Microelectronic Engineering 153 (2016) 83–87

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Self-relaxation characteristics of roll-to-roll imprinted nanogratings on plastic film

Noriyuki Unno [a,*], Tapio Mäkelä [b], Jun Taniguchi [a]

[a] Department of Applied Electronics, Tokyo University of Science, 6-3-1 Niijuku, Katsushika-ku, Tokyo 125-8585, Japan
[b] VTT Printed and Hybrid Functionalities, Tietotie 3, P.O. Box 1000, FIN-02044 VTT Espoo, Finland

ARTICLE INFO

Article history:
Received 3 November 2015
Received in revised form 29 January 2016
Accepted 31 January 2016
Available online 11 February 2016

Keywords:
Nanostructures
Thermal roll-to-roll nanoimprinting
Self-relaxation
Thermoplastics
Cellulose acetate

ABSTRACT

A strong need exists for an effective nanopatterning technique to fabricate devices of the next generation at low cost. Nanoimprint lithography (NIL) has recently received considerable attention because of its process simplicity. In particular, there are strong expectations that thermal roll-to-roll NIL (T-R2RNIL) might be permit high-throughput nanopatterning. In fabricating nanoscale patterns by T-R2RNIL, it is important to understand the transfer characteristics of the materials to permit the prediction of properties of the fabricated pattern. We previously reported the transfer characteristics of a cellulose acetate (CA) film in T-R2RNIL, and we showed that the height of the patterns obtained at temperatures near the glass-transition temperature of the polymer (T_g) was lower than that obtained at temperatures below the T_g. Moreover, we found that the replication behavior of nanoscale gratings differed from that of microscale gratings. However, we did not examine the self-relaxation behavior after T-R2RNIL. In this study, we investigated changes deformation characteristics after a prolonged development time for nano- and microspace patterns on CA film. The self-relaxation behavior was shown to depend on the process temperature for T-R2RNIL, as well as on the features of the mold. In addition, a unique pattern whose pattern density was almost double that of the original mold was obtained by T-R2RNIL at a certain temperature.

1. Introduction

For the fabrication of devices of the next generation, such as printed electronics [1–3] or optical elements [4,5], there is a strong need for effective low-cost nanopatterning techniques on plastics. In this respect, nanoimprint lithography (NIL) [6] has recently received considerable attention because of its process simplicity and high throughput. Moreover, thermal roll-to-roll NIL (T-R2RNIL) [7,8] is expected to permit more-rapid nanopatterning than the planar NIL process. In fabricating nanoscale patterns by NIL, it is important to understand the transfer characteristics of the materials to permit the prediction of the properties of the fabricated pattern. Studies on the filling motion during planar-type thermal NIL [9] have shown the existence of several modes of filling. We previously reported the transfer characteristics of a cellulose acetate (CA) film in T-R2RNIL [10], and we showed that the height of the resulting patterns at temperatures close to the glass-transition temperature of the polymer (T_g) is lower than that at temperatures below T_g as a result of the viscoelastic properties of the CA film. (We refer to this characteristic as the 'N-curve'.) In the case of T-R2RNIL, moreover, we found that the replication behavior of nanoscale gratings differed from that of microscale gratings. However, we did not examine the self-relaxation behavior and the detailed filling modes in T-R2RNIL. In the case of conventional thermal plane-to-plane NIL (T-P2PNIL), a thermoplastic film is heated above its T_g and an imprinting pressure is applied until the mold cools to a temperature below the T_g. Moreover, a belt-type mold is typically used for T-R2PNIL, and the thermal condition of the film in T-R2PNIL is similar to that in T-P2PNIL. These NIL processes ensure that there is sufficient time to heat and cool the film. It is therefore only necessary to investigate the self-relaxation behavior of the imprinted pattern at temperatures above the T_g. In the case of our T-R2RNIL process, a CA film is imprinted by using a simple machine equipped with only a roll mold and a backing roll in the imprint section. The imprinting time for T-R2RNIL is short (around 0.1 s), and the temperature of the surface of the roll mold is typically set below the T_g. Consequently, we needed to investigate the self-relaxation behavior of the imprinted pattern at below the T_g, as well as above the T_g. In this study, therefore, the long-term relaxation behavior of imprinted CA patterns at various temperatures was examined.

Here, we describe our investigations of the deformation characteristics of nano- and microspace patterns fabricated by T-R2RNIL on CA film after a prolonged development period. Furthermore, we examined the relationship between the filling mode and the results of dynamic mechanical analysis (DMA) of the CA film. It became clear that the self-relaxation behavior depends on the process temperature for T-R2RNIL,

Abbreviations: CA, cellulose acetate; DMA, dynamic mechanical analysis; NIL, Nanoimprint lithography; T_g, glass-transition temperature; T-R2RNIL, thermal roll-to-roll nanoimprinting.

* Corresponding author.
E-mail address: n.unno@rs.tus.ac.jp (N. Unno).

http://dx.doi.org/10.1016/j.mee.2016.01.042

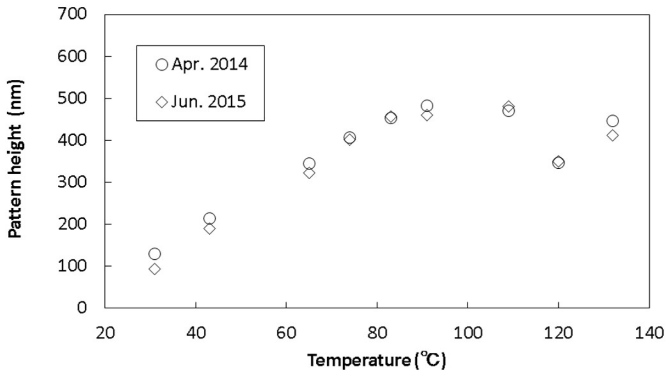

Fig. 1. The height of the pattern produced by T-R2RNIL with a micron-space mold (2200 nm) at various process temperatures. The pattern height clearly decreased after storing the samples for one year if the original process temperature was below 83 °C, which is below the T_g for the CA film.

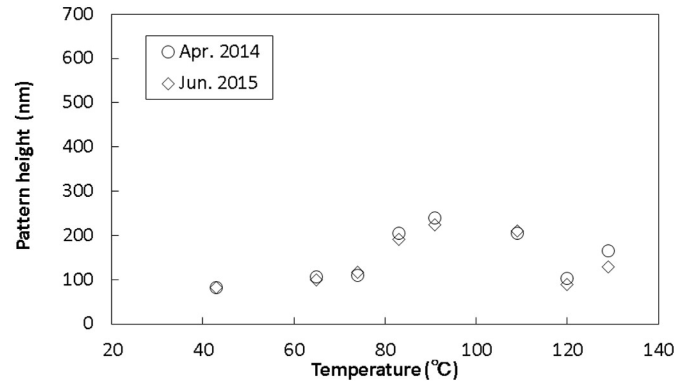

Fig. 3. The height of the pattern produced by using the narrow-space mold (710 nm). When the original process temperature was below 83 °C, the pattern height tended to decrease after one year, although the difference was small because the initial height was low.

as well as on features of the mold. Additionally, a unique mode, whose pattern density was almost double that of the space width of the original mold, was observed when T-R2RNIL was performed at a certain temperature.

2. Experimental apparatus and procedure

We investigated long-term changes in the self-relaxation behavior by using the same samples as those described in our previous paper [10]. A 90-μm-thick CA film was used as the transferred film. The imprinting force was set to 200 N, and the driving speed was kept at a constant value in the range 0.4–0.5 m/min. The contact length between the rolls was approximately 1 mm, and the calculated imprint time was therefore about 120–150 ms. After the T-R2RNIL process, the samples were stored in the atmosphere at room temperature, which was controlled at about 20 °C at all times. Molds were produced on flexible 100-μm-thick nickel film by electroplating using silicon master molds. The T-R2RNIL samples were replicated from three kinds of molds. The first mold had a line width of 900 nm, a space width of 1100 nm, and a height of 540 nm (wide-space mold). The corresponding values for the second nanograting were 500, 710, and 720 nm (narrow-space mold), and those for the third nanograting were 610, 2200, and 610 nm (micron-space mold). These molds were not coated with any release agent. T-R2RNIL process was carried out at various surface temperature of the mold from room temperature to 132 °C. Our original measurements by atomic-force microscopy (AFM, SPM-9600, Shimadzu Co.) were performed in April 2014, and those in the current study were similarly performed in June 2015. The hardness of the imprinted CA film was also measured by using a nanoindenter (DUH-211, Shimadzu Co.). We also examined the viscoelastic property of the CA film by dynamic mechanical analysis (DMA).

3. Results and discussion

Fig. 1 shows how the pattern height obtained by T-R2RNIL with the micron-space mold varied with the process temperature after patterning and more than one year later. After one year, the pattern height clearly decreased when the original process temperature was below 83 °C, that is, below the T_g of the CA film. Although the plastic deformation makes nanoimprinting possible at temperatures below the T_g, it appears that residual stresses remained in the pattern and were gradually released, resulting in a decrease in the pattern height. The maximum shrinkage ratio of the height was about 27% (from 129 nm to 94 nm) for a process temperature of 31 °C.

Figs. 2 and 3 similarly show the pattern heights for the wide- and narrow-space molds, respectively. When the process temperature was below 83 °C, the pattern height for these molds also showed a tendency to decrease after one year. On the other hand, the pattern height for a process temperature of 109 °C remained at about the same value one year after processing in all cases.

Fig. 4 shows the hardness of the CA film one year after the T-R2RNIL process. This test was performed at room temperature, and we measured the hardness at a nonpatterned area that had contacted the planar nickel surface. It became clear that the hardness of the CA film was a minimum at a processing temperature of 109 °C. The film showed little self-relaxation of the pattern height after processing at this temperature because processing of the softer film introduced less residual stress during plastic deformation. We also measured the full width at half maximum (FWHM) of the obtained pattern by AFM, as shown in

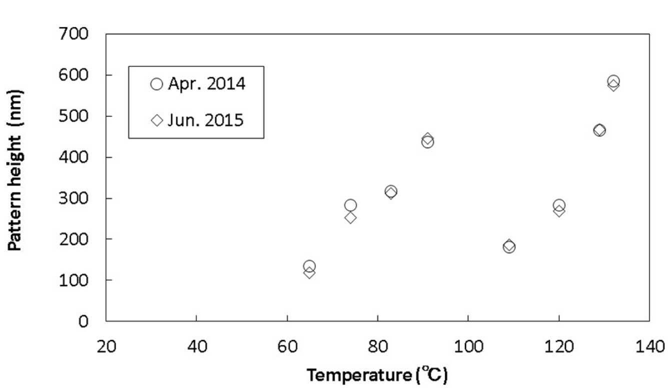

Fig. 2. The height of the pattern produced by using the wide-space mold (1100 nm). When the original process temperature was below 83 °C, the pattern height tended to decrease after one year.

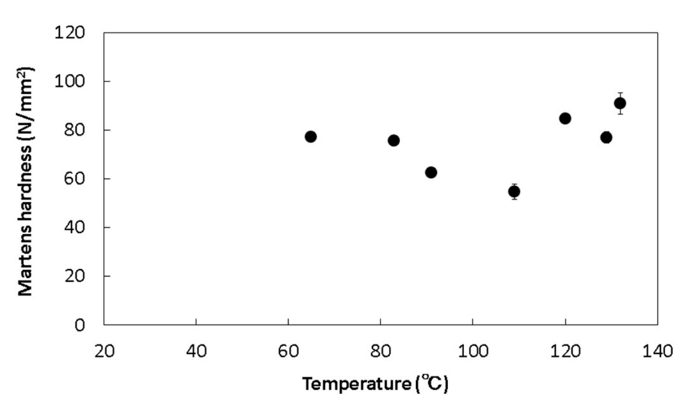

Fig. 4. The hardness of the CA film one year after the T-R2RNIL process, measured at room temperature. The hardness of the CA film initially processed at 109 °C was lower than that of CA films processed at other temperatures.