Development of Nanoimprint Lithography Template Materials using Biomass

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A template using biomass materials in nanoimprint lithography has gas permeability that is expected to reduce defects from air trapping and template damage. The dependences of indentation elastic modulus, light transmission rate and oxygen gas permeability coefficient on baking temperature of the biomass template were evaluated. It was found that indentation elastic modulus increased but light transmission rate and oxygen gas permeability decreased with increasing the baking temperature. 5 µm and 1 µm line regularly-nanostructures of master template were successfully transferred to biomass template. The gas permeable biomass template having nanostructure is expected to extend to future research, such as templates for imprinting volatile materials and solvent including materials.

Keywords: nanoimprint lithography, biomass, hydroxyl propyl cellulose, defect reduction, indentation elastic modulus, gas permeability

1. Introduction

Nanoimprint lithography techniques such as roll-to-roll [1-4] and step and flash [5-8] processes have drawn much attention because of their high volume mass production capabilities. These techniques have the advantages such as cost reduction, high resolution, high aspect ratio patterning, patterning on soft substrates, low line edge roughness (LER), and large area patterning, compared to photolithography. However, problems such as gas trapping, pattern failure, template damage, defects, resist peeling, and low throughput are present that must be resolved for the high volume mass production of semiconductor, sensor, antireflection film, and cell scaffolds materials [9-13].

A nanoimprint lithography technique using gas permeable templates is a newly developed patterning method that employs the templates with porosity, large free volume, and properties of the polymer matrix for pattern failure reduction and the improvement of nanoimprint patterning accuracy [14-16]. Figure 1 shows the nanoimprint lithography processes and the comparison of the processes using conventional quartz-based templates and gas permeable biomass templates. The monomers in resist materials are dispensed firstly onto a substrate. The monomer filled in the template patterns is exposed to UV radiation through the transparent template or thermal curing steps. After that, the resist material is demolded from the template.

In the case of using the conventional quartz-based templates, both volatile materials and solvents in nanoimprint resist are remained that often create defects and peelings in the conventional quartz-based temples without gas permeability. Outgasses such as solvents and volatile materials from imprinted materials were removed through the template by using gas permeable templates in the nanoimprint lithography techniques. In our previous studies, gas
permeable biomass templates such as cyclodextrin [17,18] and cellulose [19,20] as the raw materials and the imprint lithography processes were developed.

The fundamental material properties of the dependence of indentation elastic modulus, light transmission rates, and oxygen transmission rate on the baking temperature were evaluated in the nanoimprint lithography techniques.

2. Experimental

2.1. Material preparation for biomass template

Figure 2 shows the chemical structure and reaction of the biomass template material used in this study. The material was derived from hydroxyl propyl cellulose (Wako Pure Chemical Industries) with beta-linked disaccharide units as shown in Figure 2 (a). The hydroxyl propyl cellulose with thermal cross-linking groups in the biomass template was formed through the reaction of 2-isocyanatoethyl methacrylate (Showa Denko) (Figure 2 (b)) with hydroxyl group of hydroxyl propyl cellulose. This chemical reaction was confirmed using attenuated total reflectance Fourier transform infrared spectroscopy in our previous studies [19].

The hydroxyl propyl cellulose was blended with 2-isocyanatoethyl methacrylate and 2-butanone. The concentration of hydroxyl propyl cellulose and 2-isocyanatoethyl methacrylate in the solution was 20 wt%. After tri-ethyl amine (Kanto Chem.) was added to the solution at a concentration of 8.9 wt%, the solution was stirred at 60 °C under 1,1,1,2-tetrafluoroethane-rich atmosphere for 80 min.

Concentration of the solution was increased to over 54 wt% using vacuum oven at room temperature because the concentration was very low for use as a nanoimprint template material.

After thickening, the solution with 3 wt% AIBN was imprinted to transform line structure of master template. The minimum line width in the master template was 1 µm. Figure 3 shows preparation of the thermal cross-linkable biomass template (TCBT) using thermal nanoimprint lithography (T-NIL). T-NIL of TCBT preparation was performed using imprint test machine.
(LTNIP-5000, Litho Tech Japan). The CDS was dispensed onto a substrate. In imprint step, it was filled into the structure of the silicon template that occupied a space of 20 mm by 20 mm under load application of 3kN in 10 min at room temperature. It was then baked at 130 °C for 10 min. After deforming, the silicon template was removed from the TCBT. The structure was transferred onto the TCBT. The TCBT was observed by Scanning Electron Microscope (SEM) (SU3500, Hitachi).

Indentation elastic modulus (Eit) is one of mechanical properties analyzed in the method. Eit measurement of these films was performed using a dynamic ultra-micro hardness tester (DUH-211, Shimadzu).

2.4. Optical transparency of the TCBT films
Optical transparency of the TCBT films at wavelength 300 – 900 nm was measured using a spectrophotometer (V-650, JASCO).

2.5. Gas permeability of the TCBT films
Gas permeability of the TCBT films baked at 65 °C, 80 °C, and 110 °C was evaluated by using a gas barrier and a transmission-rate testing system (GTR-11, GTR Tec). This system uses gas chromatography (G2700T, Yanako Anal. Sys.) with a differential pressure method that can determine the oxygen transmission rate. The thickness of each sample was approximately 250 µm, and the temperature was 30 °C. The thickness of the films was measured by micrometer.

3. Results and Discussion
3.1. Mechanical Properties of TCBT films

Figure 4 shows the dependence of Eit of the films on baking temperature. The value of Eit increased with increasing baking temperature and rose rapidly at over 65 °C. It was assumed that molecular weight of the film was increased by radical reaction at over 65 °C [21]. The saturation of Eit values at 110 °C and 130 °C was estimated that solvent in these films was volatilized at these temperatures. The measurement with gas chromatograph mass spectrometer (GCMS) is needed to confirm this hypothesis.

2.2. Preparation of films for fundamental evaluation of biomass template

The TCBT was formulated in the cellulose derivative as shown in Figure 2 (c) with 2,2′-azobis(2-methylpropionitrile) (Tokyo Chem.) (AIBN) as a thermal initiator. The concentrations of the cellulose derivative and AIBN were 97 wt% and 3 wt%, respectively.

After cellulose derivative was dropped onto mold, films of TCBT were formed using a vacuum oven (AVO-310N, AS ONE). Baking conditions were 25 °C, 65 °C, 80°C, 110 °C, and 130 °C for 5 hours under diminished pressure of 0.04 MPa.

2.3. Mechanical Properties of the TCBT films
Mechanical properties of the TCBT films were studied using the indentation method.
3.2. Optical properties of TCBT films

Figure 5 shows the dependence of the light transmission rates (LTR) of the films on baking temperature. The wavelength used for UV nanoimprint lithography was 365 nm. The plot of LTR decreased with increasing baking temperature and dramatically declined at over 65 °C. We believe that the decrease of LTR is due to the production of conjugated unsaturated structures over 65 °C. It is reported that those structures were made in cellulose [22]. Over 50 % of LTR suggests that TCBT is suitable for UV nanoimprint lithography template.

3.3. Gas permeability of the TCBT films

Plot of Oxygen gas permeability coefficient (OPC) versus baking temperature is shown in Figure 6. Values at 80°C and 110°C of baking temperature were half of value at 65 °C. From these data, we believe that TCBT is suitable to gas permeable template as a substitution of quartz template which has no gas permeability [19].

With increasing baking temperature, the value of Eit increased while LTR and OPC decreased. It was suggested that agglomeration of the polymer chains in TCBT by heat caused trade-off relationship between Eit and LTR /OPC. In future studies, measurement of positron annihilation lifetime is needed in order to analyze free volume of TCBT films.

3.4. Nanoimprinted line structure on TCBT

Figure 7 shows SEM micrographs of patterned profiles of 5 µm and 1 µm line regularly-nanostructures in TCBT. This shows that structures of the master template were exactly transferred to TCBT. Thermal polymerization reaction of TCBT was carried
out at 130 °C in order to remove solvent in TCBT solution. At baking temperature of 130 °C, the measurement of TCBT films showed 2 GPa Eit and 50% LTR. Thus, it is believed that the TCBT is suitable for UV nanoimprint template. In future studies, it is necessary to observe structures of volatile materials and solvent including materials imprinted using the TCBT.

4. Conclusions

Measurement of TCBT films showed the Eit of the films dramatically increased at baking temperature of over 65 °C and the LTR of the films were over 50%. Patterned profiles of 5 µm and 1 µm line regularly-nanostructures on the TCBT were obtained. It is believed that the TCBT having gas permeability reduces defects and pattern failures in conventional UV or thermal nanoimprint lithography.

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References