feature sizes in the lateral and axial directions of the laser beams were estimated to be 23 nm and 32 nm, respectively. The estimation of the axial direction linewidth is based on the assuming that the fabricated lines have elleptical
cross-section. This result shows that the experimental linewidth aspect ratio of the axial direction to lateral direction is about 1.3.

Several 45 degree tilted measured SEM images of the freestanding nanowires fabricated by the 3D diffraction-unlimited OBL for different fabrication beam and inhibition beam conditions were measured. The estimated aspect ratios based on the the 45 degree tilted SEM measurement are between the range from 1.1 to 1.55 (Fig. 5.9) which show significant size decrease in the axial direction with the help of the inhibition beam from about 2.5. This result is amazing as there is no axial direction optical confinement used in the experiment. However, in the experiment, the light generated photo-inhibitor radicals have the ability of diffusion as molecules. This is different from the stimulated emission depletion (STED) based polymerisation confinement method where the polymerisation in the axial direction can not be confined when there is no axial direction optical confinement. This inhibitor radical diffusion contributes to the axial direction linewidth reduction. The best axial direction resolution is estimated to be less than 83 nm.

Figure 5.10 A typical SEM image of a freestanding V-shape shows the shrinkage effect on the feature size of the fabricated polymer structure. The scale bar is 200 nm.

The mechanical strength of the fabricated structures with the photo-resin should be good enough to support structure fabrication with no significant shrinkage. As
shrinkage can significantly affect the measured feature size, it is important to know the shrinkage property of the fabricated structure with the photo-resin. To test its influence to linewidth, a freestanding V-shape structure was fabricated with the writing beam intensity of 75.75 mW/cm² and the inhibition beam intensity of 0.69 μW/cm² with a scanning speed of 160 μm/s. A typical result shown in Fig. 5.10 shows no significant linewidth change of the V shape. As tension is unavoidable for freestanding structures, if shrinkage was significant, a V-shape with significant smaller linewidth at the V arm-centre was expected. The measured maximum linewidth decrease from the top to the bottom of the V-shape is 16% which shows no significant shrinkage and confirms that the method used to decrease the fabrication feature size is effective.

5.5 Resolution improvement with three-dimensional diffraction-unlimited optical beam lithography

In Ernst Abbe’s imaging theory, resolution means the distance of two objectives that can exactly be distinguished by the far field optical imaging system. Three-dimensional OBL plays the post-treatment games [58] can achieve features with size much smaller than the FWHM of the diffraction limited focal spot (the red curve of Δ off in Fig. 5.11a), however, they do not produce much smaller feature distance (the red curve of Δ off in Fig. 5.11a). So feature size could not reflect the ability of OBL to fabricate high density feature arrays. The beauty of OBL with 2PP and single-photon inhibition is the ability to realise 3D fabrication feature size and resolution far beyond the diffraction limit. As the photo-polymerisation at the ring of the doughnut-shaped inhibition beam is inhibited, the fabricated feature size can be smaller than that without the inhibition beam (the red curve of Δ on in Fig. 5.11a)
and this allows the fabrication of features with closer distance (the red curve of $\text{\Delta off}$ in Fig. 5.11a). Though feature with size far beyond the diffraction limit is the necessary but not the sufficient condition for feature distance beyond the diffraction limit, the technique which can fabricate feature down to 9 nm provides the prerequisite for high density feature array fabrication with resolution down to 100 nm or even to 50 nm.

As a most important parameter for laser fabrication, the resolution of our diffraction-unlimited OBL is judged by how close of two adjacent lines can be fabricated. Because the fabrication of the first line with the help of the inhibition beam consumed part of the photo-inhibitor, the inhibition effect for the second line fabrication was determined by the remaining local concentration of the photo-inhibitor. If the first line fabrication consumed most of the local photo-inhibitor, then the weak inhibition effect for the second line fabrication could prevent the achieving of feature size and resolution far beyond the diffraction limit. To avoid this, twice the amount of the photo-inhibitor compared with the photo-initiator was added into the photo-resin to provide sufficient photo-inhibitor concentration for high density feature fabrication.

To measure the fabrication resolution of the 3D diffraction-unlimited OBL and to demonstrate its diffraction-unlimited ability, two adjacent lines were fabricated with different centre-to-centre distances. The fabrication of two adjacent lines was performed with a fabrication beam intensity of 75.75 mW/cm² and a scanning speed of 160 μm/s. The two adjacent lines were sequentially fabricated by moving of the relative position of the photo-resin while the positions of both focal spots were fixed.

Without the help of the inhibition beam, the achieved line resolution defined by the line centre-to-centre distance is 246 nm (point A in Fig. 5.11b). This number is a bit larger than the size of 201 nm ($201 \text{ nm} = \lambda / (2 \times \text{NA} \times \sqrt{2})$, the $\sqrt{2}$ factor is the consideration of two-photon absorption) set by the Abbe’s diffraction limit for
two-photon absorption of the 800 nm wavelength fabrication beam. This is because of the finite linewidth (about 47 nm) which requires a further separation of the fabricated two lines to avoid line merging. Further improving the resolution requires the help of the photo-inhibitor.

Figure 5.1 Resolution improving by the 3D diffraction-unlimited OBL. (a) Demonstration of the linewidth decreasing and resolution improving with the inhibition beam. (b) Resolution improving versus the intensity of the inhibition laser beam. The insert SEM image shows two adjacent lines fabricated with the inhibition laser beam switching between off and on, respectively. The insert graph is the plot of the cross sectional profile of the inserted SEM image. (c) SEM images of the points B, C, D, E, F and G shown in Fig. 4b. The scale bar is 100 nm. (d) The cross sectional profile of the image G in Fig. 4c, in which the blue line is the position for obtaining the profile.

By increasing the inhibition beam intensity, the resolution decreases from 246 nm to 205 nm (point B in Fig. 5.11b) with an inhibition beam intensity of 0.57 μW/cm². This is achieved with the sufficient inhibition effect coming from the sufficient
quantity of photo-inhibitor and accompanying with the linewidth reducing by increasing the inhibition beam intensity. A further increase of the inhibition beam intensity improves the resolution beyond the diffraction limit. When the inhibition beam intensity is 1.15 μW/cm², 1.44 μW/cm², 2.02 μW/cm² and 2.31 μW/cm², the corresponding resolution is 157 nm (point C in Fig. 5.11b), 117 nm (point D in Fig. 5.11b), 87 nm (point E in Fig. 5.11b) and 57 nm (point F in Fig. 5.11b). The best resolution achieved is 52 nm (point G in Fig. 5.11b) with an inhibition beam intensity of 2.42 μW/cm², which is 1/15 of the fabrication beam wavelength and 1/5 of the resolution achievable without the inhibition beam. The cross sectional profile (Fig. 5.11d) of a line from the SEM image (picture G in Fig. 5.11c) clearly proves the successfully fabrication of lines with 52 nm resolution. The experimental data of resolution can be fitted with an empirical formula (the red curve that guides the blue experimental data in Fig. 5.11b): \( \alpha_2 / \sqrt{1+\beta_2 \times I_{inhibition} / I_S} \) with \( \alpha_2 = 252.07 \) (nm), \( \beta_2 = 2.04 \) ((μW/cm²)^{-1}). This formula reveals the diffraction-unlimited resolution that is no longer restrained by the diffraction limit of the far-field optical system. Because resolution much finer than the diffraction limit was achieved which shows the resolution improvement trend according to the formula \( \alpha_2 / \sqrt{1+\beta_2 \times I_{inhibition}^4 / I_S} \) at the nano scale, this technique is referred as a diffraction-unlimited OBL. This formula is similar to the empirical formula for the linewidth data. Compared with the linewidth decreasing formula \( \alpha_1 / \sqrt{1+\beta_1 \times I_{inhibition}^2 / I_S} \), the resolution decreasing is slower and this reflects at the different power indices of the inhibition beam intensity in the formulas. This is originated from the re-exposure of the photo-resin for two adjacent line fabrication, which requires higher inhibition beam intensity to suppress the polymerisation in the space between the two adjacent lines than the single line fabrication case. For the fabrication of two adjacent lines, a closer line distance requires higher inhibition beam intensity and this eventually leads to the slower decreasing of resolution than linewidth.
Two 3D structures were also fabricated to test the influence of shrinkage to resolution. The structures were fabricated with the fabrication beam intensity of 45.45 mW/cm$^2$ and a scanning speed of 20 μm/s. The inhibition beam is off. The structures are woodpile photonic crystals (PCs, Fig. 5.12). The line centre-to-centre distances of these two structures are 400 nm and 500 nm. The designed size of these two structures is 20 μm by 20 μm with a height about 3 μm. The measured top surface sizes of these two structures are 19.24 μm by 19.60 μm and 19.20 μm by 19.72 μm. This indicates a less than 5% influence of shrinkage to resolution.

![SEM images of two woodpile PCs fabricated by the 3D diffraction-unlimited OBL.](image)

**Figure 5.12** The SEM images of two woodpile PCs fabricated by the 3D diffraction-unlimited OBL.

In principle, this diffraction-unlimited OBL based on 2PP and single-photon inhibition can infinitely reduce the linewidth and improve resolution. However, a further increase of the inhibition beam intensity can lead to destruction of the structure after the developing process. This is because that the linewidth is too small to withstand the inevitable tension for freestanding lines fabricated with the inhibition beam intensity larger than 2.42 μW/cm$^2$.

Because of the competitive mechanism of initiator radical reacting with the inhibitor radical and the monomer, polymerisation monomer conversion degree at the doughnut-shaped ring is tuned down to the threshold. But it is not a zero value. This can lead to increased linewidth for two adjacent line fabrication than single line
fabrication. Figure 5.13a shows the average linewidth of the two adjacent lines shown in Fig. 5.11b and Fig. 5.11c. This experimental result confirms the larger linewidth. Though the influence of re-exposure for two lines sequentially fabricated at the same diffraction-limited local area can increase both lines’ width compared with single line fabrication (Fig. 5.13a), it also experimentally worse the uniformity (picture G in Fig. 5.11c) and leads to disintegrated lines if the inhibition beam intensity was further increased. With this reason, materials with stronger mechanical strength and facilitating more uniformity feature fabrication can benefit further size reducing and resolution improvement. This could be the future direction for 3D OBL with feature size of 5 nm and resolution of 10 nm.

![Figure 5.13 Average linewidth of two adjacent lines (corresponding to Fig. 5.11b) and that of the single line (corresponding to Fig. 5.7d).](image)

Uniformity is extremely important for lines with small linewidth to survive. As forces such as tension in 3D features is unavoidable, non-uniform structure means non-uniform forces in the structure. The non-uniform forces play a bad role for thin line surviving even the average linewidth is large (Fig. 5.13b). For line with linewidth down to 20 nm, if the single monomer size is 5 nm, more or less a monomer can significantly change the mechanical performance at the local position and result to
disintegrated line. In principle, our diffraction-unlimited OBL based on 2PP and single-photon inhibition can infinitely reduce the linewidth and improve resolution. But based on the current photo-resin, line with linewidth smaller than 9 nm can not survive. Except the limited mechanical strength of the photo-resin, even though it is good enough, reasonable laser intensity fluctuation induced non-uniformity might be one of the main reasons. The fabrication of two adjacent lines worses the uniformity as observed in picture G in Fig. 5.11c. This might because of that each of the lines were affected by two times exposure of both the fabrication beam and the inhibition beam. Also, compared with single line, non-symmetrical local environment for each of the two adjacent lines can induce non-uniformity during the developing process.

**Figure 5.14** Schematic of a vertically integrated nano-circuit (a), comprising an X-shaped coupler (b) and a Y-shaped splitter (c). The scale bars for all images are 100 nm.

Freestanding nanowires, which are generated by the 3D diffraction-unlimited OBL, are the buliding blocks for 3D nanophotonic devices [112]. As an illustration, nano-splitters (Y-shape junctions, Fig. 5.14c) and nano-couplers (X-shape junctions,
Fig. 5.14b) which are two of the basic structures for 3D integrated photonic and optoelectronic devices were fabricated by using the new photo-resin. The X-shaped nano-coupler (with feature size of 14 nm, Fig. 5.14b) and the Y-shaped nano-splitter (with the feature size of 38 nm, Fig. 5.14c) were fabricated with the intensity of 75.75 mW/cm² of the fabrication beam and scanning speed of 160 μm/s. The intensity of the inhibition beam is 2.31 μW/cm² for the fabrication of the X-shaped coupler and 0.69 μW/cm² for the fabrication of the Y-shaped splitter, respectively. The structures built at different depths of the medium enable the vertical integration of nanophotonic devices with a scalable high density in the third dimension. In terms of feature dimensions achieved by EBL and the 3D diffraction-unlimited OBL, the equivalent integration circuit densities are estimated as $10^{10}$ N/mm³, and $10^{15}$ N/mm³, respectively, which implies that a 3D nanophotonic circuit produced by the 3D diffraction-unlimited OBL is five orders of magnitude higher than that by EBL.

**Figure 5.15** Schematic of the fabrication of 3D complex structures constituted by building components with different sizes and resolutions. The Y-shapes are connected to a frame. A clear shadow coming from the coating of gold can be seen on the surface of the cover slip. The scale bar is 100 nm.
Though the never better feature size and never finer resolution in 3D diffraction-unlimited OBL were realised by the 3D OBL combining with 2PP and single-photon inhibition, the cost of this 3D diffraction-unlimited OBL system is low as no extraordinary optical element is required. It also benefits this 3D OBL for a portable system for industry application. This 3D nanolithography system also facilitates the fabrication of complex structures constituted by building components with different size and resolution magnitudes. To demonstrate this ability, two freestanding Y-shape junctions at different depths were fabricated at different conditions and are shown in Fig. 5.15. The intensity of the writing beam and the inhibition beam and the scanning speed used to fabricated the Y arm of 1, 2, 3 and 4 (Fig. 5.15) is 75.75 mW/cm², 1.15 μW/cm², 140 μm/s; 75.75 mW/cm², 1.15 μW/cm², 120 μm/s; 75.75 mW/cm², 0 μW/cm², 140 μm/s; and 75.75 mW/cm², 1.15 μW/cm², 100 μm/s. This wide scale compatibility provides the incomparable convenience for industry required device fabrication.

5.6 Chapter conclusion

To the conclusion, by developing a new photo-resin which is suitable for 3D OBL to improve the farbication resolution with two-photon polymersiation and single-photon inhibition strategy, the 3D diffraction-unlimited OBL demonstrated in this work shows the amazing ability to fabricate 3D features with a size down to 9 nm and a resolution down to 52 nm which is no longer constrained by the diffraction limit of the far field optical system but the properties of the material. This indicates the feasibility and promising of applying far field optics with ordinary optical elements to nanofabrication which supports the nanoscience and nanotechnology with the fabrication feature size and resolution matching the scale ranged from 1 to 100 nm.
Chapter 5

The 3D diffraction-unlimited OBL is currently the first nanofabrication method targeting the nanometre resolution with arbitrary 3D structure fabrication ability which can widely impact the nanofabrication community. This technology can be used for different purposes in different disciplines including nanophotonics and nanoelectronics to fabricate 3D nanostructures.
Chapter 6

Three-dimensional optical beam lithography of lead selenide microstructures with the bottom-up strategy

6.1 Introduction

Bulk rock-salt lead selenide (PbSe) is a typical narrow electronic bandgap semiconductor with a direct bandgap of 0.27 eV. Except a refractive-index as high as 4.82 at 6 microns [113] and a third-order nonlinear refractive-index at the magnitude of $10^{-13}$ cm$^2$/W [114], PbSe exhibits unique optical and electrical properties. Unique properties such as the multi-exciton generation [115], the high carrier mobility and the thermal-electric property with a thermoelectric figure-of-merit value larger than 1 [116] makes it a highly promising material in photonics, nano-electronics and nano-thermal-electrics.

Three-dimensional (3D) optical beam lithography (OBL) which uses a focused laser beam for direct writing has become a wide-implemented enabling technology for the fabrication of 3D photonic devices [2, 10, 11]. However, the fabrication of 3D structures made by materials with a narrow electronic bandgap and a high refractive-index such as PbSe by 3D OBL is challenged due to single-photon absorption of the material and refractive-index mismatch with a commonly used 3D OBL such as the one used in Chapter 3 and Chapter 5.

In this chapter, to provide functional photonic device application with a high refractive-index platform having unique optical and electrical properties, the
fabrication of 3D PbSe micro or nano structures with OBL in a solution based photo-resin is presented. This approach takes the advantages of 3D OBL and avoids the problems of the strong aberration and the long excitation wavelength for 3D OBL in a bulk PbSe. In Sec. 6.2 the concrete challenges to fabricate structures made by PbSe with 3D OBL are discussed. Sec. 6.3 introduces the development of the photo-resin. The fabrication results and discussions are presented in Sec. 6.4.

6.2 The basic challenges and considerations of fabricating structures made by lead selenide with three-dimensional optical beam lithography

The main challenges of 3D fabrication with OBL in a bulk narrow bandgap semiconductor, i.e. the PbSe, for the top-down strategy come from the narrow electronic bandgap and the high refractive-index of PbSe. Two-photon OBL is performed in a material, which absorbs the excitation photon via a two-photon process. As the two-photon process is proportional to square of the light intensity in the focal volume, the laser induced lithography can be controlled to occur only at the focal volume of the excitation light beam. It is this property that enables the 3D fabrication ability with a high fabrication resolution for two-photon OBL. However, two-photon OBL fabrication in a bulk PbSe material requires the excitation wavelength longer than 5 microns as the electronic bandgap of the bulk PbSe is 0.27 eV. This longer than 5 microns excitation wavelength does not facilitate the fabrication system manipulation and is a hurdle to sub-micron fabrication resolution. Furthermore, the refractive-index value of 4.82 at the wavelength of 6 microns causes a big problem for 3D OBL in the bulk PbSe. As two-photon OBL uses a high
numerical-aperture (NA) objective lens to focus the excitation laser beam into the fabricated material, the refractive-index of the objective immersion oil (normally about 1.52 for 1.4 NA objective) is much smaller than 4.82. For 3D OBL in a material with a refractive-index much larger than that of the immersion oil, when the excitation focal spot is moved deeply into the material, the excitation focal spot is more defocused, more elongated and distorted [20]. This hinders the achieving of high resolution, symmetric and depth unaffected fabrication with 3D OBL, which is clearly shown in Fig. 6.1a. For PbSe, the large refractive-index mismatch requires strong aberration compensation, which means a big challenge for 3D OBL in a bulk PbSe for the top-down strategy.

**Figure 6.1** A comparison of the top-down strategy and the bottom-up strategy for the fabrication of PbSe material by two-photon DLW. From left to right, the excitation focal spot was moved deeper with an increment of 10 μm. (a) Top-down strategy in PbSe bulk material. (b) Bottom-up strategy in a photo-resin. The insert shows a detailed view of the focal spot.
Except the top-down strategy, the bottom-up strategy is also widely used to fabricate micro or nano scale structures. In this work, as the top-down strategy encounters the problems for materials with a narrow electronic bandgap and a high refractive-index, the bottom-up strategy is utilised to fabricate 3D PbSe micro or nano scale structures by 3D OBL. The basic concept is as follows: First, the basic chemical components to form PbSe need to be put into the fabrication photo-resin in advance. Then, under the irradiation of the fabrication laser beam, the basic components in the photo-resin generate PbSe to form the designed PbSe micro or nano scale structures. To avoid possible trouble from the significant refractive-index mismatch, the developed photo-resin should have a low refractive-index (Fig. 6.1b). To enable 3D fabrication, the photo-resin is required to have no single-photon absorption but two-photon absorption at the excitation wavelength.

6.3 Sample preparation and fabrication

Based on the considerations in Sec 6.2, in this experiment, Pb with the form of lead oleate (PbOA) and Se with the form of TOPSe (Se dissolves in trioctylphosphine) were dissolved in an organic solution 1-octadecene (ODE). This organic solution has high solubility of PbOA and TOPSe, which allowed the formation of PbSe with sufficient amount of Pb and Se elements at the local position of the excitation laser beam focal spot. The refractive-index of ODE was 1.44. After dissolving of PbOA and TOPSe, the final solution based photo-resin has a refractive-index about 1.50 which serves as a low refractive-index platform for two-photon OBL of PbSe without aberration compensation. ODE is a colourless solution and had no single-photon absorption at the laser wavelength ranging from 500 nm to 800 nm. This provided the possibility of fabricating 3D PbSe structures in ODE with two-photon OBL. TOPSe
in ODE is also a colourless solution. Pure PbOA is a wax-like solid. After dissolving PbOA and TOPSe in ODE, the final photo-resin is a transparent and colourless solution (Fig. 6.2a). Figure 6.2b shows the absorption spectrum of the photo-resin, TOPSe precursor and PbOA precursor. The absorption spectra of both PbOA and TOPSe precursors in Fig. 2b show an absorption band edge at the wavelength of 410 nm and 340 nm separately. The photo-resin shows an absorption band edge at the wavelength of 400 nm, which shows no single-photon absorption at the wavelength range from 500 nm to 800 nm.

Figure 6.2 Synthesised photo-resin for the PbSe material fabrication based on the bottom-up strategy via two-photon DLW. (a) A photograph shows that the photo-resin is transparency and colourless. (b) The absorption spectrum of the photo-resin, TOPSe precursor and PbOA precursor.

The process to prepare the precursors is similar to the synthesising of PbSe semiconductor quantum dots (QDs) [80]. To be concrete, the preparation process is as follows: For the preparation of PbOA as the precursor of the fabrication photo-resin with a maximum dissolve of Pb elements, a mixture of PbO (0.506 g), oleic acid (1.280 g) and technological grade ODE (2.300 g) was stirred and heated to 120 °C for 1 hour under the vacuum. After that, the mixture was switched to nitrogen gas and the temperature of the mixture was allowed to increase to 180 °C. The mixture was kept
at 180 °C for 15 mins in a three neck flask under the nitrogen gas. Then, the mixture was quickly cooled down to the room temperature with the protection of the nitrogen gas. The mixture of PbOA in ODE was centrifuged to remove the small amount of the un-dissolved PbO. The obtained solution after the centrifugation was PbOA dissolved in ODE, which is a colourless solution. The concentration of PbOA was about 0.5 mol/L. The TOPSe solution was prepared by dissolving excessive amount of selenium (0.358 g) in trioctylphosphine (TOP, 3.220 g). The mixture of Se and TOP was centrifuged to remove the un-dissolved Se. The concentration of TOPSe was about 1.0 mol/L. At the room temperature, the Pb mixture and the Se mixture were mixed together with a volume ratio 1 to 1, which corresponds to a mole ratio of 1:2. This mole ratio rather than 1:1 contributed to the faster formation of PbSe with high chemical efficiency [117]. To guarantee fully mixing of these two precursors, the final mixture was allowed to be vigorously shaken in a sealed glass vial. The final mixture was used as the fabrication photo-resin. A drop of the photo-resin was sandwiched between two cover slips separated by about 60 μm with thick sticky-tapes. The sample was then used for the two-photon OBL.

At the room temperature, the mixed PbOA and TOPSe in ODE can form PbSe with a very slow reaction rate. The formed PbSe has a dark colour and thus can change the colour of the mixture from almost colourless to dark brown. This is because of the formation of PbSe nano-particles in the photo-resin. However, as the reaction rate is slow, this can only be observed at a time at least 12 hours after the mixing of PbOA and TOPSe in ODE, which leaves a long enough time interval to finish the fabrication in this mixed solution based photo-resin.

An OBL system, which is the same as the one used for the polymer PC fabrication in Chapter 3 was used to fabricate PbSe structures in the prepared photo-resin. A laser beam with a wavelength of 580 nm was used as the OBL excitation source for two-photon absorption. Under the excitation of a femtosecond (fs) pulsed laser beam
with a wavelength of 580 nm, the photo-resin can emit red light which shows an evidence of two-photon absorption as there is no single-photon absorption. A bright spot coming from the emission of the photo-resin at the excitation focal spot was observed with a confocal placed charge-coupled device (CCD) camera before a long pass filter with cutting wavelength at 600 nm. This can only be observed when the excitation focal spot was inside the photo-resin and this confirms the emission is a two-photon absorption induced process. For these reasons, the 580 nm wavelength light was select for two-photon OBL. After fabrication, the sample can be annealed at 120 °C for 5 min. The cover slip without the stick of the fabricated structure was mechanically taken off with care then the whole down cover slip with the fabricated structure attached was immersed into the washing pure toluene solution for 5mins to remove the un-solidified photo-resin and to reveal the fabricated structures. The fabricated structure was finally dried in air at the room temperature.

6.4 Three-dimensional optical beam lithography of PbSe structures

Under the irradiation of the fs pulsed laser beam with a wavelength of 580 nm, PbSe can be formed instantly. This laser induced instant formation of PbSe in the photo-resin enables the fabrication of PbSe structures in a solution based photo-resin and facilitates the successful fabrication of narrow bandgap semiconductor materials by two-photon OBL. By fixing the position of the excitation focal spot and moving the position of the photo-resin with a scanning stage, two-dimensional (2D) structures can be fabricated. A home-made confocal microscopy with a CCD camera based on the laser fabrication system is used to monitor the laser fabrication process. From the CCD camera, the fabrication process can be monitored at the real time. A typical picture shows the fabrication of lines with a dark colour (Fig. 6.3a). The significant
refractive-index change at the fabricated line position indicates the formation of the material with high refractive-index contrast. The experimental achieved linewidth in Fig. 6.3b is about 900 nm which confirms the sub-micron fabrication resolution. To show the 3D fabrication ability, pillars with a height about 12 microns (Fig. 6.3c) were fabricated by moving the scanning stage vertically away from the objective. Three-dimensional structure with different layers (Fig. 6.3d) was also fabricated to show it 3D fabrication ability. As a linearly polarised beam was used to do the fabrication, lines at different layers fabricated along perpendicular directions shows significant linewidth differences due to the non-symmetrical property of the laser beam focal spot.

**Figure 6.3** Fabrication of the PbSe structures by two-photon DLW in the photo-resin. (a) A typical picture taken during the fabrication process from the CCD camera. (b) The SEM images of two dimensional lines. (c) The SEM images of pillars with a height of about 12 μm. (d) The SEM images of 3D structure with different layers. (e) The SEM images of the two dimensional structures after fabrication and annealing. All the scale bars are 1000 nm.
However, as can be seen from the scanning electron microscopy (SEM) images (Figs. 6.3b, 6.3c and 6.3d), the fabricated structure surface is rough. This originates from the fast reaction rate of PbOA with TOPSe under the irradiation of the fs pulsed laser beam which leads to the uncontrolled growth of PbSe within the volume of the focal spot. To make it smoother, the sample was annealed at 120°C for 5 mins after the fabrication and before washing out. The structure after the annealing (Fig. 6.3e) is much smoother and the feature size of the line is reduced as well compared with Fig. 6.3b, which shows an effective way to improve the quality of the fabricated structure.

Laser induced PbSe formation in the ODE solution based photo-resin enables the 3D OBL of PbSe micro or nano structures and the mechanism of the PbSe formation under the irradiation of laser is a concerned topic. Here, there are two possible mechanisms that may account for the PbSe instant formation in the excitation focal spot. The first one is local heat driven PbSe formation. At the focal region, due to the light energy concentration by the objective lens, the local temperature at the volume of the focal spot can be increased. This local high temperature means a high chemical reaction rate and makes the instant formation of PbSe possible. For the PbOA and TOPSe mixed solution in ODE, after the triggering of the nucleation of PbSe in 170 °C, it takes 5 mins for the PbSe nano-particles to grow to a size about 6 nm in 120°C. This process has been proved by the PbSe QD synthesis with the wet chemical method [80]. Compared with this, according the line fabrication scanning speed of 20 μm/s, it takes about 50 ms to finish the line fabrication with a one-micron length. It is observed that a line can be fabricated at a scanning speed of 100 μm/s. So if high temperature is the only reason to induce PbSe instant formation, the local temperature should be much higher than 120 °C. However, the boiling point of ODE is 314 °C. As no bubbles were observed during the fabrication process, the local temperature should not be high enough to independently induce instant PbSe formation though it partially contributes to the local instant PbSe formation. The other possible mechanism is the reduction of Pb²⁺ to Pb⁰ under the irradiation of an intense laser beam. Compared with
the reaction rate of Pb$^{2+}$(OA) with TOPSe, Pb$^0$ can react with TOPSe much faster [118]. If Pb$^0$ can be formed instantly with the irradiation of an intense laser beam, the reaction of Pb(OA) with TOPSe to form PbSe under the intense laser excitation can be significantly accelerated. This is possible as metal ions can be reduced in an organic solution by laser irradiation [119-123]. With a local higher temperature in the focal region and an accelerated reaction rate of PbOA with TOPSe under the irradiation of intense laser, PbSe can be formed instantly in the focal volume.

Figure 6.4 (a) Energy dispersive spectrum of the fabricated PbSe structures. (b) The HRTEM image of the fabricated PbSe structures.

It is important to confirm the formation of the PbSe by the two-photon OBL. The energy dispersive spectrum (EDS) of the fabricated structure was measured and is shown as Fig. 6.4a. From the EDS measurement, Pb and Se elements can be identified with an atomic ratio of Pb and Se 1.07:1. This almost 1 to 1 ratio of Pb and Se confirms that the formed structure is mainly constituted with a nearly equal amount of the Pb and Se elements. The slightly larger amount of Pb can be explained as a Pb-rich structure surface due to the low utilisation rate of Se in the photo-resin [117]. There are also carbon and oxygen elements that can be identified with tiny amount. These are residual organic molecules attached at the surface of the fabricated structure. To show the crystal structure of the fabricated PbSe structures, high resolution transmission electron microscopy (HRTEM) image was shown in Fig. 6.4b. The HRTEM image confirms the formation of PbSe with a rock salt phase.
The fabricated structures were measured with a ZEISS Supra 40 VP Field Emission Scanning Electron Microscope. Before the measurement, the sample was coated with a gold layer with the thickness of 2-3 nm. The EDS measurement was performed at a fabricated PbSe block at an area of \(20 \times 20 \, \mu \text{m}^2\) to reduce random error. Because Pb and Se are the main heavy element ingredients of the fabricated structure, the atomic ratio measured by the EDS is quantitative. The HRTEM was performed at a FEI Tecnai F30 Transmission electron microscope.

### 6.5 Chapter conclusion

To conclude, it is the first time that 3D micro or nano structures made by narrow bandgap and high refractive-index PbSe material were fabricated by two-photon OBL. The method in this chapter shows the promising way to fabricate 3D narrow electronic bandgap and high refractive-index semiconductor structure based on the bottom-up strategy, which is otherwise challenged for the top-down strategy. This work shows the great potential of applying 3D OBL to fabricate 3D micro or nano structures made by PbSe with a never higher refractive-index, high nonlinearity and unique optical and electrical properties for applications in photonics and electronics such as energy harvesting, nano heat transfer, SE controlled device applications and high performance infrared photonic devices.
Chapter 7

Conclusion

7.1 Thesis conclusion

An appropriate three-dimensional (3D) fabrication method can provide photonic applications with functional devices that have different geometrical configurations and are made by different materials with different properties. Three-dimensional optical beam lithography (OBL) is one of the most promising candidates. This thesis contains a detailed investigation on 3D OBL. The aim of studying 3D OBL in this thesis is to fully support photonic applications with 3D functional photonic devices. The support is provided from three essential aspects as the following:

1. Demonstration of enhancing spontaneous emission (SE) in 3D low refractive-index photonic crystals (PCs) fabricated by 3D OBL with a designed defect. By inducing a plane defect in the middle of a PC fabricated by two-photon OBL, the photonic LDOS at the local position of the defect is tuned from significant decreasing to obvious increasing. It was shown that PCs fabricated by two-photon OBL can have photonic LDOS designed by the PC structure geometrical parameters and three-dimensional OBL can well support local photonic environment designing for the fabricated photonic devices with designed local structure geometries.

2. Development of 3D diffraction-unlimited OBL with resolution down to the nanometre range for extending the working wavelength range of the photonic
devices for photon manipulation applications. A comprehensive work including theory and experiment on breaking the diffraction barrier to achieve optical nanolithography was done. It is the first time to demonstrate in experiment that 3D two-beam OBL based on ordinary optical elements can achieve 9 nm feature size and 52 nm resolution. This work witnesses the beginning of 3D diffraction-unlimited OBL with nanometre resolution and undoubtedly can extend the available shortest working wavelength of the photonic devices fabricated by single-beam 3D OBL to a shorter wavelength.

3. Fabricating 3D structures made by narrow electronic bandgap and high refractive-index materials with unique optical and electronic properties which is highly desired for photonic device applications. With the bottom-up strategy, 3D structure formed by PbSe was successfully fabricated by two-photon OBL. By 3D OBL, it is the first time to fabricate 3D structures made by PbSe with electronic bandgap as narrow as 0.27 eV and a never higher refractive-index of 4.8 at 6 μm for a bulk material.

The photonic LDOS change induced SE modification for PCs fabricated by two-photon OBL was investigated. To study the SE modification by PCs quantitatively and to get reliable comparison information of SE modification for PbSe/CdSe core-shell quantum dots (QDs) in PCs and in a reference system, an accurate method to put the QDs into the PCs and the reference system was developed with a controllable amount of the integrated QDs. This method is based on the linking of the QDs to the surface of the PC structure with a molecule. The SE decay of the QDs in PCs shows the photonic LDOS determined property and this is confirmed by the theory. With a designed plane defect in the geometrical centre of a PC, significant SE enhancing with an average of 15% lifetime shorter was achieved at the local position of the defect. A significant change of lifetime from about 20% longer to 15% shorter due to the designed defect indicates that photonic LDOS can be designed by
changing the local structure geometry. This result demonstrates the ability for 3D OBL to support SE manipulation with designed photonic LDOS by designing the local structure geometry.

The diffraction nature of light prevents the application of photonic devices fabricated by 3D diffraction-limited OBL at some wavelength range. To extend the working wavelength range of the photonic devices fabricated by the 3D diffraction-limited OBL, both theoretical and experimental work were done to develop a technique for 3D OBL breaking the diffraction barrier to get nanometre resolution. The strategy for achieving diffraction-unlimited OBL is to use the super-resolution photoinduced-inhibition nanolithography (SPIN). To facilitate the material development, a dynamical model was established firstly to investigate the SPIN. The theoretical work shows that photo-polymerisation with the assistance of photo-inhibition can provide two-beam OBL with smaller feature size and finer resolution compared with those of the single-beam OBL. For material development, side effects such as photo-inhibition induced polymerisation should be avoided as much as possible. To prevent photo-inhibitor consuming induced non-uniformity, sufficient amount of the photo-inhibitor should be included in the photo-resin. With the enlightenment of the theoretical work, a photo-resin equipped with large two-photon absorption cross-section initiator, high mechanical strength monomers and high efficiency photo-inhibitor with a sufficient amount was successfully developed. With this photo-resin and with the assistance of an inhibition beam, smaller feature size and finer resolution were achieved compared with that without the inhibition beam. It is the first time to demonstrate that 3D OBL can have nanometre resolution, which is no longer constrained by the diffraction limit. The smallest feature size and best resolution is 9 nm and 52 nm which is 1/88 and 1/15 of the fabrication beam wavelength, respectively. For this 3D diffraction-unlimited OBL, the linewidth and resolution, which decrease with the increasing of the photo-inhibition beam intensity, satisfy a formula of $\frac{\alpha_1}{\sqrt{1 + \beta_1 \times I_{\text{inhibition}}^4 / I_s}}$ and
\[ \alpha_2 \left/ \sqrt{1 + \beta_2 \times I_{\text{inhibition}} / I_S} \right. \] respectively at the nanometre scale and show the diffraction-unlimited property of this technique. With this diffraction-unlimited 3D OBL, the working wavelength of the functional photonic devices can be greatly extended. This technique also shows the great potential for the next generation photonic device applications as it provides a resolution in the nanometre range with 3D fabrication ability.

Undoubtedly, 3D functional photonic devices made by materials with a narrow electronic bandgap and a high refractive-index can be used for a number of applications with better performance. However, materials with a narrow electronic bandgap and a high refractive-index are not suitable for fabrication with 3D OBL based on the top-down strategy. To fabricate 3D functional photonic devices made by materials such as PbSe, 3D OBL of micro or nano scale structures made by narrow bandgap and high refractive-index materials based on the bottom-up strategy was proposed in this thesis. It is the first time that 3D structures made by PbSe with an electronic bandgap as narrow as 0.27 eV and a refractive-index as high as 4.8 at 6 microns were fabricated with two-photon OBL. By dissolving Pb and Se elements in an organic solution to make the photo-resin, laser irradiation of the photo-resin can induce instant formation of PbSe in the focal volume of the focal spot and thus fabricate 3D PbSe structures. As the photo-resin is designed to have no single-photon absorption at the visible range and a moderate refractive-index which matches the refractive-index of the objective lens immersion oil, single-photon induced absorption and high refractive-index required aberration compensation are avoided. Two-photon response of the photo-resin to the excitation laser beam in the focal volume enables 3D fabrication of PbSe structures. The method used in this thesis to fabricate 3D PbSe structures proposes a general method to fabricate narrow electronic bandgap material by 3D OBL. This work provides functional photonic devices with narrow electronic
bandgap and high refractive-index materials having unique optical and electrical properties for better performance and new applications.

7.2 Future work

For the future work of this thesis, two potential directions could be future investigation. One is to manipulate SE at the visible wavelength range with photonic devices fabricated by 3D diffraction-unlimited OBL. The other is to develop 3D diffraction-unlimited OBL to fabricate structures made by materials with a high refractive-index.

7.2.1 Spontaneous emission manipulation at the visible wavelength range

Because two-photon OBL used in Chapter 3 could not fabricate a PC working at the visible wavelength range, the SE manipulation with PCs shown in that chapter was done at the near infrared wavelength range. Three-dimensional diffraction-unlimited OBL developed in this thesis shows the promising of fabricating, photonic devices working at the visible wavelength range. Therefore, an important work need to be done first for this direction is to fabricate functional photonic devices such as PCs working at the visible wavelength range by using the 3D diffraction-unlimited OBL. Then, SE manipulation at the visible wavelength range is ready to be explored. The first is to use the photonic devices fabricated by 3D diffraction-unlimited OBL to
manipulate the SE from a single nano-emitter. A single nano-emitter can be detected by photo-detectors when it emits at the visible wavelength range rather than at the near infrared wavelength range because the photo-detectors working at the visible wavelength range are much more sensitive than that at the near infrared range. The other is to study the electromagnetic interaction of two or multi nano-emitters by manipulate their local photonic environment. For example, for fluorescence resonance energy transfer, the electromagnetic interaction of two nano-emitters in the energy transfer system is mediated by the virtual photon exchange between the emitters. By changing the photonic LDOS at the space where these two emitters are located, the fluorescence resonance energy transfer could be manipulated.

7.2.2 Fabrication of three-dimensional structures with high refractive-index material by diffraction-unlimited optical nanolithography

Photonic devices with high refractive-index materials are more powerful to manipulate photons such as manipulate photon emission than that with low refractive-index materials. The fabrication of PCs in As$_2$S$_3$ glass reported by the reference [26] and the fabrication of PbSe structure in this thesis represent the fabrication of high refractive-index 3D structures with wide and narrow electronic bandgap materials by OBL, respectively. As the same situation for 3D OBL in polymer, the resolution for fabricating structures with high refractive-index materials by single-beam OBL limits the working wavelength range of the fabricated photonic device due to the diffraction. Thus, the development of 3D diffraction-unlimited OBL to fabricate photonic devices made by high refractive-index materials with nanometre resolution is the other future direction. As the two-beam OBL in low refractive-index polymer demonstrated in this thesis shows the amazing ability to break the diffraction
limit and achieve nanometre resolution, the two-beam strategy for resolution improving can also be used for the high refractive-index material case with different resolution improving mechanisms. For wide electronic bandgap materials, the top-down strategy can still be used with requirements including an appropriately designed developing process and a complex aberration compensation process for both the writing beam and the doughnut-shaped beam. An appropriate mechanism for the doughnut-shaped beam to decrease the fabrication feature size and improve the fabrication resolution in wide bandgap high refractive-index material is the most important and challenged part. The designed mechanism should facilitate high density structure fabrication as well as nanometre sized feature generation.

The method developed in this thesis for 3D fabrication of narrow electronic bandgap materials can be used as the basis for the fabrication of high refractive-index narrow bandgap materials with nanometre resolution via the two-beam strategy. No aberration compensation is required for this bottom-up strategy. But converse to the light induced instant PbSe formation, the mechanism for light induced instant PbSe deformation with another wavelength is desired. This also requires a full understanding of the mechanism for the light induced instant PbSe formation. With an appropriate formation and deformation mechanism, two-beam OBL can produce 3D structures made by high refractive-index and narrow bandgap materials with resolution within the nanometre range.


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