

Fabrication of Thermally Durable Sub-wavelength Periodic Structures upon Inorganic–Organic Hybrid Materials by Nano-imprinting

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We fabricated sub-wavelength periodic structures by thermal nano-imprinting using our original functionally modified inorganic–organic hybrid materials. The fabricated structures exhibited excellent uniformity and surface smoothness over a large imprinted area. In addition, optical transmittance is more than 90% within visible wavelength regions after heat treatment for 2 h at 300 °C. These nano-imprinted periodic structures showed high thermal durability without any structural changes after heating for 2 h at 200 °C, which is superior to commercially available organic imprinting materials. These nano-imprinted sub-wavelength periodic structures using our original inorganic–organic hybrid materials offer great potential for several applications in microphotonic and nanophotonic devices. [DOI: [10.1143/JJAP.46.3704](https://doi.org/10.1143/JJAP.46.3704)]

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1. Introduction

Nano-imprinting, which uses a rigid or elastomeric mold for the simple fabrication of various nanostructures, offers excellent features such as patterns smaller than 10 nm over a large area. It is an attractive, low-cost alternative to photolithography and other lithographic techniques, particularly for applications in microphotonics, nanophotonics and electronics.^{1–7)} The nano-imprinting methods can be broadly classified into two types depending on the curing properties of imprinted materials: UV-based and thermal-based nano-imprinting methods. In general, organic materials such as poly(methyl methacrylate) (PMMA) have been mostly studied for nano-imprinting. They have shown good imprinting behavior because of their UV-induced and thermally induced curability. However, these organic imprinted materials present limitations in direct applications as devices because of their low thermal durability. For that reason, organic imprinted materials have been used only as resists, which requires a rather complex process for direct application to microdevices and nanodevices. Consequently, they increase fabrication costs. For those reasons, thermally durable imprinted materials have attracted much attention in recent years for direct applications and have been extensively examined.

Recently, inorganic–organic hybrid materials fabricated by sol–gel processes were found to exhibit better properties than those of organic materials in terms of thermal stability, chemical resistance, and mechanical strength, once fully cured.^{8,9)} In particular, inorganic–organic hybrid materials showed high efficiency of photoinduced and thermally induced polymerization upon feasible modification of the organic functional moiety such as photopolymerizable and thermopolymerizable groups in sol–gel processing.^{8–10)} In addition, the inorganic–organic hybrid materials show high optical transparency in the visible-wavelength regions. Therefore, these outstanding inorganic–organic hybrid materials offer great potential as nano-imprinting materials

for direct application to microphotonic and nanophotonic devices. Moreover, UV-curable inorganic–organic hybrid materials have already demonstrated their candidacy as imprint materials for nano-imprinting.^{11,12)}

In this paper, we introduce thermally curable inorganic–organic hybrid materials with thermal stabilities higher than those of UV-curable inorganic–organic hybrid materials. Then we present sub-wavelength periodic structures fabricated using these materials and thermal nano-imprinting. Finally, we describe the high thermal durability of nano-imprinted sub-wavelength periodic structures upon thermally curable inorganic–organic hybrid material films.

2. Experimental Methods

Transparent thermally curable inorganic–organic hybrid material films were prepared using 3-glycidoxypropyltrimethoxysilane (GPTS; Aldrich Chemical) and diphenylsilane diol (DPSD; TCI) as precursors. Barium hydroxide monohydrate (BH; Aldrich Chemical) was used as a catalyst to promote a condensation reaction between the two precursors. The GPTS and BH were mixed at 80 °C; DPSD was added continually to the mixture for 2 h to prevent self-condensation of DPSD and phase separation. The solution was kept at 80 °C for another 2 h to advance the reaction. Subsequently, methanol, a by-product of the condensation reaction, was removed by vacuum heating. The solution was cooled to room temperature and filtered through a 0.45- μ m-diameter pore filter to remove BH. Finally, the epoxy-modified inorganic–organic hybrid materials were obtained in the form of a clear solution. Aluminum acetylacetonate [Al(acac)₃] of 1 wt % was added as a thermal curing agent to the epoxy-modified inorganic–organic hybrid materials. After stirring the solution for 1 h at room temperature, homogeneous thermally curable inorganic–organic hybrid materials were obtained. These thermally curable hybrid solutions were spin-coated onto cleaned glass substrates and wafers. The coated films were then subjected to thermal-based nano-imprinting. In addition, the structural evolutions related to chemical changes of the thermopolymerization in the thermally curable inorganic–organic hybrid materials

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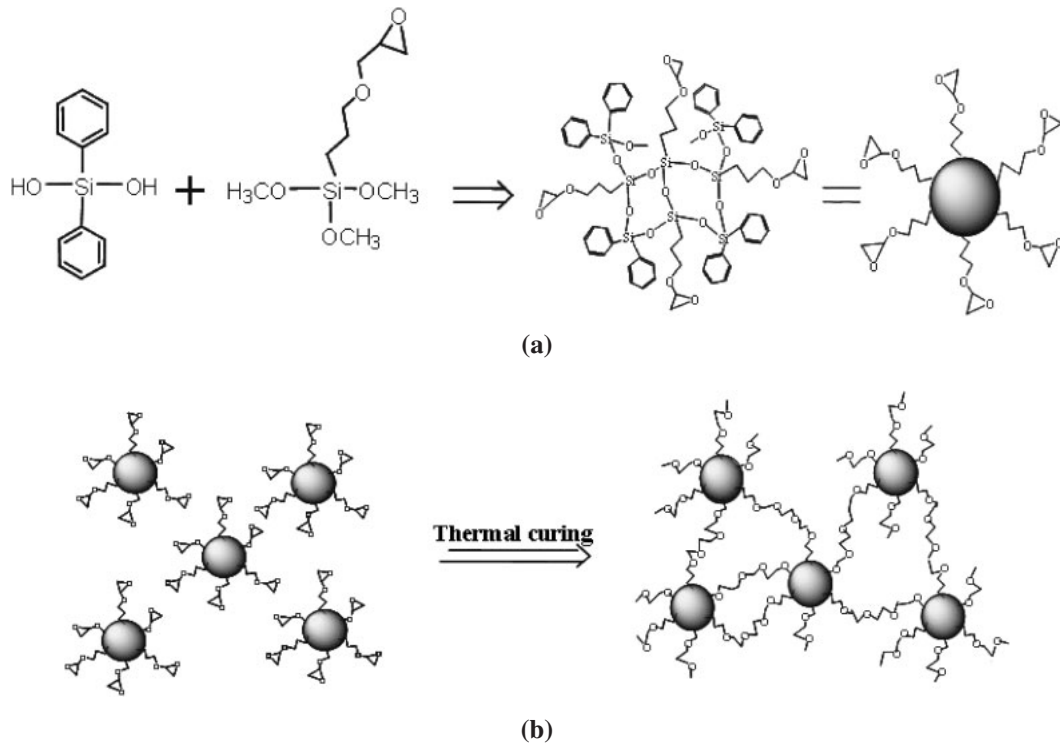


Fig. 1. Fabrication of thermally curable inorganic-organic hybrid materials. (a) Synthesis of nanoscale epoxy-modified oligosiloxane resin from GPTS and DPSD. (b) Fabrication of thermally curable inorganic-organic hybrid materials from epoxy-grafted oligosiloxanes. (Circles indicate oligosiloxane with siloxane bonds)

films were examined by Fourier-transform infrared microscopy (FT-IR; IRT-3000, JASCO). The nano-imprinted sub-wavelength periodic structures and their surface structural changes, depending on the temperature increase, were observed by scanning electron microscopy (SEM; S-4300, Hitachi). The thermal stability and optical transparency of the thermally curable inorganic-organic hybrid material films were examined, respectively, through measurement of the thermal decomposition by thermal gravimetric analysis (TGA) and ultraviolet-visible spectrum (UV-vis) transmission analysis.

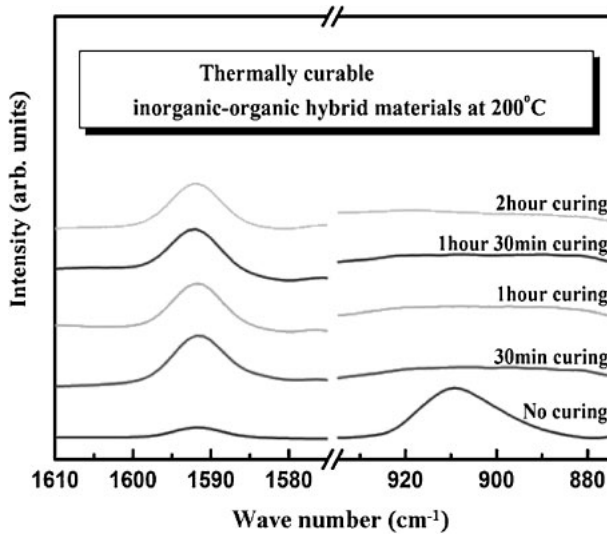
3. Results and Discussion

DPSD and GPTS were chosen to synthesize the desired materials. DPSD has silanol groups that can react with the alkoxy groups in organoalkoxysilane. GPTS has a polymerizable epoxy group. Therefore, epoxy-grafted oligosiloxane can be synthesized via a condensation reaction between the silanol group of DPSD and the methoxy group of GPTS. Used as a condensation catalyst, BH induces a condensation reaction between the two silanes, even without the hydrolysis of silane precursors. In addition, epoxy rings are preserved during the condensation reaction using BH. Generally, the epoxy ring is easily opened in the presence of basic catalysts at temperatures over 60 °C. However, the use of BH as a basic catalyst had no effect on epoxy ring opening in this experiment. BH can act as an efficient catalyst that activates the nucleophilic attack of silanol, but does not change the pH of the solution. Because BH does not dissolve in solvent or water, a neutral condition is maintained. Thus, BH has a catalytic effect only on the condensation reaction. By employing DPSD and BH, epoxy-grafted oligosiloxanes can be synthesized easily via a

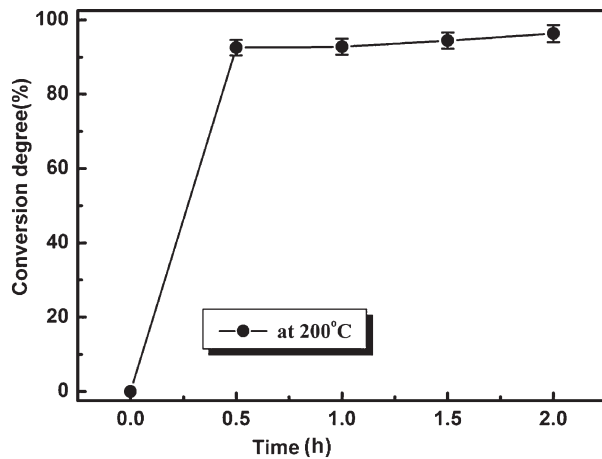
modified sol-gel reaction. The fabrication of thermally curable inorganic-organic hybrid materials using epoxy-grafted oligosiloxanes can be achieved by crosslinking epoxy groups. These reactions are illustrated in Fig. 1.

To analyze the degree of conversion of epoxy groups in thermally curable inorganic-organic hybrid materials, which is extremely important in thermal nano-imprinting processes and in the final structure of inorganic-organic hybrid materials, FT-IR was applied. The FT-IR measurements were performed in the 4000–500 cm^{-1} range with 4 cm^{-1} resolution. Indirectly, FT-IR shows that polymerization or crosslinking of epoxy groups occurred during the thermal curing process. The bands at 910 cm^{-1} , assigned to epoxy groups, decreased after thermal curing. Figure 2(a) shows from which the degree of epoxy ring opening can be calculated the band intensities at 910 cm^{-1} normalized to unchanged phenyl peaks (1590 cm^{-1}). Most epoxy rings are opened after adding $\text{Al}(\text{acac})_3$ and curing. Figure 2(b) shows the conversion degrees of epoxy groups as a function of curing time. The conversion degree of the epoxy groups is greater than 90% after 30 min at 200 °C. It increases up to 96% with increasing curing time. This indicates that thermopolymerization occurs efficiently in the inorganic-organic hybrid materials under heat treatment. Therefore, the thermal nano-imprinting method can be applied efficiently because of the efficient thermal curability of our original inorganic-organic hybrid materials.

Figure 3 shows the fabrication route of sub-wavelength periodic structures for thermally curable inorganic-organic hybrid material films. The figure shows that, before thermal nano-imprinting, prebaking at 150–200 °C was required for efficient nano-imprinting of the resin-type inorganic-organic hybrid material films. The prebaking time was dependent on



(a)



(b)

Fig. 2. (a) FT-IR spectra and (b) the conversion degree of epoxy ring band in thermally curable inorganic-organic hybrid materials as a function of curing time.

the prebaking temperature. After prebaking, thermal nano-imprinting could be simply applied to the thermally curable inorganic-organic hybrid material films. The silica mold used for thermal nano-imprinting was fabricated by photolithographic processing including two-beam holographic interference and dry-etching. The pitch and depth of the mold used were, respectively, around 430 and 140 nm. Table I shows that the imprinting pressure was 3–5 kN and that the imprinting temperature was 200 °C. The imprinting time was controlled in accordance with the procedure of the imprinting step. In step 1, pressing with a low pressure of 3 kN easily imprinted the resin-state films at room temperature. In step 2, the pressure was increased slightly to 5 kN and the temperature to 200 °C in order to fabricate the sub-wavelength periodic structure via the initiation of the thermal curing of resin-state inorganic-organic hybrid material films. In step 3, a pressure of 5 kN and temperature of 200 °C, maintained for 1500 s, resulted in efficient solidification through thermal curing of the nano-imprinted sub-wavelength periodic structure on the inorganic-organic hybrid material films. Finally, the sub-wavelength periodic

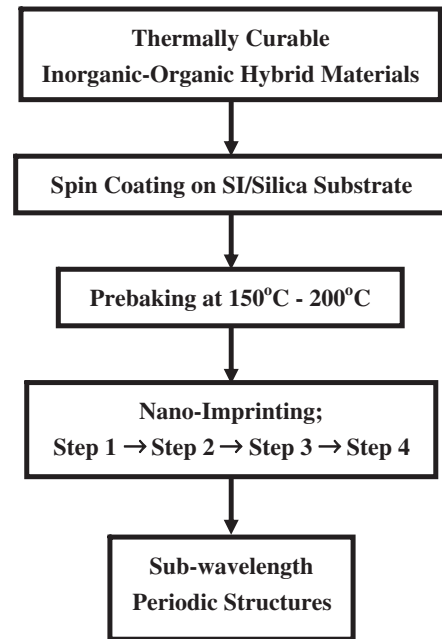


Fig. 3. Fabrication route of sub-wavelength periodic structures on thermally curable inorganic-organic hybrid material films by thermal nano-imprinting.

Table I. Nano-imprinting conditions for fabrication of sub-wavelength periodic structure upon thermally curable inorganic-organic hybrid material films.

	Step 1	Step 2 (Increase)	Step 3 (Maintain)	Step 4 (Decrease)
Pressure (kN)	3	3 → 5	5	5 → 0
Temperature (°C)	20	20 → 200	200	200 → 20
Imprinting time (s)	60	240	1500	600

structures were obtained after decreasing the pressure and temperature and then releasing the imprinted inorganic-organic hybrid material films from the mold.

Figure 4 shows SEM images of (a) a perspective view, (b) a perspective and cross-sectional view, and (c) a cross-sectional view of the sub-wavelength periodic structure fabricated on thermally curable inorganic-organic hybrid material films by thermal nano-imprinting. The nano-imprinted sub-wavelength periodic structures exhibited good imprintability and a uniform homogeneity. The period and depth of imprinted sub-wavelength periodic structures were nearly 430 and 140 nm, respectively, which are almost the same as those of the silica mold used.

These nano-imprinted sub-wavelength periodic structures were then heat-treated at various temperatures to investigate their thermal durability; their surface structural changes were observed using SEM. Figure 5 shows cross-sectional SEM images of sub-wavelength periodic structures imprinted upon thermally curable inorganic-organic hybrid material films for various heating temperatures. Figure 5 shows that the sub-wavelength periodic structures fabricated at temperatures up to 200 °C were stable; no surface structural changes were detected. However, slight surface structural changes were caused by heat treatment at 300 °C. Such structural changes increased sharply because of greater thermal decomposition of inorganic-organic hybrid material

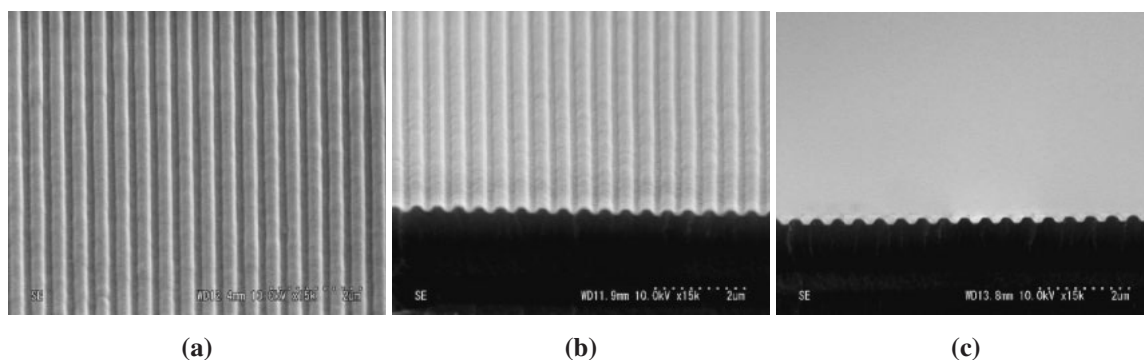


Fig. 4. SEM images of (a) perspective view, (b) perspective + cross-sectional view and (c) cross-sectional view of sub-wavelength periodic structure fabricated using thermal nano-imprinting upon thermally curable inorganic–organic hybrid material films.

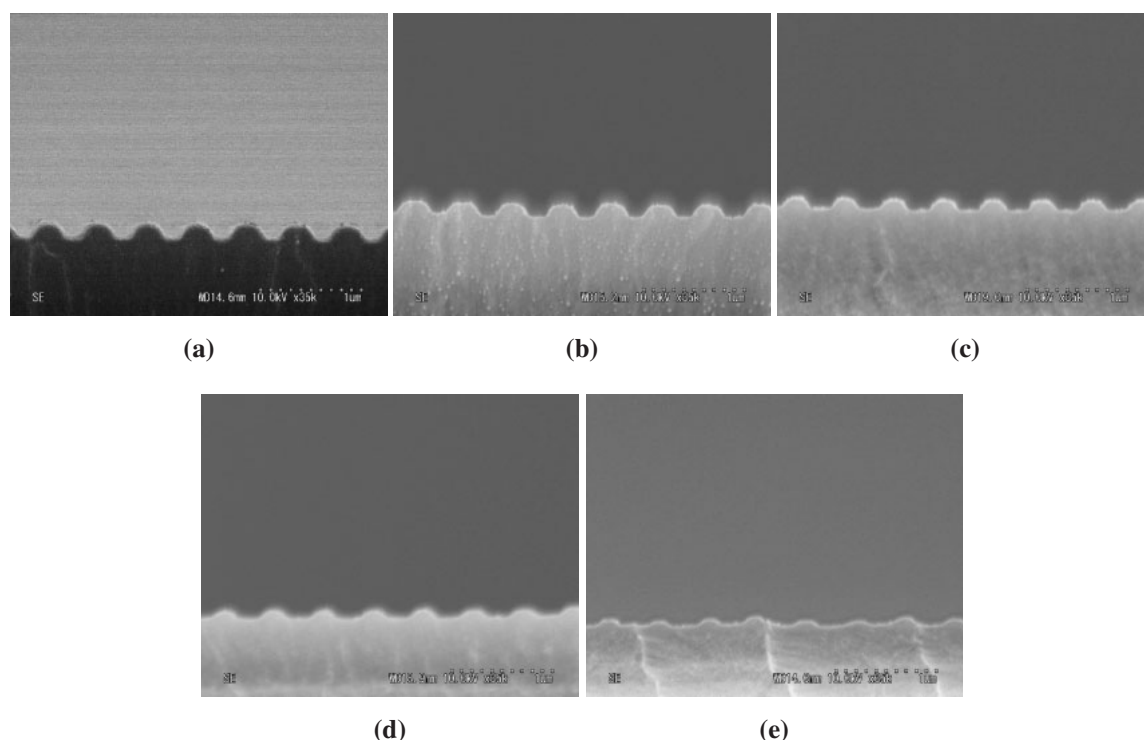


Fig. 5. Cross-sectional SEM views of sub-wavelength periodic structures imprinted upon thermally curable inorganic–organic hybrid material films for various heating temperatures. (a) After imprinting at 200 °C, and after heat treatment for (b) 2 h at 200 °C, (c) 2 h at 300 °C, (d) 2 h at 400 °C, and (e) 2 h at 500 °C.

films with increasing temperature. Using the SEM images shown in Fig. 5, we numerically analyzed the surface structural changes of the nano-imprinted sub-wavelength periodic structure as a function of temperature. Before analyzing the surface structural changes of the sub-wavelength periodic structure, we first investigated the thermal stability of the inorganic–organic hybrid materials by TGA under the conditions of a heating rate of 5 °C min⁻¹ in nitrogen. Figure 6(a) shows the dynamic thermogravimetric curves of the thermally curable inorganic–organic hybrid materials. Rapid weight loss was not apparent until 300 °C. A 5% weight loss, which is the basic value for the evaluation of the thermal stability of optical materials, was detected at around 350 °C. This temperature is much higher than those of general organic materials because of the increased decomposition temperature attributable to chemical bonding between the functional organic moiety and oligosiloxanes.

Therefore, these thermally curable inorganic–organic hybrid materials with high thermal stability present a high possibility of optical application. Figures 6(b) and 6(c) show the height and width changes of the nano-imprinted sub-wavelength periodic structures as functions of temperature. The height and width of the fabricated sub-wavelength periodic structures were not changed by heating for 2 h at 200 °C. However, their height and width decreased slightly after heating for 2 h at 300 °C and then decreased greatly after a further 2 h at 400 °C because of the thermal decomposition of organic groups. Finally, the height and width had almost disappeared after another 2 h at 500 °C. These surface structural modifications of the sub-wavelength periodic structures on thermally curable inorganic–organic hybrid material films agreed with the TGA curve shown in Fig. 6(a), and the fabricated sub-wavelength periodic structures exhibited higher thermal durability.

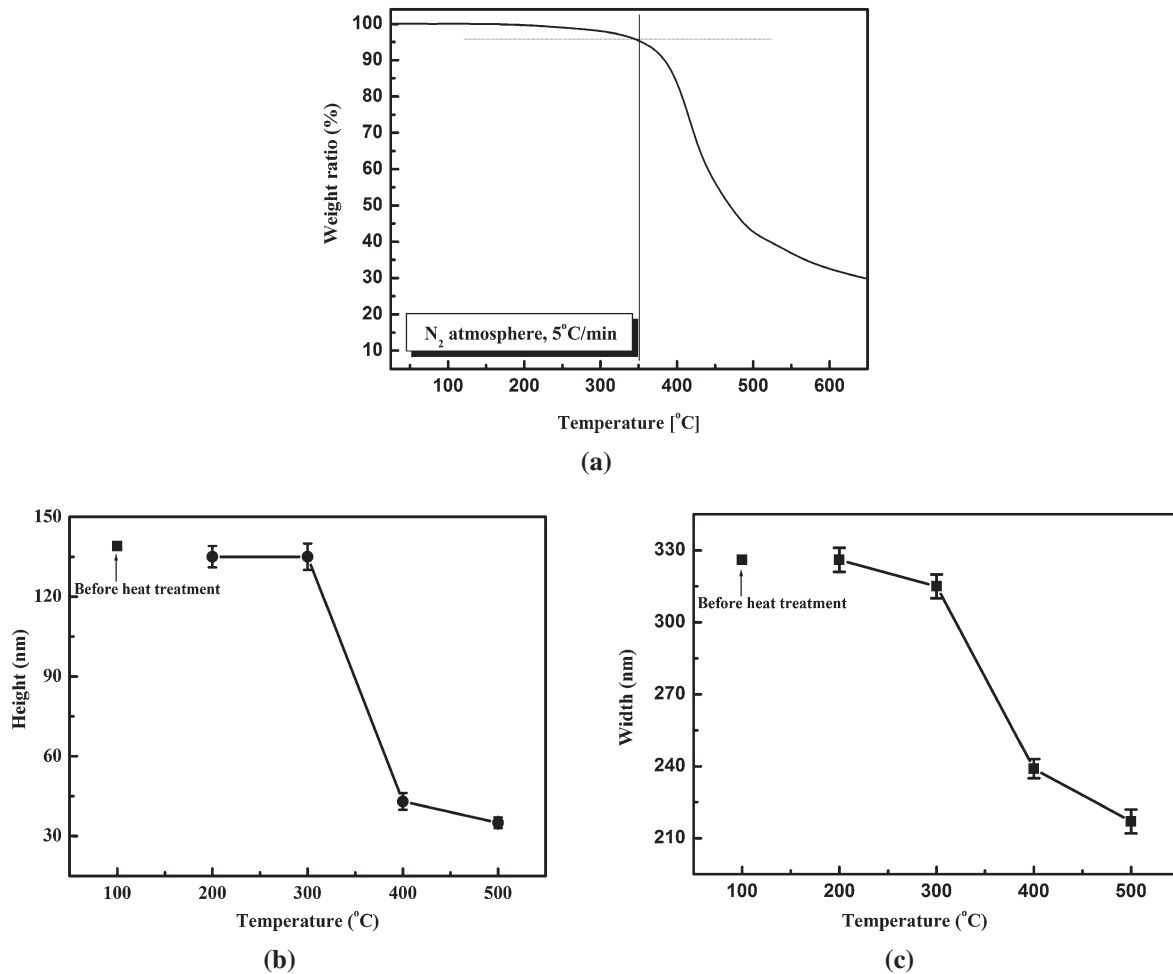


Fig. 6. Thermal dependence of (a) TGA spectra and (b) height and (c) width of sub-wavelength periodic structures imprinted upon thermally curable inorganic–organic hybrid material films versus heating temperature.

In addition, we measured the thermal durability of the optical transmission of thermally curable inorganic–organic hybrid material films within visible-wavelength regions by UV–vis transmission analysis. Thermally curable inorganic–organic hybrid material films were prepared on quartz substrates and then heat-treated for 2 h at 200 or 300 °C. Figure 7 shows the curve of transmission versus wavelength for the thermally curable inorganic–organic hybrid material films with thicknesses of around 1–2 μm. The light transmission through the thermally curable inorganic–organic hybrid material films is of good quality. Optical transmission within visible-wavelength regions is greater than 90% after heating for 2 h at 200 and 300 °C.

4. Conclusions

We fabricated well-defined sub-wavelength periodic structures upon thermally curable inorganic–organic hybrid material films by thermal nano-imprinting. The fabricated sub-wavelength periodic structures exhibited higher thermal durability than do general organic nano-imprinted materials. The thermally curable inorganic–organic hybrid material films showed optical transparency of greater than 90% within visible-wavelength regions; the thermal durability of transmission was also very high. Consequently, our original thermally curable inorganic–organic hybrid materials with high thermal durability are offered as potential nano-

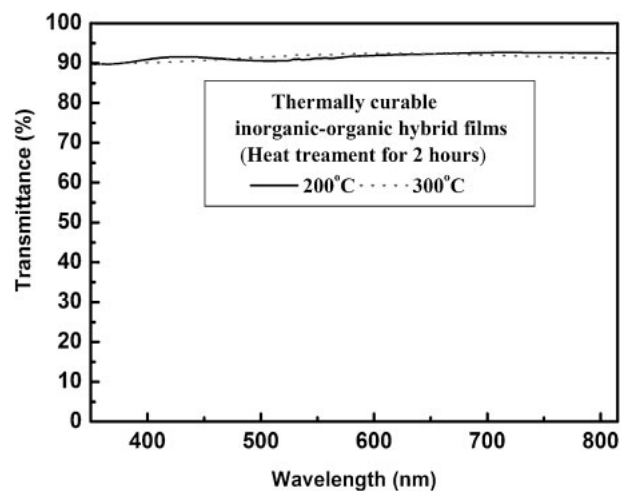


Fig. 7. Curves of transmission versus wavelength for thermally curable inorganic–organic hybrid material films.

imprinted materials that can be applied directly to micro-photonics and nanophotonics devices.

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- 1) S. Y. Chou, P. R. Krauss, and P. J. Renstrom: *Science* **272** (1996) 85.
- 2) L. Zhuang, L. Guo, and S. Y. Chou: *Appl. Phys. Lett.* **72** (1998) 1205.
- 3) H. Schiff, R. W. Jaszewski, C. David, and J. Gobrecht: *Microelectron. Eng.* **46** (1999) 121.
- 4) Y. Xia and G. M. Whitesides: *Angew. Chem., Int. Ed.* **37** (1998) 550.
- 5) Y. Xia, J. A. Rogers, K. E. Paul, and G. M. Whitesides: *Chem. Rev.* **99** (1999) 1823.
- 6) Z. Yu, P. Deshpande, W. Wu, J. Wang, and S. Y. Chou: *Appl. Phys. Lett.* **77** (2000) 927.
- 7) I. Martini, S. Kuhn, M. Kamp, L. Worschech, A. Forchel, D. Eisert, J. Koeth, and R. Sijbesma: *J. Vac. Sci. Technol. B* **18** (2000) 3561.
- 8) T. H. Lee, J. H. Kim, and B. S. Bae: *J. Mater. Chem.* **16** (2006) 1657.
- 9) T. H. Lee, J. H. Kim, and B. S. Bae: *Polym. Mater.: Sci. Eng. Prepr.* **94** (2006) 551.
- 10) D. J. Kang, W. S. Kim, and B. S. Bae: *Appl. Phys. Lett.* **87** (2005) 221106.
- 11) W. S. Kim, K. B. Yoon, and B. S. Bae: *J. Mater. Chem.* **15** (2005) 4535.
- 12) W. S. Kim, D. G. Choi, and B. S. Bae: *Nanotechnology* **17** (2006) 3319.