Temperature effects on pinpoint photopolymerization and polymerized micronanostructures

Kenji Takada, Koshiro Kaneko, Yu-Dong Li,[a] and Satoshi Kawata
Department of Applied Physics, Osaka University, Suita, Osaka 565-0876, Japan

Qi-Dai Chen and Hong-Bo Sun[b]
State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, 2699 Qianjin Street, Changchun 130012, People's Republic of China

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The spatial resolution in pinpoint two-photon photopolymerization of radical-type resins was found to be improved by varying the liquid sample temperature from a critical value T_c. For SCR-500 and NOA-61, the currently widely used resins, T_c is around room temperature. The improvement of spatial resolution by temperature decrease was attributable to restraint radicals diffusion; while the voxel size reduction versus temperature increase was considered as arising from enhanced chain termination. Furthermore, temperature plays an important role in size tuning of polymerized structures, for example, a photonic crystal blueshifted its working wavelength for 50 and 400 nm when heated at 200 and 300 °C, respectively, indicating the possibility to precisely tailor the photonic bandgap by means of thermal processing. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2834365]

Since the first demonstration of femtosecond laser light for photonic crystal (PhC) fabrication,[1] the approach has been broadly utilized for modeling and prototyping complicated three-dimensional (3D) micronanocomponents in optics[2–4] and mechanics[5–7] either by means of pinpoint two-photon photopolymerization of resins[1,4–8] or by photoionization of transparent dielectrics.[2,3,9] It is particularly worthy to mention that the fabricating accuracy has recently reached around 10 nm[4] with the assistance of optical nonlinearity,[10–12] i.e., two-photon absorption effect,[1] and chemical nonlinearity, i.e., thresholding effect,[13] as well as with the aid of material nonlinearity, i.e., the polymer network shrinking effect.[10] The advance makes the femtosecond laser fabrication a real nanotechnology that enables devices of size less than 100 nm in at least one dimension. The reasonably high fabrication accuracy, together with the capability of arbitrarily prototyping complex 3D geometry may lead to the concept of *designable nanofabrication*. Polymer micronanoelectromechanical systems and micro-optical integrated circuits are two examples with immediate application potential. However, deep insight into photopolymerization chemistry and understanding of physical performance of nanostructured polymers are indispensable before this dream comes true. For instance, it has been considered that lowering the temperature of photopolymerization may significantly improve the fabrication spatial resolution due to suppression of radicals' diffusion and Brownian motion of small molecules. However, so far there is no experimental data to support this supposition that has until now been taken for granted. In this letter, we find that reducing temperature tends to reduce voxel size but the effect is not as pronounced as to be practically useful. On the contrary, increasing temperature leads to considerable improvement of the spatial resolution. Furthermore, a postfabrication thermal processing was found to irreversibly blueshift the photonic bandgap of polymer PhC structures.

Shown in Fig. 1(a) is an optical microscope-adaptive cooling and heating setup. The temperature of the inner chamber is continuously adjustable from −193 to 650 °C with an accuracy of ± 0.5 °C by balancing the flow rate of

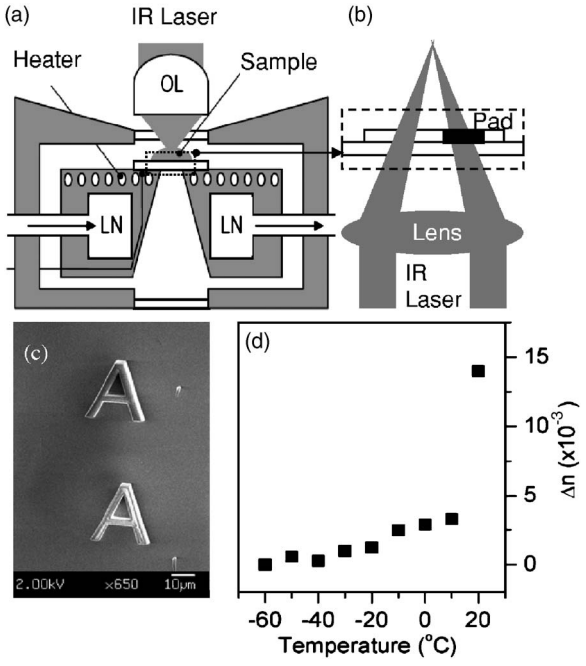

FIG. 1. Photopolymerization and photopolymerized structures under low temperature. (a) Schematic illustration of the temperature controlling block, LN: liquid nitrogen, OL: objective lens. (b) A dual-beam interference system for characterizing the refractive index change of the laser-exposed pad as the sample temperature is increased from below freezing point of the resin to RT. (c) SEM image of a two-photon polymerized letter "A," which underwent the temperature varying sequence prior to sample rinsing. (d) The resin refractive index change versus temperature, indicating the occurrence of polymerization.

[a]Currently with: College of Physics, Nankai University, 94 Weijin Street, Tianjin 300071, China.
[b]Author to whom correspondence should be addressed. Electronic mail: hbsun@jlu.edu.cn and hbsun@ieee.org.

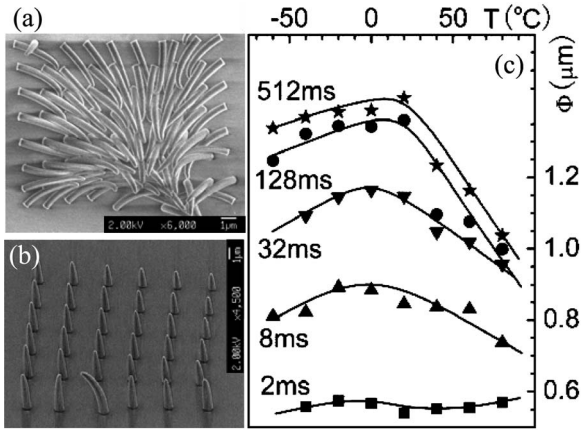

FIG. 2. Spatial resolution investigation by means of voxel formation. (a) Long voxels and (b) approximately half-truncated voxels produced by the ascending scan approach. The applied laser pulse energy is 8 nJ. (c) Lateral voxel sizes under varied temperatures. Each point is obtained by averaging data from six identical experiments.

the liquid nitrogen and the heating power. The top and bottom glass windows of the setup permit simultaneous incidence of the femtosecond laser for fabrication and the illuminating light for *in situ* observation of the sample production process. Because of a thermally resistive gap between the top window and the sample platform, a long working distance objective lens was needed. In the current research, a numerical aperture (NA)=0.55, 40× lens was employed to focus the femtosecond laser pulses of 82 MHz repetition rate, 80 fs pulsewidth, and 780 nm wavelength for micronanofabrication. 3D scanning was realized by a piezoelectric stage with motion accuracy better than 1 nm. The resins, SCR-500 (JSR, Japan) and NOA 61 (Norland Optical Adhesive), were adopted. The temperature-dependent polymerization degree was evaluated by a dual-beam interference system [Fig. 1(b)]. As a test of the newly built setup, a letter "A" was written,[4] gradually cooled to −80 °C and then recovered to room temperature (RT), rinsed by ethanol, and finally imaged by scanning electron microscope (SEM). The well-defined letter shape [Fig. 1(b)] verifies that the temperature-varying setup works properly.

Low-temperature photopolymerization, by which better fabrication spatial resolution has been expected, was first investigated. The underlying mechanism is the suppression of local photoinduced radicals and small molecules, and the reduction of their Brownian motion.[14] These temperature sensitive processes have been considered as the most likely factor to cause voxel expansion.[13] Shown in Fig. 2(a) is a SEM image of voxels produced by means of ascending scan, their size revealing the information of the spatial resolution.[15] Since it is difficult for long voxels to stand self-supported because of the low NA induced slim shape, we carefully reduced voxel lengths to near to their half maximum [Fig. 2(b)] by adjusting the position of the focal spot,[15] from which the lateral diameter was measured. The decrease of the lateral voxel diameters versus temperature falling from room temperature to −60 °C is not astonishing [Fig. 2(c)]. The rate of voxel size reduction is 0.8–1.1 nm/°C. The freezing point of the SCR 500 resin is −50 °C, while voxels were formed by laser writing in resins that were frozen to −60 °C. It is interesting to know in which state, liquid ($T>-50$ °C) or solid ($T<-50$ °C), does the polymerization occur. In the test system [Fig. 1(b)] constructed inside the temperature-variation setup [Fig. 1(a)], a probe light beam is passed through a 500 μm thick pad that was pinpoint exposed at −60 °C, and interfered with a reference beam. These two beams are the same as that used for fabrication but with one-order weaker power. The interference fringes, monitored by a photodetector, shifted when the sample temperature rose, from which the relative refractive index change, or Δn between the exposed and the bare regions was deduced [Fig. 1(d)]. The laser irradiated pad volume and other part of the sample underwent identical temperature variation. Therefore, the only interpretation of the origin of Δn is that polymerization takes place since it is known that the refractive index increases by around 0.02 after photopolymerization for SCR 500. This implies that radicals are produced from pinpoint exposure in the frozen resin but the polymerization does not

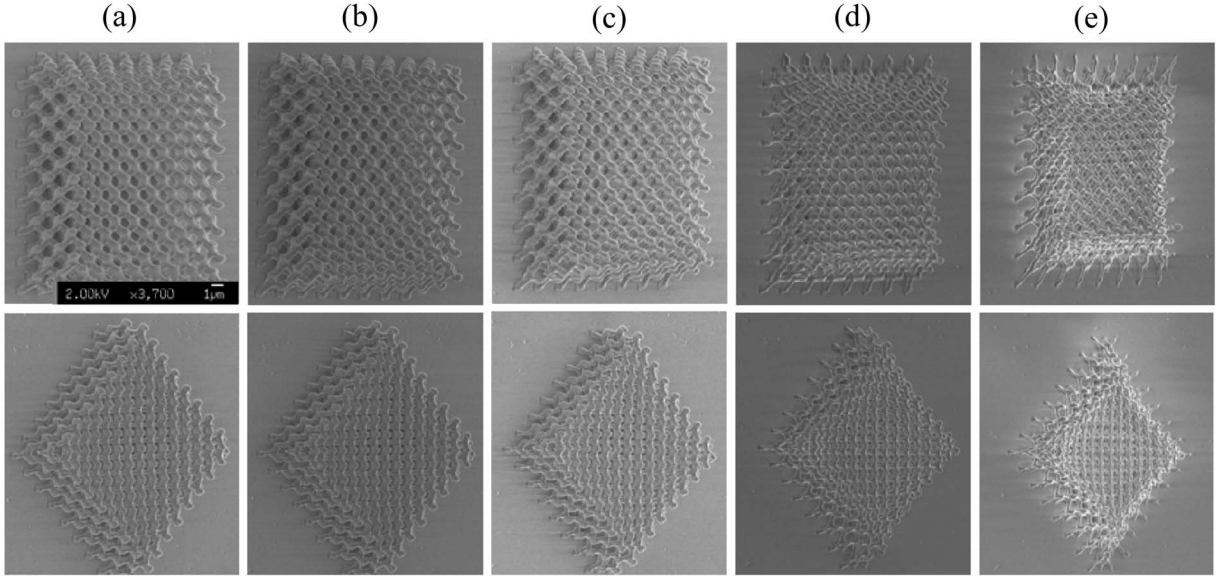

FIG. 3. SEM images of diamond-lattice PhCs heated under different temperatures for 30 min: (a) as fabricated at RT, (b) 150 °C, (c) 200 °C, (d) 250 °C, and (e) 300 °C.

proceed significantly until an appropriate temperature is provided, e.g., more than 10 °C in the current study. The above phenomenon indicates the technical possibility of performing pinpoint two-photon writing from frozen solid resins so that floating and distortion occurring in the course of laser scanning is minimized.

Following the tendency of voxel size increase versus T increase from −60 to 20 °C, we expect that further rise of temperature brings about larger voxels. However, a pronounced decrease, a tendency opposite to the prediction, has been experimentally attained in course of T lifting from 20 to 80 °C. In case of 512 ms exposure, the voxel size of 1.42 μm at 20 °C is lowered to 1.04 μm at 80 °C, i.e., a 27% reduction. The reduction rates for 128, 32, and 8 ms exposures are 26%, 17%, and 13%, respectively. In order to understand this unusual phenomenon, the kinetics of photoinitiated polymerization has to be considered. Polymerization reactions occur mainly after the laser irradiation, of which the task is generation of radicals [$R^{\bullet}$, Eq. (1)] from initiator molecules (I). The important stages of polymerization, propagation [Eq. (2)], and termination [Eq. (3)], are both favored by enhanced diffusional effects associated with temperature.[16,17] A T increase enhances the mobility of the reactive chain ends, e.g., $M_1^{\bullet}, M_2^{\bullet}, M_m^{\bullet}, M_n^{\bullet}$ in Eqs. (2) and (3), and therefore leads to the reduction of their "lifetimes."

$$\text{Radical creation: } I \xrightarrow{2\hbar\nu} 2R^{\bullet}, \tag{1}$$

$$\text{Chain propagation: } R^{\bullet} + M \rightarrow M_1^{\bullet},\ M_1^{\bullet} + M \rightarrow M_2^{\bullet} \ldots$$
$$M_n^{\bullet} + M \rightarrow M_{n+1}^{\bullet}, \tag{2}$$

$$\text{Chain termination: } M_m^{\bullet} + M_n^{\bullet} \rightarrow M_{m+n};$$
$$M_m^{\bullet} + M_n^{\bullet} \rightarrow M_m + M_n. \tag{3}$$

Temperature accelerated termination is well known in photopolymerization.[16] The similar temperature dependence of voxel size was found on NOA 61, for which it happens T_C is also around RT. Scherzer and Decker[17] found recently from a real-time fourier transform infrared spectroscopy (FTIR) study varying temperature up to 160 °C that the induction period strongly decreased at higher temperature, and enhanced termination processes led to a decrease of the polymerization rate. In laser micronanofabrication, higher concentration of the short-chain polymer units results in less cross-linked or loose voxels, of which the surrounding portion is easier to be removed in the rinsing process, contributing to smaller voxel size. In other words, the fabrication spatial resolution is improved.

Not only the photopolymerization process itself is affected by temperature, but also some characteristics of photopolymerized structures are sensitive functions of temperature. Figure 3(a) shows a diamond-lattice PhC structure consisting of balls of 580 nm, rods of 500 nm, and a period of 2.5 μm. This was rapidly heated (>50 °C/min) from RT to series of target T's: 50, 100, 150, 200, 250, and 300 °C. After holding at these temperatures for 30 min, the sample was rapidly cooled to RT for FTIR characterization. No visible shape change appears until treated at 200 °C [Fig. 3(c)], above which PhC structures shrunk inwards, and the rods become thinner. If we define a shrinkage rate as the ratio of the top-layer period of heated PhCs to that of unheated samples, a maximum of 85% shrinkage has been obtained at 300 °C [Fig. 4(a)]. The shrinkage leads to a significant blueshift of the bandgap center wavelength, for example, by approximately 50 nm at 200 °C and 400 nm at 300 °C [Fig. 4(b)]. Thermal processing within an appropriate temperature range, e.g., 100 °C $<T<$ 200 °C not only makes the structures mechanically more robust, but also moves their bandgap position. Careful selection of the processing conditions may be useful for precisely tuning the working wavelength of polymer PhCs while maintaining lattice shape.

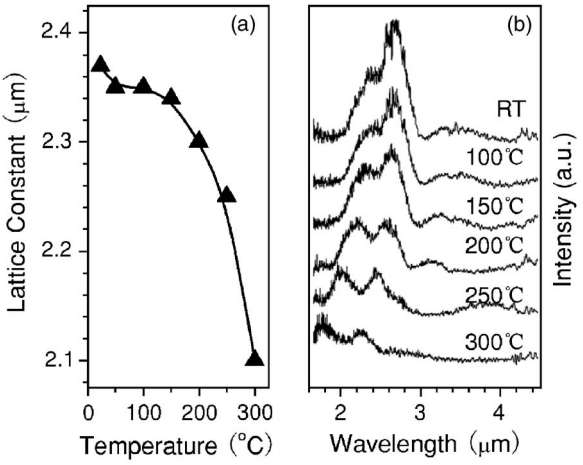

FIG. 4. (a) The treatment temperature-dependent lattice constants of the heated PhC. (b) Reflection spectra of the PhC structures treated under different temperatures.

In summary we find temperature—sensitivity of fabrication spatial resolutions and feasibility of initiating polymerization in the frozen state of resins in pinpoint two-photon photopolymerization, as well as a huge shrinking effect of micro-polymer structures upon heating. These will help a deep insight and broad use of the technology.

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