Optical and thermal characterization on micro-optical elements made by femtosecond laser writing

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ABSTRACT

Femtosecond laser polymerization of photonic crystals (PhCs) and diffractive micro-optical elements which can be easily integrated into complex 3D geometries of micro-fluidic chips is analysed in IR spectral domain. Thermal properties of such 3D optical elements and patterns were investigated by thermal imaging, IR spectroscopy and a heat-wave method using absorption-heating with visible light. Thermal imaging allows a simple in situ judgement on a 3D fabrication quality of photonic crystals and is simpler compared with scanning electron imaging. Photonic stop gaps at IR spectral range were clearly observed and IR mapping at the specific spectral wavelength reveals spatial uniformity of PhCs. Potential to use IR imaging with spectral IR plasmonic filters for sensor applications is discussed.

Keywords: laser fabrication, photonic crystals, IR imaging, temperature diffusivity, IR sensors, plasmonics

1. INTRODUCTION

Direct laser writing of micro-optical elements and photonic crystals (PhC) has become a mature technology after suitable optical materials such as organic-inorganic hybrid resists have been developed over the last decade.1–10 Resolution of laser polymerized structures down to tens-of-molecules has been achieved.11 There is an increasing need for in situ monitoring as well as for assessment of the structuring quality of micro-patterns made by laser writing. While some of applications in the field of laser writing such as fabrication of scaffolds for cell growth12, 13 does not require very high resolution and surface quality, PhC and micro-optical applications should meet very stringent requirements for the surface finish and ideally without post-processing procedures.

Infra-red imaging is one of the suitable techniques to inspect quality of PhC since usually they have photonic stop bands (PSB), with transmission considerably reduced along certain directions, is in IR spectra region. Formation of PSB occurs due to periodic pattern of PhC and inspection of reflectivity would bring out structural perfection of the interior regions of PhC, which can be not well developed in the chemical wet bath processing step. Since polymerization can be carried out by a local heating delivered with a micrometer precision, IR

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monitoring of laser fabrication is a promising technique to clarify a photo-thermal or/and photo-physical nature of laser induced modifications.\textsuperscript{12, 14–18}

Here, we show use of IR imaging and spectroscopic characterization of PhCs polymerized by direct laser writing with fs-laser pulses. Also, fs-laser structured regions inside polyimide (PI, the Kapton H) film were investigated for thermal transport properties.

2. EXPERIMENTAL: SAMPLES AND PROCEDURES

Woodpile PhC structures were polymerized by direct laser writing in SZ2080 sol-gel resist with photoinitiator Bis (Michlers ketone 4,4-bis(dimethylamino)benzophenone) as we reported earlier.\textsuperscript{15–17, 19–22} Figure 1 shows images of the PhC patterns of different pitch, hence with different volume filling factor. Such woodpile structures are expected to have a reflectivity at wavelengths approximately twice the period. Such 3D PhC structures are good test samples for transmission and reflection tests at 2-5 µm spectral range.

Structural morphology of samples was inspected with scanning electron microscopy (SEM).
Figure 3. (color online) (a) Transmission spectra integrated over 650 - 4000 cm$^{-1}$ spectral window. (b) Reflection spectra and IR image mapping (in transmission) at specific wavelengths; arrows pointing to the image insets. The same nomenclature is used in panels (a) and (b) and 6-9 structures corresponds to I-IV in Fig. 1. One woodpile occupies a 100 × 100 µm$^2$ footprint.

IR imaging was carried out with a photon-type IR camera Indigo Phoenix coupled with CCD InSb sensor operating in 3-5 µm spectral range and equipped with optics operating down to 3-4 µm spatial resolution. The Fourier transform IR (FTIR) spectral imaging was carried out with a PerkinElmer Spotlight 3000 setup which include of a spectrometer (Spectrum One, PerkinElmer Inc.) an IR microscope, the automatic xyz-stage with a sample holder, and detector linear array 16 × 1 of Mercury Cadmium Telluride (MDT) sensor; a square pixel size was ∼ 6.25 µm. Spectral analysis was carried out with 4 cm$^{-1}$ spectral resolution, averaging of 16 scans, and a baseline substraction at each pixel.

Heat wave method of modulated thermal excitation and synchronized detection$^{23-28}$ was used for comparison with spectral imaging and FTIR measurements. A femtosecond (fs) laser structuring of Kapton H (a derivative of polyimide PI) ∼ 75 µm-thick film was carried out by 150 fs/800 nm laser pulses at irradiance above the dielectric breakdown threshold to alter its thermal properties. Focusing objective lens had numerical aperture of NA = 0.5. A grating patterns with different periods 10, 20 µm were recorded at different depth inside the PI film over a 760 × 760 µm$^2$ footprint; a central window of not structured part was left to monitor temperature distribution in the 120 × 140 µm$^2$ area. The heat-wave optical illumination was placed at the depth of laser structured region; more details about the method and laser structuring were published elsewhere.$^{28}$

3. RESULTS

IR imaging and mapping of PhC structures at specific wavelengths is presented next together with temperature diffusion in fs-laser structured PI film.

3.1 Spectral imaging

Figure 2 shows integrated IR radiation image of woodpile structures. A difference of the contrast is discernable. Interference is observed in the smallest period $p_{xy} = 1.7$ µm woodpiles. Difference in black body emission of the micro-structures is caused by the PhC stop gap formation at specific wavelengths and emissivity of the structured material, SZ2080. Emissivity depends on surface properties, direction of imaging, wavelength and for patterns like PhC with large surface-to-volume ratio can be different from the bulk material.

Spectral mapping at selective wavelengths was carried out and is summarized in Fig. 3. Spectrally integrated transmission was almost featureless as shown in Fig. 3(a). However, there were strong reflection regions (Fig. 3(b))
Figure 4. (color online) (a) Transmission image at the photonic stop-gap of the structure No. 2. (b) Transmission spectra presented in units of absorbance \( \text{Abs} = -\lg(T/T_0) \), where \( T_0 \) is the intensity of the input light, \( T \) is the intensity of the transmitted light through the sample; arrow shows the stop gap spectral position of the structure No. 2. One woodpile occupies a 100 \( \times \) 100 \( \mu \)m\(^2\) footprint.

Figure 5. (color online) The amplitude and phase images of the fundamental Fourier component (at frequency of temperature modulation). The excitation was delivered by focused 630 nm wavelength laser at \( \sim 0.2 \) Hz modulation frequency. Scales are arbitrary and were optimized for visibility of the polymerized cage around a woodpile structure. One woodpile occupies a 50 \( \times \) 50 \( \mu \)m\(^2\) footprint.

which were dependent on the period of the woodpiles: smaller period caused stronger reflection at shorter wavelengths (larger wavenumbers) as expected from the Maxwell scaling. Strong modulation of the reflectivity was observed around 3000 cm\(^{-1}\) and tunability of reflection by period of the structure is clearly demonstrated. The measurements were carried out with FTIR spectrometer in reflection.

It is usually easier to detect spectral position of the stop gap of PhC in reflection. Figure 4 shows the same imaging (a) data together with direct measurement of the transmission using FTIR spectrometer. Formation of the stop gaps is also clearly recognizable in the transmission spectra and indicates a good quality of 3D laser writing and structural uniformity of the structures retrieved after a wet-bath development. Capillary forces of the wet processing are critical in achieving high spatial resolution\(^4,7,29\) of the 3D patterns since their mechanical strength is reduced at low volume fraction of the polymer.\(^8,30–32\)

3.2 Heat wave method
Temperature diffusivity measurements by a modulated heat wave excitation with a synchronized detection by (i) direct measurement using a thermocouple or by (ii) imaging is an additional tool to investigate thermal
properties at nano-/micro-scale.  

Figure 5 shows the amplitude and phase images at the Fourier component frequency which is equal to the modulated illumination (a heat source). The large mesh cage was laser polymerized around one of the woodpile structure. Such cage allows to make 3D PhC inside the bulk volume of the resist and after development a proportional all directional re-scaling of the 3D PhC structure occurs due to capillary forces. This caged PhD was illuminated to modulate its temperature and IR imaging was used to monitor temperature diffusivity. The darker appearance of the cage in amplitude image indicates that its emissivity and temperature are different from the PhC. The Stefan-Boltzmann law defines the radiated power per unit area \( j = \varepsilon \sigma T^4 \), where \( \sigma \) is the Stefan-Boltzmann constant, \( T \) is the absolute temperature, and \( \varepsilon \) is the emissivity. This illustration shows a possibility to use different 3D structures made of the same material and to explore contrast in IR imaging due to differences in their IR reflectivity (the previous section) and emissivity.

Another example of control over the black body radiation via nano-/micro-structuring of material by changing its temperature diffusivity and emissivity is shown in Fig. 6. Two different period gratings in PI film show different thermal emission patterns and temperature diffusivity. Laser structuring changes PI properties and, hence, a heat transport. Temperature increases at the laser modified regions as can be judged from the amplitude and phases contour plots (Fig. 6(c,d)).

The Kapton and PI are popular plastics used for hinges in micro-electro mechanical systems (MEMS) and control of its temperature diffusivity is important for the valve actuation. Since PI has no melting point laser structuring by ultra-short laser pulses can be used for high precision modifications in the volume of the polymer matrix.

4. DISCUSSION

FTIR measurements requires bulky equipment and sophisticated highly sensitive and cooled detectors to perform at around 10 \( \mu \)m wavelengths which are close to the thermal noise at normal conditions. IR selective filters for extraordinary transmission (up to 15 – 20%) using plasmonic hole patterns can be implemented as discussed next. Such filters can be used with much simpler imaging IR CCD cameras.
Sensing in the IR spectral range around 10 µm (1000 cm\(^{-1}\)) wavelength where molecular fingerprinting is possible by surface enhanced IR absorption (SEIRAS). Extraordinary transmission through plasmonic metal mesh can be used to enhance IR absorption of particular narrow molecular peaks as we demonstrated for the azobenzene and SF\(_6\) gas.\(^{35,36}\) At those IR wavelengths the required resolution of the hole mesh arrays is not demanding and simple mask projection lithography or thin film ablation by fs-laser irradiation can be used to fabricate IR absorption enhancing surfaces.\(^{37-39}\)

For fabrication of IR metal meshes for extraordinary transmission around 2-4 µm in SEIRAS applications, resolution of micro-fabrication should be considerably higher and lithography masks have to be fabricated via electron beam lithography (EBL) step which is usually considered forbidding in practical sensing applications. A laser ablation could be used down to the hole sizes of several hundreds of nanometers with period approximately twice larger and is a promising method for IR sensing.

The Wien’s law links the temperature and the peak wavelength of the corresponding black body emission:

\[ \lambda_{\text{max}} = \frac{b}{T}, \]

where \(b = 2.8977685(51) \times 10^{-3}\) m.K and \(T\) is the absolute temperature, e.g., \(T = 1000\) K produces emission which peaks at \(\lambda_{\text{max}} \approx 2.9\) µm \(\equiv 3448\) cm\(^{-1}\).

Sensing of CO\(_2\) with current atmospheric level approaching 400 ppm is required with sensitivity better than 10 ppm (by volume). CO\(_2\) has absorption bands around 650-700 cm\(^{-1}\) and 4.2 µm (2380 cm\(^{-1}\)). Other greenhouse gases and ozone have bands within the spectral range which is matching the resolution capabilities of direct laser writing in photo-polymers. Hybridization of PhC with plasmonic metal coatings\(^{40}\) can prove successful strategy to create field enhancement and modulation of IR transmission/reflection. Expanding the concept of IR sensors one can envisage similar performance as recently demonstrated for chemical sensing with Morpho butterfly structures via reflectivity changes at visible wavelengths.\(^{41}\)

5. CONCLUSIONS

Thermal imaging at IR wavelengths and spectral mapping showed that PhC structures exhibit strong reflectivity changes near spectral locations of the photonic stop gaps. This feature can be used in thermal imaging to filter and/or detect specific wavelengths at near-IR range. Since 3D PhD are volumetric structures, they can be tailored for sensing in gas or liquid by monitoring their IR reflectivity/transmission.

As THz and IR detection becomes more a widely spread technology, direct detection at the specific spectral window using plasmonic extraordinary transmission has strong application potential. Commercial IR and THz (0.2-0.4 THz) people security scanners are passive and already operate without additional illumination and detect black body radiation which is quite weak. Such technology does not require check points and monitors people remotely. Creation of IR and THz filters is a fast growing area of engineering.

Temperature localization at nanoscale is very interesting phenomena which can help to understand light localization on nano-structures used in surface enhanced Raman scattering,\(^{42-44}\) creation of high resolution 3D PhC structures by direct laser write with well controlled light and heat delivery.\(^{6,11,18,45-48}\) Temperature to electricity converters is yet another strongly sought after technology required to decrease thermal energy pollution and working by engineering the thermal conductivity and temperature diffusivity at a nanoscale.

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