Chemical Engineering Journal 161 (2010) 289–292

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Micromold fabrication for flexible display application

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ARTICLE INFO

Article history:
Received 12 October 2007
Received in revised form 26 March 2010
Accepted 30 March 2010

Keywords:
Cellulose acetate
Micropattern
Flexible display

ABSTRACT

Uniform size, height and poreless micropattern fabrication on a flexible substrate becomes an important factor for electronic paper development. Recently, thin and flexible display has been a main target in display industry. Therefore, for the future industrial application, non-petroleum based and environmentally friendly thin and flexible micromold development is an essential technology for flexible display application. For this application, existence of micro or nanopores is drawback due to the reduction of transmittance by light scattering and leak of carrier solvent. The liquid–liquid demixing process made porous structure of the cellulose acetate (CA) film. The resulting CA films were optically turbid due to the light scattering by the pores. Single solvent process provides optically transparent and smooth surface films. Line, honeycomb, and square shapes of photoresist patterns were fabricated on the silicon wafer with different heights (2 μm and 20 μm). The replicas of the CA-patterns have about the same sizes and heights with respect to those of the photoresist patterns. The cross-sectional field emission scanning electron microscope images exhibit the pore-free CA mold.

1. Introduction

A major biomacromolecule of the plant cell walls is cellulose, which has been utilized as a major natural resource. Cellulose has been discovered as a smart material having piezoelectric property [1]. This material has advantages including naturally abundant, cheap, biodegradable, flexible, optically transparent, light weight, and easy to modify the chemical structure. Developing display device with this smart material might have huge impact in the display industry. Since cellulose acetate (CA) film is optically highly transparent, it is applicable as a substrate mold for electronic paper device. For this application the pattern size and height should be controllable and uniform. Another requirement is that the carrier solvent should not leak out from the mold.

To satisfy the application for replica process, the polymer material should have a high modulus to withstand deformation and should not stick with the master-mold material. Widely using master-mold material is a poly(dimethylsiloxane) (PDMS). Transcription method with PDMS [2] was utilized to produce porous CA honeycomb pattern. However, the pores are not desirable for optical device application due to the light scattering from the pores. The brittleness and the thermal instability of the PDMS mold are limiting factors for its wide application. Silicon wafer mold could be a ideal mold due to easy fabrication of the mold, strength of the mold, and easy modification of the silicon wafer surface. Using SiO_2 and silicon wafer master mold, fluoropolymer mold was fabricated with tensile modulus of approximately 1.6 GPa.

Recently, flexible displays have been a huge attraction for various display field including electronic books, electronic newspapers, wearable computer screens, and smart identity cards. Several technologies were proposed for fabricating thin flexible displays. One of the particle-based displays is based on moving color spheres in glass or elastomeric cavities and electrophoresis inside small capsules [3]. Chen et al. [4] demonstrated the fabrication of a bendable active-matrix-array sheet with less than 0.3 mm thick, high pixel density (160 pixels × 240 pixels), and high resolution. An electrowetting technology was reported for the rapid manipulation of liquids on a micrometer scale [5].

In this paper, we report the effect of liquid–liquid demixing process and single solvent process on the film pore formation, pore-free uniform size and uniform height CA mold fabrication process with various master mold patterns.

2. Experimental

Dimethylacetamide (99%, DMAc), acetone (98%) and CA (98%) were purchased from Aldrich company and used without further purification. The acetyl content of CA is 39.8 wt.%, and the molecular weight of the CA is 30,000. Developer and photoresists (SU-8) having various viscosities were purchased from Microchem. company. The schematic view of photoresist master pattern and CA pattern fabrication process was shown in Fig. 1. A photoresist was spin-coated onto the silicon wafer substrate and pre-heated at 95 °C for 3 min. The thin film was irradiated with UV-light (365 nm) for

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1385-8947/$ – see front matter
doi:10.1016/j.cej.2010.03.084

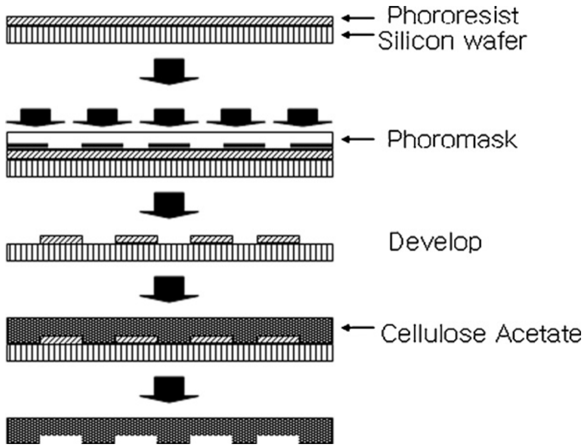

Fig. 1. Schematic view of the photoresist master pattern and CA micro-pattern fabrication process.

10 s with patterned photomask and post-baked at 95 °C for 3 min. After those processes, the unexposed area was washed away using a developer (1-methoxy-2-propanol acetate).

Meanwhile, various combinations of CA solutions were prepared. About 12 g of CA were dissolved into the mixture of 50 mL acetone and 50 mL DMAc solvent. For the single solvent effect, 12 g of CA were dissolved into the 100 mL acetone. The resulting solutions were spin-coated onto the silicon wafer for studying pore effect on the solvent demixing process and single solvent process. The resulting film fabricated with liquid–liquid demixing process was whitish and milk color. However, the film fabricated with single solvent was clear and transparent. The surface and cross-sectional structures of the films were investigated using field emission scanning electron microscope (FESEM, S-4300 Hitachi). To fabricate pore-free various shapes of CA patterns, acetone solution was used. The CA solution was poured onto the photoresist mold and dried using spin coater (Laurell, EDC2-100) at room temperature for a few minutes. After that, the film was peeled off from the mold and investigated the structure using FESEM.

3. Results and discussion

Light attenuation being combination of absorption and scattering in the fabricated optical devices is a key factor for display device, such as guided wave device, electronic paper, and prism sheet. Surface and inside material's morphologies and structures are a major factor governing the light attenuation. The pore structures of the casted CA films were investigated to obtain the information of solvent effect [6] and additive effect by adding different molecular weight polyethylene glycol [7] and zirconium dioxide [8]. Liquid–liquid demixing process offers large morphological variations as a function of the ratio of the two solvents [9]. When the pore size is bigger than the dimension of the wavelength, the porous materials scatter light [10]. Hence, existence of the pores bigger than the dimension of the visible light wavelength is a negative impact for the optical device application. In this research, two solvent mixtures having low boiling point solvent (acetone, 68 °C) and high boiling point solvent (DMAc, 162 °C) were utilized to investigate the dual solvent effect on the film structure. The cross-sectional FESEM image of the CA film fabricated using liquid–liquid demixing solvent is shown in Fig. 2(a) and, in greater detail, enlarged view is exhibited in Fig. 2(b) representing the detailed pore sizes and pore distribution. The CA film thickness was about 80 μm. The micro- and nano-pores of the film were uniformly distributed throughout the film.

The surface FESEM image of CA film fabricated using acetone/DMAc solvent corresponds in Fig. 3(a), while the surface image of the CA film fabricated with single solvent (acetone) corresponds Fig. 3(b). Large number of micro- and nano-pores was distributed throughout the surface of the film as shown in Fig. 3(a). However, no micro- or nano-pores exist on the film surface, and relatively

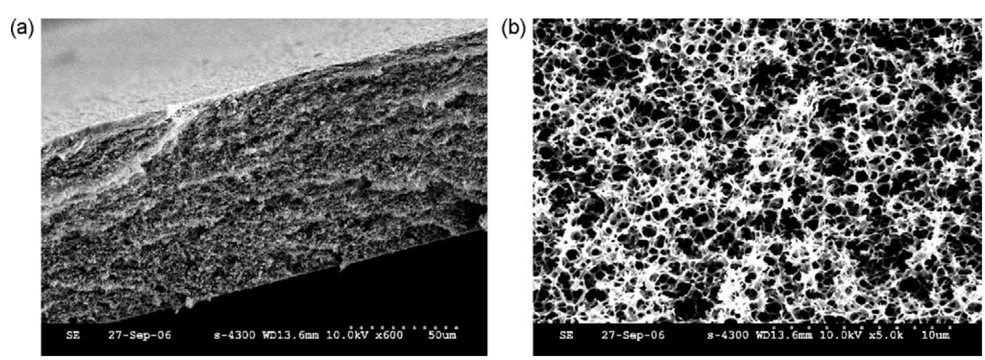

Fig. 2. FESEM cross-sectional images of CA film fabricated using a dual solvent.

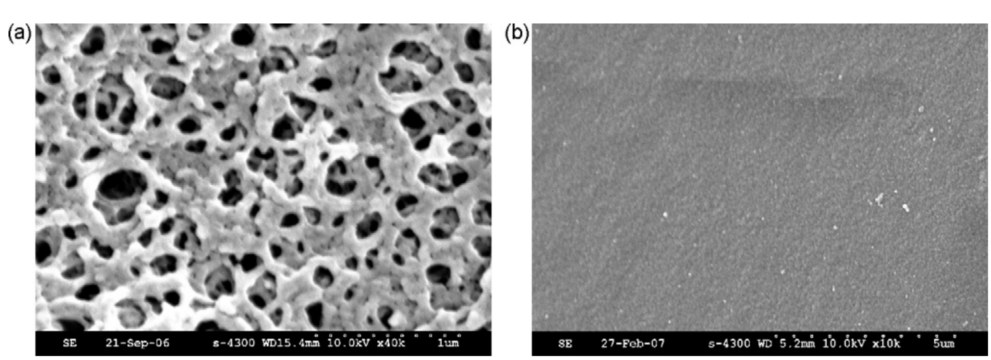

Fig. 3. FESEM surface images of the CA films for using (a) a dual acetone/DMAc (1:1 volume ratio) solvent and (b) single acetone solvent.

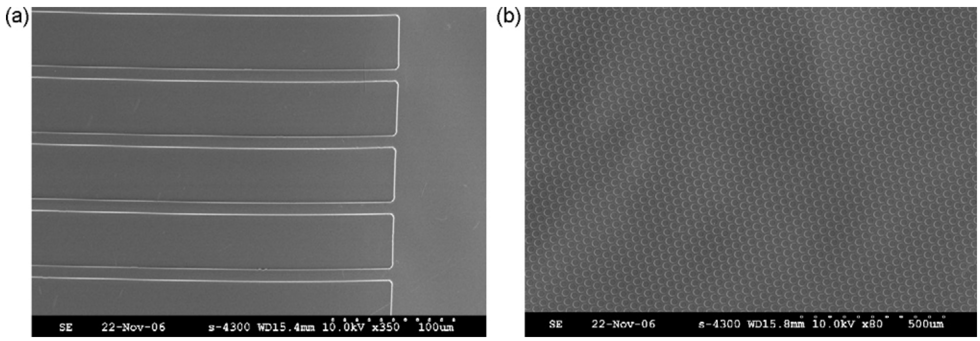

Fig. 4. The FESEM images of (a) line-patterned and (b) honeycomb patterned CA surface image after peeling off the CA film from the photoresist micro-pattern.

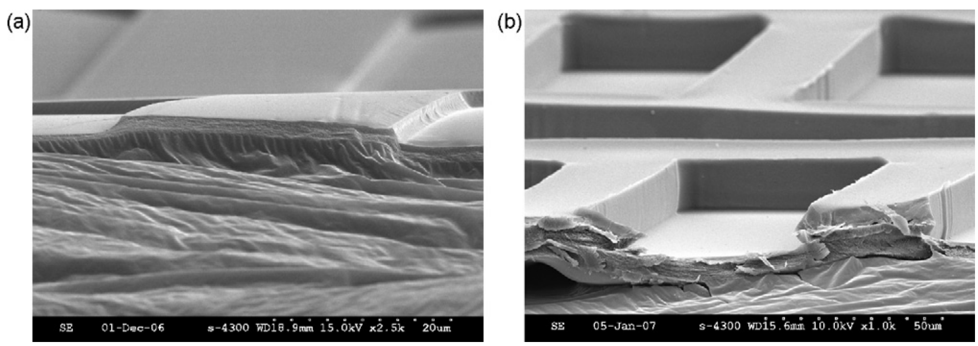

Fig. 5. The cross-sectional FESEM images of CA pattern. The square heights are about 2.1 μm and 20.5 μm, respectively.

smooth surface film was obtained with acetone solution. The film produced by acetone/DMAc mixture was turbid, but the film made using acetone solution was clear and transparent.

Transparent polymer honeycomb pattern was fabricated using water droplet with different humidity, temperature, and moving speed [10]. Fabricated pore sizes were changed from 300 nm to 5 μm depending on liquid film thickness. Honeycomb patterned cellulose acetate pattern was fabricated using water in oil emulsion under saturated water vapor [11]. The pore sizes of the honeycomb patterned CA film were from 1 μm to 100 μm. CA honeycomb patterns were fabricated using water microspheres at the air–polymer solution interface and PDMS micromold [2]. Fig. 4(a) represents the multiple line patterns of CA film. Defect free and clear patterns were obtained with this method. The line width and height were about 20 μm and 2 μm, respectively. To fabricate uniform size and height of honeycomb patterns, photoresist micromold was used. Fig. 4(b) shows uniform size and defect-free honeycomb structures. The resulting film was transparent indicating pore-free film. In addition, when CA solution was cast on the second template followed by evaporation of acetone, this second process also gave the same structure. Repeated use of the mold did not change the pattern shape or structure.

In the electronic paper, each cell acts as a pixel. Nakamura et al. proposed approximately 20–30 μm cell depth on the 1 mm flexible sheet [12]. The cell depth is very import for this device due to the device operating voltage will depend on the cell depth. Therefore, fabrication of transparent flexible sheet with controllable cell depth is important in this display device. Two different heights (2 μm and 20 μm) of the photoresist master-pattern were prepared. The fabrication process was used in the same manner as former method, such as pouring solution, evaporating solvent, and peeling off the film. The cross-sectional views of CA square patterns were shown in Fig. 5(a) and (b). The heights of the CA patterns were about 2.1 μm and 20.5 μm and were about the same compared with the master pattern heights. This result indicates that there was no significant shrinkage after final pattern formation.

4. Conclusions

Large morphology change of CA film was observed when a binary solvent mixture (acetone/DMAc) was employed during the film fabrication process. Liquid–liquid demixing process produced micro- and nano-pores both in the surface and inside of the film. The films fabricated using solvent demixing process were optically opaque. Therefore, it is not adequate method to apply optical device. The films with single solvent process were optically transparent. Photoresist pattern was utilized as a master pattern to fabricate line, honeycomb, and square pattern of CA. The photoresist pattern heights were 2 μm and 20 μm. The resulting heights of the CA-patterns were about the same compared with the master pattern. The resulting patterns were transparent, defect-free, and pore-free. Therefore, the CA is a promising material for flexible display device.

Acknowledgement

This work has been performed under the support of Korea Research Foundation (KRF, EAPap Actuator) in Korea.

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