Evaluation of Scratch Durability of Moth-eye Structures Made of High Hardness Ultraviolet Curable Resin

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Displays such as smartphones and personal computers suffer from deterioration in contrast due to reflection from fluorescent lamps and sunlight, and deterioration in visibility from scratches and fingerprints. There is a need for high-performance antireflection films. To realize such an antireflection film, we focused on the moth eye structure. In this study, an Anti-reflection structure (ARS) film was fabricated with ultraviolet nanoimprint lithography using the newly developed UV curable resin. The ARS film was subjected to scratch testing using steel wool. The change in shape, optical properties and antifouling properties were evaluated. The reflectance of the ARS film was about 0.4%, and the transmittance was over 90%. Contact angle measurements were used to evaluate the antifouling properties of the ARS film. The contact angle and sliding angle were >150° and 12° after the 30th scratch test, respectively.

Keywords: UV-NIL, Anti-reflection, High abrasion resistance, Moth-eye

1. Introduction

Anti-reflection structure (ARS) films are useful in displays for preventing the reflection of light. Touch panel devices such as smartphones and other devices require ARS films which are resistant to breakage and contamination upon physical contact. Ultraviolet nanoimprint lithography (UV-NIL) [1,2] is an effective method for mass producing ARS films. ARS films made of conventional resin are subject to scratching and dirt adhesion upon physical contact. A newly developed ultraviolet (UV) curable epoxy resin with high hardness (9H: pencil hardness) and antifouling properties was developed for ARS films to overcome these problems [3-7]. However, this newly developed resin has a strong adhesive force. For this reason, ARS films have been produced by the partial filling method [8-10], which involves incompletely filling the resin. In the previous study, the antifouling properties and durability of ARS films produced from high-hardness UV curable resin were evaluated.

In this study, an ARS film was fabricated by UV-NIL using the newly developed UV curable resin. The ARS film was then subjected to scratch testing with steel wool to evaluate its change in shape, optical properties and antifouling properties. Contact angle measurements were used to evaluate the antifouling properties. Scanning electron microscopy (SEM) was used to evaluate the durability.

2. Materials and methods

2.1. Preparation of master mold

An oxygen ion beam was applied to a glassy carbon (GC) substrate (Tokai Carbon Co., Ltd., Tokyo) using an ion beam apparatus (EIS-210ER, Elionix Inc., Tokyo) to prepare the master mold for the ARS film. The master mold was square with dimensions of 2 cm × 2 cm. The processing conditions were an ion-beam acceleration voltage of 800 V, an oxygen gas flow rate of 3.0 sccm, an irradiation period of 90 min, and processing was carried out at room temperature. We performed an operation to aid the release of the master mold of the ARS film. Using a Cr evaporator (VPC-260F, Ulvac Kiko, Inc., Japan), a 30-nm-thick Cr layer was vacuum deposited on the master mold. The Cr layer

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was then allowed to react with oxygen in the atmosphere for 1 h to form \( \text{Cr}_2\text{O}_3 \). The Cr oxide layer was then immersed in a fluorine-based silane coupling agent (Optool DSX, Daikin Industries, Ltd., Japan) for 1 h, and subjected to liquid phase treatment. Gas phase treatment was carried out at room temperature to increase the adhesion between the Optool and master mold. After that, the baking temperature was 120 °C and the baking time was 5 min [11]. Following this, rinsing was carried out by immersion (NOVEC 7300, 3M Japan Ltd., Japan) for 1 min to remove any dirt and release the agent. Finally, the mold was washed with pure water.

2.2. Production of ARS film and steel wool scratch testing

Figure 1 shows the UV-NIL process for preparing the ARS film using the partial filling method. The newly developed UV curable resin was deposited dropwise on the master mold, and a polyester film (Cosmoshine A 4300, Toyobo Co., Ltd., Japan) was then covered on the master mold (Fig. 1(a)). In the partial filling method, the adhesiveness of the resin was high, so the filling time was intentionally reduced from that reported, and no pressure was applied. The resin was cured with UV light at 70 °C and an UV dose of 10 J/cm² (Fig. 1(b)). The ARS film was then removed from the master mold (Fig. 1(c)) and baked at 100 °C for 30 min to impart the ARS film with antifouling properties (Fig. 1(d)). Scratch testing was then conducted using steel wool (# 0000, Nippon Steel Wool Co., Ltd., Japan) under a load of either 125 g/cm² or 250 g/cm² (Fig. 1(e)). The number of rubbings was set to 1 round. Evaluation was carried out after the 5th, 20th, and 30th scratch test.

2.3. Evaluation method

Reflectance spectra (specular reflection at an incident angle of 5° in the wavelength region of 300–1000 nm) and transmittance spectra were obtained using an UV-visible-infrared spectrophotometer (Solidspec-3700, Shimadzu Corporation, Japan) equipped with an integrating sphere mode. The shape of the master mold and ARS film before and after scratch testing were observed by SEM (ERA-8800FE, Elionix Inc., Japan).

The contact angle [12-20] was measured using a fully automatic contact angle meter (DM-701, Kyowa Electronic Instruments Co., Ltd., Japan) to evaluate the antifouling properties. The sliding angle was also measured.

3. Results and discussion

3.1. Preparation of master mold

Figures 2(a) and (b) show SEM images of the top of the ARS master mold and a tilted view at 75°, respectively. Figure 2(c) shows the reflectance spectrum of the ARS master mold. The height, diameter and pitch of the ARS master mold were 650 nm, 70 nm and 115 nm, respectively. The reflectance of the master mold was about 0.1% at 550 nm.

3.2. Fabrication of the ARS film

Figures 3(a) and (b) show SEM images of the top and a tilted view at 75° of the ARS film. The height, diameter and pitch of the ARS film were 480 nm, 150 nm, and 200 nm, respectively. The reflectance of the ARS film was about 0.1% at 550 nm.

3.3. Evaluation of master mold and ARS film

The haze was calculated using Eq. 1.

Haze [%] = (Diffuse transmittance [%])/(Total light transmittance [%])×100

(1)

3. Results and discussion

3.1. Preparation of master mold

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3.2. Fabrication of the ARS film

Figures 3(a) and (b) show SEM images of the top and a tilted view at 75° of the ARS film. The height, diameter and pitch of the ARS film were 480 nm, 150 nm, and 200 nm, respectively. This height was lower than that of the master mold because of the partial filling technique. The reflectance of the ARS film was about 0.4% and the transmittance was 90% at 550 nm. Figure 3(c) shows the reflectance and transmittance spectra of the ARS film. The contact
angle was >150° and as such could not be precisely determined.

3.3. Evaluation results

Figures 4(a)–(c) and Figs. 5(a)–(c) show SEM images of the top and a tilted view at 75° of the ARS film. Figures 4(a)–(c) show SEM images after the 5th, 20th, and 30th scratch test at 125 g/cm², respectively. Figures 5(a)–(c) show SEM images after the 5th, 20th, and 30th scratch test at 250 g/cm².
The results of haze are shown in Table 2.

Figures 6(a) and (b) show the reflectance and transmittance of the ARS film after scratch tests at 125 g/cm² and 250 g/cm², respectively. Figure 6 shows that as the load/cm² increased, and as the number of scratch tests increased, the reflectance increased and the transmittance decreased. However, under all scratch test conditions, the reflectance was ≤0.7%. Table 2 shows that the haze tended to increase with both the load/cm² and number of scratch tests. The haze of the PET film was 4%, so the haze of the ARS film was low.

Table 1. Load/cm², height, diameter, pitch, and contact angle after scratch tests under various loads.

|                         | master mold | ARS film | 125 g/cm² | 250 g/cm² |
|-------------------------|-------------|----------|-----------|-----------|
|                         | 5th time    | 20th time| 30th time | 5th time  | 20th time | 30th time |
| height [nm]             | 650         | 480      | 440       | 420       | 415       | 400       | 380       | 370       |
| diameter [nm]           | 70          | 150      | 160       | 165       | 175       | 170       | 175       | 220       |
| pitch [nm]              | 115         | 200      | 210       | 230       | 240       | 230       | 235       | 265       |
| contact angle [°]       | over 150    | 152.8    | 152.6     | 152.8     | 153.8     | 152.7     | 148.4     |

Table 2. Haze results.

| ARS film | 125 g/cm² | 250 g/cm² |
|----------|-----------|-----------|
|          | 5th time  | 20th time | 30th time | 5th time  | 20th time | 30th time |
| Haze     | 1.351     | 4.221     | 2.586     | 4.092     | 1.812     | 3.680     | 5.387     |

After the 5th, 20th, and 30th scratch test at 250 g/cm², respectively. Table 1 shows the load/cm², height, diameter, pitch and contact angle at the rubbing time. Table 1 shows that as the load/cm² and number of scratch tests increased, the height decreased and the diameter and pitch increased.

This occurred because the tip of the ARS had scraped off, so the pitch became wider by chipping or needle breaking. The contact angle is <150°, which was after the 30th scratch test at a load of 250 g/cm². At 125 g/cm², no significant decrease in contact angle was observed after the 30th scratch test. At 250 g/cm², the contact angle decreased by about 4° after the 30th test compared with after the 5th test. The sliding angle was 12° after the 30th scratch test at 250 g/cm², but was 0° under all other scratch test conditions. The sliding angle measures liquid removability, and thus has no correlation with the contact angle.

The results of haze are shown in Table 2.

Figures 6(a) and (b) show the reflectance and transmittance of the ARS film after scratch tests at 125 g/cm² and 250 g/cm², respectively.

Figure 6 shows that as the load/cm² increased, and as the number of scratch tests increased, the reflectance increased and the transmittance decreased. However, under all scratch test conditions, the reflectance was ≤0.7%. Table 2 shows that the haze tended to increase with both the load/cm² and number of scratch tests. The haze of the PET film was 4%, so the haze of the ARS film was low.

4. Conclusion

A high performance ARS film was fabricated by UV-NIL and the partial filling method using the newly developed high hardness resin. The change in shape with increasing load/cm² and number of scratch tests were confirmed. The ARS film had a reflectance of about 0.4% and a transmittance of >91%. The ARS film was subjected to scratch tests at different load/cm². The ARS height decreased.
during the scratch test, but the reflectance remained at ≤0.6% and the transmittance was >90%, regardless of the load/cm² and number of scratch tests. The haze was 5.4%, and the contact angle was 148°. These results show that the reflectance was low even when the contact angle did not indicate super water repellency. However, the value of the haze increased. When the contact angle did indicate super water repellency, the reflectance increased only 0.2% compared with before the scratch test, and the haze increased by 4%. This anti-reflection film potentially has various purposes. In future, we intend to adjust the shape of the master mold, make a moth-eye film with low reflectance and antifouling properties, and evaluate the antifouling properties in greater detail. The ARS film may have potential in touch panels.

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