

Direct laser writing of three-dimensional narrow bandgap and high refractive-index PbSe structures in a solution

Zongsong Gan,^{1,2} Yaoyu Cao,¹ Min Gu^{1,2,*}

¹Centre for Micro-Photonics Swinburne University of Technology, P.O. Box 218 Hawthorn, VIC 3122, Australia

²Centre for Ultrahigh-bandwidth Devices for Optical Systems (CUDOS), Faculty of Engineering and Industrial Science, Swinburne University of Technology, P.O. Box 218 Hawthorn, VIC 3122, Australia
*mgu@swin.edu.au

Abstract: Three-dimensional (3D) micro/nano structures made of narrow electronic bandgap semiconductor materials have important applications in a wide range of disciplines. Direct laser writing (DLW) provides the unparalleled advantage to fabricate 3D arbitrary geometric structures at the micro and nano meter scale. The fabrication of 3D structures within bulk narrow electronic bandgap semiconductor materials by DLW is challenged for the top-down strategy due to their narrow bandgap and high refractive index. Here, we report on the bottom-up strategy for the fabrication of 3D micro/nano structures made from PbSe with an electronic bandgap as narrow as 0.27 eV and a refractive index as high as 4.82 in a solution.

©2013 Optical Society of America

OCIS codes: (160.6000) Semiconductor materials; (140.3450) Laser-induced chemistry; (160.4670) Optical materials; (220.4241) Nanostructure fabrication; (220.4610) Optical fabrication.

References and links

1. M. Straub and M. Gu, "Near-infrared photonic crystals with higher-order bandgaps generated by two-photon photopolymerization," *Opt. Lett.* **27**(20), 1824–1826 (2002).
2. M. S. Rill, C. Plet, M. Thiel, I. Staude, G. von Freymann, S. Linden, and M. Wegener, "Photonic metamaterials by direct laser writing and silver chemical vapour deposition," *Nat. Mater.* **7**(7), 543–546 (2008).
3. P. Galajda and P. Ormos, "Complex micromachines produced and driven by light," *Appl. Phys. Lett.* **78**(2), 249–251 (2001).
4. K. Ohlinger, Y. Lin, Z. Poole, and K. P. Chen, "Undistorted 3D microstructures in SU8 formed through two-photon polymerization," *AIP Advances* **1**(3), 032163 (2011).
5. J. Serbin and M. Gu, "Superprism phenomena in waveguide-coupled woodpile structures fabricated by two-photon polymerization," *Opt. Express* **14**(8), 3563–3568 (2006).
6. M. D. Turner, G. E. Schröder-Turk, and M. Gu, "Fabrication and characterization of three-dimensional biomimetic chiral composites," *Opt. Express* **19**(10), 10001–10008 (2011).
7. S. Wong, M. Deubel, F. Pérez-Willard, S. John, G. A. Ozin, M. Wegener, and G. von Freymann, "Direct laser writing of three-dimensional photonic crystals with a complete photonic bandgap in chalcogenide glasses," *Adv. Mater.* **18**(3), 265–269 (2006).
8. E. Nicoletti, D. Bulla, B. Luther-Davies, and M. Gu, "Generation of $\lambda/12$ nanowires in chalcogenide glasses," *Nano Lett.* **11**(10), 4218–4221 (2011).
9. A. Rodenas, G. Zhou, D. Jaque, and M. Gu, "Rare-earth spontaneous emission control in three-dimensional lithium niobate photonic crystals," *Adv. Mater.* **21**(34), 3526–3530 (2009).
10. M. Bass, *Handbook of Optics*, 2nd ed., Vol. 2 (McGraw-Hill 1994). This can also be found at <http://refractiveindex.info/?group=CRYSTALS&material>.
11. I. Moreels, Z. Hens, P. Kockaert, J. Loicq, and D. Van Thourhout, "Spectroscopy of the nonlinear refractive index of colloidal PbSe nanocrystals," *Appl. Phys. Lett.* **89**(19), 193106 (2006).
12. H. Kobayashi, H. Kanbara, M. Koga, and K. Kubodera, "Third-order nonlinear optical properties of As₂S₃ chalcogenide glass," *J. Appl. Phys.* **74**(6), 3683–3687 (1993).
13. R. J. Ellingson, M. C. Beard, J. C. Johnson, P. Yu, O. I. Micic, A. J. Nozik, A. Shabaev, and A. L. Efros, "Highly efficient multiple exciton generation in colloidal PbSe and PbS quantum dots," *Nano Lett.* **5**(5), 865–871 (2005).
14. D. Parker and D. J. Singh, "High-temperature thermoelectric performance of heavily doped PbSe," *Phys. Rev. B* **82**(3), 035204 (2010).
15. B. P. Cumming, A. Jesacher, M. J. Booth, T. Wilson, and M. Gu, "Adaptive aberration compensation for three-dimensional micro-fabrication of photonic crystals in lithium niobate," *Opt. Express* **19**(10), 9419–9425 (2011).

16. H. I. De Lasa and B. S. Rosales, *Advances in Chemical Engineering* (Academic Press, 2009) pp. 37–67.
17. J. Ouyang, C. Schuurmans, Y. Zhang, R. Nagelkerke, X. Wu, D. Kingston, Z. Y. Wang, D. Wilkinson, C. Li, D. M. Leek, Y. Tao, and K. Yu, “Low-temperature approach to high-yield and reproducible syntheses of high-quality small-sized PbSe colloidal nanocrystals for photovoltaic applications,” *ACS Appl. Mater. Interfaces* **3**(2), 553–565 (2011).
18. W. W. Yu, J. C. Falkner, B. S. Shih, and V. L. Colvin, “Preparation and characterization of monodisperse PbSe semiconductor nanocrystals in a noncoordinating solvent,” *Chem. Mater.* **16**(17), 3318–3322 (2004).
19. J. Joo, J. M. Pietryga, J. A. McGuire, S. H. Jeon, D. J. Williams, H. L. Wang, and V. I. Klimov, “A reduction pathway in the synthesis of PbSe nanocrystal quantum dots,” *J. Am. Chem. Soc.* **131**(30), 10620–10628 (2009).
20. T. Rajh, D. M. Tiede, and M. C. Thurnauer, “Surface modification of TiO₂ nanoparticles with bidentate ligands studied by EPR spectroscopy,” *J. Non-Cryst. Solids* **207**, 815–820 (1996).
21. M. C. Thurnauer, T. Rajh, D. M. Tiede, P. S. Lakkaraju, A. Sousa, A. D. Garnovskii, D. A. Garnovskii, B. O. Roos, C. Vallance, and B. R. Wood, “Surface modification of TiO₂: correlation between structure, charge separation, and reduction properties,” *Acta Chem. Scand. A* **51**, 610–618 (1997).
22. L. Murrini, F. Conde, G. Leyva, and M. I. Litter, “Photocatalytic reduction of Pb(II) over TiO₂: New insights on the effect of different electron donors,” *Appl. Catal. B* **84**(3-4), 563–569 (2008).
23. L. Murrini, G. Leyva, and M. I. Litter, “Photocatalytic removal of Pb(II) over TiO₂ and Pt–TiO₂ powders,” *Catal. Today* **129**(1-2), 127–135 (2007).
24. A. M. Smith and S. Nie, “Semiconductor nanocrystals: Structure, properties, and band gap engineering,” *Acc. Chem. Res.* **43**(2), 190–200 (2010).
25. M. Nirmal and L. Brus, “Luminescence photophysics in semiconductor nanocrystals,” *Acc. Chem. Res.* **32**(5), 407–414 (1999).

1. Introduction

Direct laser writing (DLW) which uses a focused laser beam has become a wide-implemented enabling technology for the fabrication of three dimensional (3D) complex structures at the micro or nano meter scale [1–6]. However, the materials suitable for 3D DLW are mainly wide electronic bandgap materials such as As₂S₃ chalcogenide glass [7, 8] and LiNbO₃ crystal [9] or organic photoresins such as SU8 [4], Ormocer [5] and IP-L [6] that absorb the writing laser energy via a two-photon process. When DLW is applied to fabricate 3D structures inside narrow electronic bandgap materials, it encounters the problem of single-photon absorption which disables the 3D fabrication ability of DLW. Compared with wide electronic bandgap materials, narrow electronic bandgap materials normally have much higher refractive index [10]. This could also be a challenge to operate DLW in the narrow electronic bandgap materials due to the refractive index mismatch. Because of these reasons, even though narrow electronic bandgap materials have unique optical and electrical properties that are highly desired for a wide range of applications, the fabrication of their 3D structures by DLW has not been demonstrated. In this work, we demonstrate the fabrication of 3D structures made of lead selenide (PbSe) as a typical example of the narrow electronic bandgap materials by conducting DLW in a solution, which avoids the problems of the refractive index mismatch and the long excitation wavelength of the DLW in the top-down fabrication approach.

As a typical narrow electronic bandgap material, Bulk rock-salt PbSe has a bandgap as narrow as 0.27 eV. It has a refractive index as high as 4.82 at 6 microns [10], which should be the dielectric material that has the largest refractive index value at 6 microns within the current materials used for DLW. The third-order nonlinear refractive index of PbSe is at the magnitude of 10⁻¹³ cm²/W [11], which is about one order of magnitude larger than that of As₂S₃ chalcogenide glass [12]. In addition, PbSe exhibits unique optical and electrical properties such as the multi-exciton generation [13], the high carrier mobility and the unique thermal-electric property with a thermoelectric figure-of-merit ZT value larger than 1 [14] which makes it a highly promising material applicable in photonics, nano-electronics and nano-thermal-electrics. So the successful fabrication of 3D PbSe structures can greatly facilitate 3D device applications that can utilize the unique intrinsic properties of PbSe, which is otherwise unavailable for wide electronic bandgap materials.

2. The challenges to fabricate PbSe structures with two-photon direct laser writing

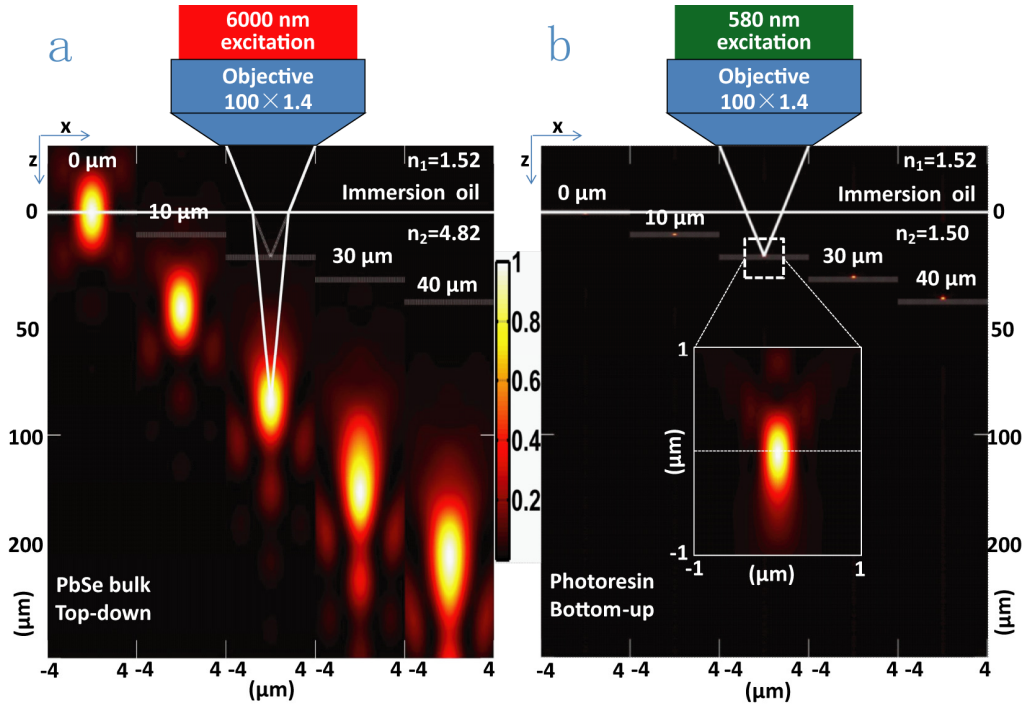


Fig. 1. A comparison of the top-down strategy and the bottom-up strategy for the fabrication of PbSe material by two-photon DLW. From left to right, the excitation focal spot was moved deeper with an increment of 10 μm . (a) Top-down strategy in PbSe bulk material. (b) Bottom-up strategy in a photoresin. The insert shows a detailed view of the focal spot.

The main challenges of 3D fabrication with DLW in bulk semiconductor PbSe for the top-down strategy come from the narrow electronic bandgap and the high refractive index of PbSe. Two-photon DLW is performed in a material which absorbs the excitation photon via a two-photon process. However, two-photon DLW in bulk PbSe requires the excitation wavelength longer than 5 microns as the bandgap of bulk PbSe is 0.27 eV. This excitation wavelength of longer than 5 microns does not facilitate the manipulation of the DLW fabrication system and is the hurdle to sub-micron fabrication resolution. Further, the refractive index value of 4.82 is also a big problem for 3D DLW in bulk PbSe. As DLW 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 DLW in a material with refractive index much larger than that of the immersion oil, when the excitation focal spot was moved deeply into the material, the excitation focal spot was more defocused, more elongated and distorted [15]. This hinders the achieving of symmetric, high resolution and depth unaffected fabrication with DLW, which is clearly shown in Fig. 1(a). The large refractive-index mismatch requires strong wave-front aberration compensation, which means a big challenge for 3D DLW in bulk PbSe.

3. Experiment

3.1 Photoresin development

In this work, as the top-down strategy encounters the problems in narrow bandgap and high refractive-index materials, the bottom-up strategy is utilized to fabricate 3D PbSe micro/nanostructures by DLW and the basic concept is as follows: First, the basic chemical components

to form PbSe need to be put into the fabrication photoresin beforehand. Then, under the irradiation of the fabrication laser beam, the basic chemical components in the photoresin can produce PbSe to form the designed PbSe micro/nano- structures. To avoid possible trouble from the significant refractive index mismatch, the developed photoresin should have a low refractive index (Fig. 1(b)). To enable 3D fabrication in the photoresin, the photoresin is required to have no single-photon absorption but two-photon absorption at the excitation wavelength. Based on these considerations, 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) in this experiment. This organic solution had a high solubility of PbOA and TOPSe which allowed the formation of PbSe with sufficient amount of Pb and Se elements in 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 mixture had a refractive index about 1.50 which served as a low refractive index platform for the DLW of PbSe without aberration compensation. ODE was a colorless solution and had no single-photon absorption at the laser wavelength from 500 nm to 800 nm. This provided the possibility of fabricating 3D PbSe structures in ODE. TOPSe in ODE was also a colorless solution. Pure PbOA was a wax-like solid. After dissolving PbOA and TOPSe in ODE, the final photoresin was a transparent and colorless solution (Fig. 2(a)).

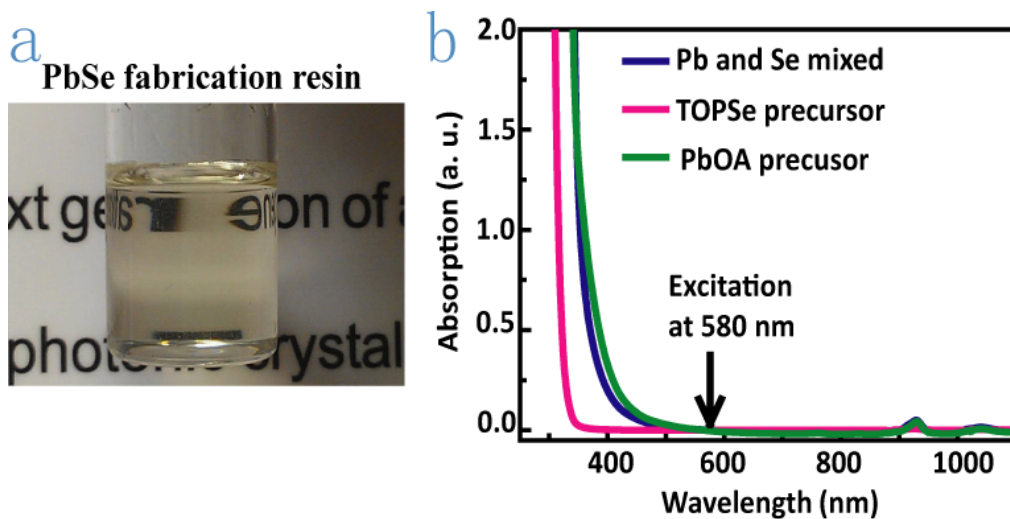


Fig. 2. Synthesised photoresin for the PbSe material fabrication based on the bottom-up strategy via two-photon DLW. (a) A photograph shows that the photoresin is transparency and colorless. (b) The absorption spectrum of the photoresin, TOPSe precursor and PbOA precursor.

For the preparation of PbOA as the precursor of the fabrication photoresin with a maximum dissolve of Pb elements, a mixture of PbO (0.506 g), oleic acid (1.280 g) and technological grade 1-octadecene (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 was a colorless 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 (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 fast formation of PbSe with high chemical efficiency [16]. 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 photoresin.

Figure 2(b) shows the absorption spectrum of the photoresin, TOPSe precursor and PbOA precursor. The absorption spectra of both PbOA and TOPSe precursors in Fig. 2(b) show an absorption band edge at the wavelength of 410 nm and 340 nm separately. The photoresin show an absorption bandedge at the wavelength of 400 nm, which confirms no absorption in the wavelength range from 500 nm to 800 nm. A laser beam with a wavelength of 580 nm was used as the DLW excitation source for two-photon absorption. Under the excitation with a wavelength of 580 nm, the photoresin can absorb 580 nm light via two-photon absorption and trigger the formation of PbSe within the focal spot volume.

3.2 Two-photon direct laser writing of PbSe structures

At the room temperature, the mixed PbOA and TOPSe in ODE can form PbSe with a slow reaction rate. The formed PbSe has a dark color and thus can change the color of the mixture from colorless to dark brown. This is because of the formation of PbSe nano-particle in the photoresin. 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 use DLW in this photoresin.

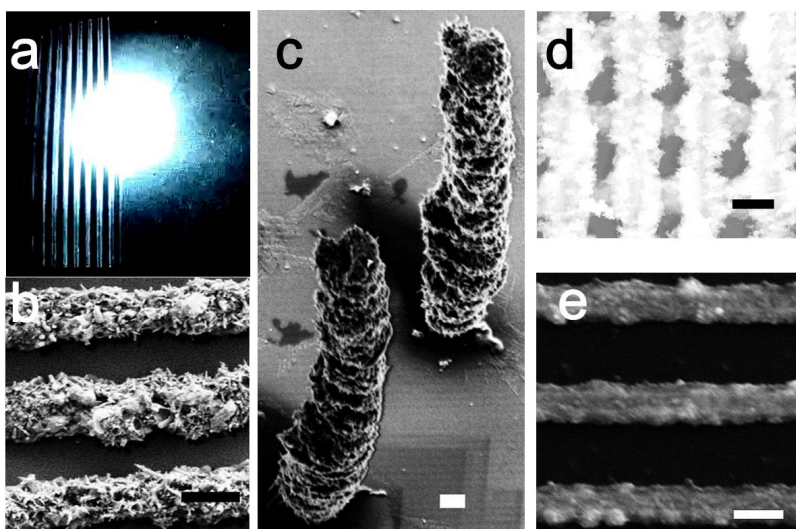


Fig. 3. Fabrication of the PbSe structures by two-photon DLW in the photoresin. (a) A typical picture taken during the fabrication process from the CCD camera. (b) The SEM images of two dimensional lines. (c) The SEM images of pillars with a height of about 12 μm . (d) The SEM images of 3D structure with different layers. (e) The SEM images of the two dimensional structures after fabrication and annealing. All the scale bars are 1000 nm.

Under the irradiation of a femtosecond (fs) pulsed laser beam with wavelength 580 nm, PbSe can be formed instantly. This laser induced instant formation of PbSe in the photoresin enables the fabrication of PbSe structures in a solution and facilitates the successful fabrication of narrow bandgap semiconductor materials by two-photon DLW. By moving the relative position of the photoresin with a scanning stage, two-dimensional structures can be fabricated. A home-made confocal microscopy with a charge-coupled device (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 dark color (Fig. 3(a)). The significant refractive index change at the position of the fabricated lines indicates the formation of the high refractive-

index material. The experimental achieved linewidth in Fig. 3(b) is about 900 nm which confirms the sub-micron fabrication resolution. To show the 3D fabrication ability, pillars with a height about 12 microns were fabricated by moving the scanning stage vertically away from the objective (Fig. 3(c)). We also fabricated 3D structures with different layers (Fig. 3(d)). As we used a linearly polarized beam to do the fabrication, lines at different layers fabricated along perpendicular directions (top layer and the second layer in Fig. 3(d)) shows significant linewidth differences (the top layer linewidth is about 900 nm, the second layer linewidth is about 500 nm.) due to the non-symmetrical property of the laser beam focal spot. However, as can be seen from the scanning electron microscopy (SEM) images (Figs. 3(b), 3(c) and 3(d)), 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 annealing (Fig. 3(e)) is much smoother and the feature size of the line is reduced as well compared with Fig. 3(b), which shows an effective way to improve the quality of the fabricated structure.

A drop of the photoresin was sandwiched between two cover slips separated by about 60 μm with thick sticky-tapes. The sample was then used for the two-photon DLW. A femtosecond pulsed 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 photoresin with a high numerical-aperture oil immersed objective lens (Olympus, NA = 1.4, 100 \times) to induce PbSe formation. The sandwiched sample was affixed to a 200 \times 200 \times 200 μm x-y-z piezoelectric scanning stage (P562, Physik Instrumente) for fabrication. A mechanical shutter, 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 was monitored with real time by a charge-coupled device (CCD) camera. A red lamp was used as an illumination source for the CCD camera. The 3D structure was fabricated on the up surface of the down cover slip by controlling the moving of the scanning stage. After the fabrication, the sample was 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 5 mins to remove the un-solidified photoresin and to reveal the fabricated structure. The fabricated structure was finally dried in air at the room temperature.

The fabricated structures were measured with a ZEISS Supra 40 VP Field Emission Scanning Electron Microscope (SEM). Before the measurement, the sample was coated with a gold layer with the thickness of 2-3 nm.

2.3 Confirmation of PbSe formation

It is important to confirm the formation of the PbSe structure by two-photon DLW. The energy dispersive spectrum (EDS) of the fabricated structure was measured and shown as Fig. 4(a). 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 utilization rate of Se in the photoresin [17]. 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 PbSe structure. To show the crystal structure of the fabricated PbSe structures, high resolution transmission electron microscopy (HRTEM) image was shown in Fig. 4(b). The HRTEM image confirms the formation of PbSe with a rock salt phase.

The EDS measurement was performed at a fabricated PbSe block at an area of 20 \times 20 μm^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.

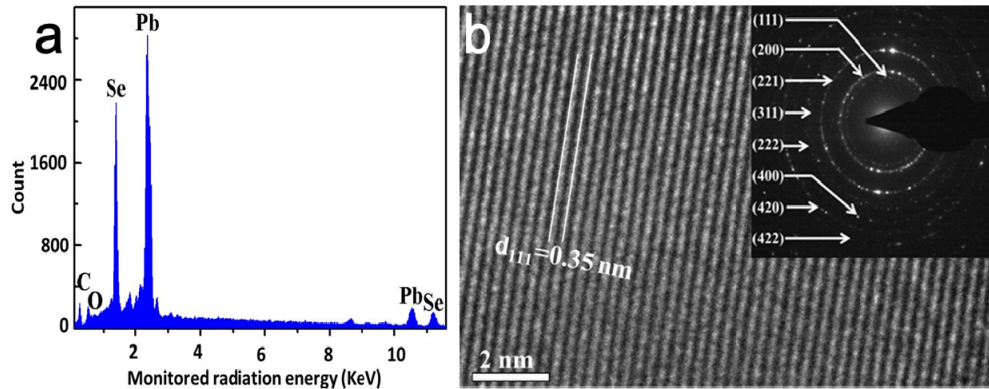


Fig. 4. (a) Energy dispersive spectrum of the fabricated PbSe structures. (b) The HRTEM image of the fabricated PbSe structures.

3. Discussion

The mechanism of the PbSe formation under the irradiation of the fs pulsed laser beam can be explored in two aspects. The first one is the local heat driven PbSe formation. At the focal region, due to the light energy concentration, the local temperature can be increased. This local high temperature means a high chemical reaction rate and makes the instant local 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 quantum dots synthesis with the wet chemical method [18]. In our experiment, it takes about 50 ms to finish the line fabrication within one micron length according to the line fabrication scanning speed of 20 $\mu\text{m/s}$. It is observed that lines can be fabricated at a scanning speed of 100 $\mu\text{m/s}$. If high temperature is the only reason to induce PbSe instant formation, the local temperature should be much higher than 120°C. The other possible mechanism is the reduction of Pb^{2+} to Pb^0 under the irradiation of an intense laser beam. Compared with the reaction rate of $\text{Pb}^{2+}(\text{OA})$ with TOPSe, Pb^0 can react with TOPSe much faster [19]. If Pb^0 can be formed instantly with the irradiation of the intense laser beam, the reaction of $\text{Pb}(\text{OA})$ 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 [16, 20–23].

4. Conclusion

In conclusion, to the best of our knowledge, we have, for the first time, demonstrated the two-photon bottom-up DLW for the fabrication of 3D micro/nano-structures made of the narrow bandgap and high refractive-index PbSe material. It should be noticed that other metal ions such as Cd^{2+} , Sn^{2+} , and Zn^{2+} can also be dissolved in ODE with the form of MOA where M is the metal element and the elements S and Te can also be dissolved in TOP to form TOPS and TOPTe [24, 25]. The 3D fabrication platform similar to the method we have used to fabricate PbSe in this work, should be applicable to generate other kinds of 3D narrow bandgap semiconductor micro/nano-structures.

Acknowledgment

This work is supported by the Australian Research Council (ARC) Centre for Ultrahigh-bandwidth Devices for Optical Systems (CUDOS) (project number CE110001018).