Advanced Nanoimprinting Material for Liquid Crystal Alignment

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Keywords : LC alignment, Nanoimprint lithography, SFG

Abstract

To promote liquid crystal application of nanoimprint lithography, a polymer with new concept is proposed. The material consists of a polyamic acid for good LC alignment and an epoxy resin for good imprinting. The result of sum-frequency generation (SFG) vibrational spectroscopy proves that this material is a functionally gradient material. This material shows excellent capability as a nanoimprinting material as well as an LC alignment layer.

1. Introduction

The nano-sized surface groove created clearly by a suitable method can promote LC order [1-4] and it is not accompanied with surface impurities, a cause of a bad optical quality, unlike the rubbing. Nanoimprint lithography (NIL) has been applied to various areas of electronics, photonics, and magnetic device because it can produce more easily and simply nanosize patterns with high-throughput and high precision [5-9]. NIL will enable us to precisely get an expected surface anisotropic direction and surface LC anchoring strength by controlling the pitch and the depth on a mold, which is hardly possible in the conventional rubbing process. However, the NIL has been little applied to LC alignment technology. To promote LC application of NIL, we must choose an appropriate material, which has a good imprinting characteristics under lower pressure and temperature and a good LC alignment characteristics with high anchoring energy and thermal stability. Polyimide currently used as the standard rubbing alignment layer, has very good characteristics. However, it is not suitable for imprinting due to high glass transition temperature [Tg]. Imprinting in such high temperature may affect color filter resin having lower Tg. Therefore, a new organic material having lower Tg is needed crucially for nano-imprinting LC alignment technology. Here, we embodied ideally a functionally gradient material, of which the top surface is made of mostly the material for LC alignment and inner part is made of mostly material for imprinting and proved that this is a functionally gradient material. In addition, we estimated the capability of this material as a nanoimprinting material as well as an LC alignment layer.

2. Experimental

Our hybrid type organic material consists of a polyamic acid (planar or homeotropic type) and a kind of epoxy resin with solvents of N-Methylpyrrolidone /Ethylene glycol butyl ether/γ-Butyrolactone=59/33/8 as shown in Fig. [10-12]. Here, polyamic acid (PAA, PIA-XXXX, Chisso Co. Ltd) is for good LC alignment and epoxy resin with polyester amic acid (PEA) is for easy imprinting. This new polymer film was baked in hot plate of 80 °C for 3 min for removal of solvents and prebaked on hot plate of 165 °C for 10 min for epoxy resin cross-linking reaction. The post baking for polyimidization reaction was performed for

30 min in 220 °C on hard and flat metal plank upholding the sample in imprinting equipment. In order to know whether this is a functionally gradient material or not, we used sum-frequency generation (SFG) vibrational spectroscopy and judged whether in the surface, imide CO groups from polyimide exist. SFG spectroscopy is one of powerful surface analytical probes [13]. The pitch and the height of the quartz mold pattern manufactured by electron beam were 400 nm and 120 nm, respectively. HPI film was pressed under 8 MPa for 5 min in 185°C by the mold with an imprinting-machine (X-200-NV, SCIVAX Corp.), according to the general imprinting conditions. Subsequently, it was cooled down below the glass transition temperature of it and separated.

3. Experiment and Discussion

Figure 2 shows the SFG spectra of a planar hybrid film, and its individual components—PAA(planar type), PEA and Epoxy films—in the range of C=O stretches taken with SSP polarization combination. The spectrum obtained from the PAA film exhibits two imide CO stretches: the antisymmetric (~1740 cm^{-1}) and symmetric (~1780 cm^{-1}) stretch vibrational modes for two coupled CO associated with each imide ring as expected [13], while that from the Epoxy film does not show the signals of the imide CO groups. In the spectrum of the hybrid film, however, the peaks of the imide CO do appear, indicating that the imide rings are protruding out of the surface. Noteworthy is almost the same magnitude of the intensity obtained from the hybrid film as that from the PAA film despite a small amount of the component fraction of PAA—10 % in the hybrid film. Therefore we expect that the planar type hybrid film — the hybrid-type polymer film—is not a functionally uniform but gradient layer of which the top surface has the characteristics of PAA dominantly as shown in Fig. 3. Figure 4 shows the SFG spectra of a homeotropic hybrid film, and its individual components—PAA(homeotropic type), PEA and Epoxy films—in the range of C=O stretches taken with SSP polarization combination. The result is similar to almost it obtained from a planar hybrid film, and its individual components—PAA(planar type), PEA and Epoxy films. Therefore, we expect that the homeotropic type hybrid film—is also not a functionally uniform but gradient layer. To check it more surely, we fabricated LC cell using the homeotropic type hybrid film and then, obtained a microscopic image under crossed polarizer as shown in Fig. 5. Very good darkness, indicating good vertical LC alignment is shown.

Finally, we check the capability of nanoimprinting of this HPI film. Figure 6 shows atomic force microscopy (AFM, SPM-9500J3, Shimadzu Corp.) images of HPI film pattern transferred from nano sized mold feature. The pitch and the height of the pattern on HPI film substrate transferred from the mold were 398 nm and 118 nm, respectively. Some difference in the pitches between the mold and HPI substrate is due to some difference in thermal expansion between them. This picture proves that HPI film is excellent materials for NIL.

To find the suitable conditions to get an excellent LC alignment is very important work. In LC alignment by the linear groove, LC anisotropic surface anchoring energy coeffecient is determined by only its pitch and depth by the following relationship [1-4]:

$$w = \frac{1}{2} k A^2 \left(\frac{2\pi}{\lambda}\right)^3, \qquad (1)$$

where λ is the groove pitch, k is the NLC elastic constant, and A is the groove depth. In our experiment, we could get $w \approx 10^{-4} J/m^2$ from eq. (1) in $\lambda = 400$ nm and $A = 120$ nm with the $k \approx 6\times10^{-12}$ N. This value stands comparable with it by rubbing and indeed, good darkness without almost any light leakage in crossed polarizer was shown in this condition. We can make the mold with deeper depth to obtain higher anchoring energy. However, it may generate totally the reduction of brightness in LCD by the difference of retardation due to thickness difference between an embossed region and a depressed one. Thus, we guess that the groove depth not to exceed 100 nm will be good for electro-optics of LCD and so then, much desirably the surface anchoring energy should be controlled by just only the groove pitch.

4. Summary

A hybrid type polymer with new concept is proposed for liquid crystal application of nanoimprint lithography. The result of sum-frequency generation (SFG) vibrational spectroscopy proves that this material is a functionally gradient material. This material shows excellent capability as a nanoimprinting material as well as an LC alignment layer.

5. Acknowledgements

The authors thank to Mr. K. Shimmo of Nippon Sheet Glass Co., Ltd. for providing nano-imprinted mold and Dr. Y. Mitsuhashi for his continuous help and encouragement.

6. References

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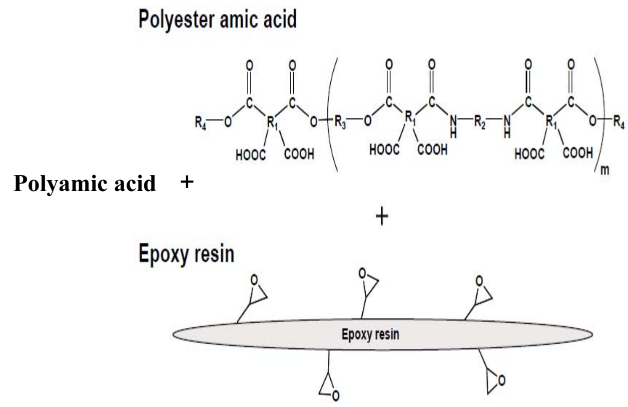

Fig. 1. A new hybrid type polyimide consists of a polyamic acid for LC alignment and an epoxy resin with polyester amic acid for easy nano-imprinting lithography.

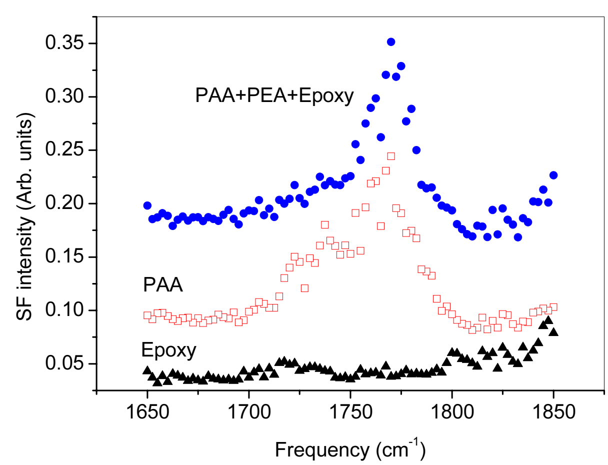

Fig. 2. SFG spectra of the HPI, PAA(planar type), Epoxy spin-coated films with the SSP polarization combination.

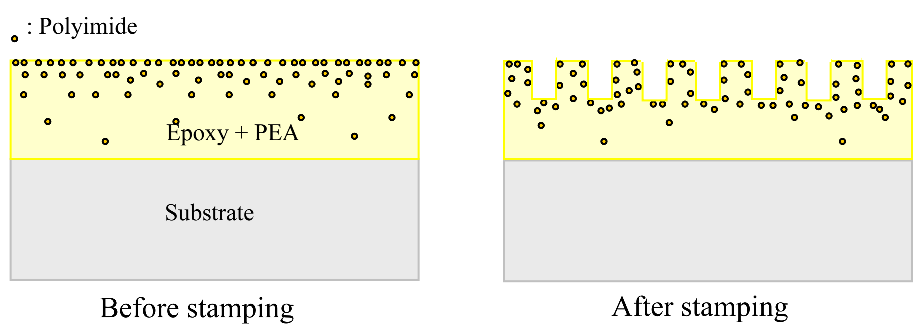

Fig. 3. Schematic diagram of a new planar type hybrid film for nanoimprinting LC alignment layer

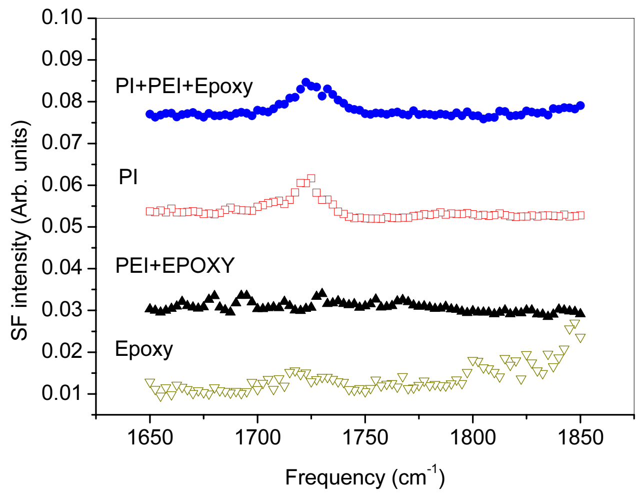

Fig. 4. SFG spectra of the HPI, PAA(homeotropic type), Epoxy spin-coated films with the SSP polarization combination.

Fig. 5. Microscopic image of LC cell using a homeotropic type hybrid film for nanoimprinting LC alignment layer.

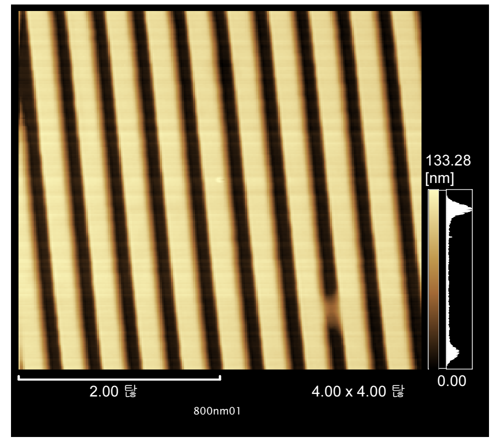

Fig. 6. Atomic force microscopic (AFM) image of HPI substrate transferred from mold pattern.