Microelectronic Engineering 197 (2018) 33–38

Contents lists available at ScienceDirect

Microelectronic Engineering

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

Research paper

Tough and antifouling antireflection structures made by partial-filling ultraviolet nanoimprint lithography

Hikari Eto[a], Shin Hiwasa[b], Jun Taniguchi[a,*]

[a] Department of Applied Electronics, Tokyo University of Science, 6-3-1 Niijyuku, Katsusika, Tokyo 125-8585, Japan
[b] Autex Co., Ltd., 16-5 Tomihisa-chou, Shinjuku-ku, Tokyo 162-0067, Japan

ARTICLE INFO

Keywords:
Antireflection structures
Nanoimprint lithography
Antifouling property
Scratch resistance

ABSTRACT

Ultraviolet nanoimprint lithography (UV-NIL) is the most effective technique for the mass fabrication of antireflection structure (ARS) films. For the use of ARS films in mobile phones and tablet PCs, which are touch-screen devices, it is important to protect the films from fingerprints and dust. In addition, as the nanoscale ARS that is touched by the hand is fragile, it is very important to obtain a high abrasion resistance. To solve these problems, a UV-curable epoxy resin has been developed that exhibits antifouling properties and high hardness. However, because the developed epoxy resin has a high adhesive strength, ARS films should be fabricated by the partial-filling technique, where partial filling refers to an incomplete filling ratio of the resin. Thus, in this study, ARS films fabricated by means of partial-filling UV-NIL using a UV-curable resin with antifouling properties and high hardness are presented. The fabricated ARS films are evaluated for abrasion resistance and antifouling properties by the steel wool test and wiping test, respectively. Moreover, the reflectance of the ARS films is also evaluated. The high abrasion resistance ARS films are shown to withstand a load of 250 g/cm^2 in the steel wool scratch test, and the reflectance is less than 0.4%. Hence, high abrasion resistance ARS films can be fabricated using a very high hardness resin by partial-filling UV-NIL. Furthermore, dirt is shown to be washed away from the ARS films after wiping 20 times with water containing ethanol.

1. Introduction

Antireflection structure (ARS) films are used to suppress the surface reflection of flat panel display, mobile phones and tablet PCs. In particular, moth-eye ARS exhibits a high performance in preventing light reflection. Ultraviolet nanoimprint lithography (UV-NIL) is the most effective technique for the mass fabrication of ARS films. However, considering the contact with fingers, such as in a touch-screen display, since the ARS is a nano-ordered structure, it is assumed that the structure is broken owing to contact and oil stains, such as the adherence of fingerprints. It is difficult to use an ARS film on a touch-screen display because the antireflection effect tends to be lost and the reflectance tends to increase owing to the breakage of the structure and dirt. Thus, to realize usage on the touch-screen display, it is extremely important to fabricate the ARS with antifouling properties that does not break its structure and adhere to dirt, such as fingerprints, even if it is touched. In recent years, coatings that are resistant to scratching [1–6] and antifouling nano patterns [7–9] have been reported. From the scratch reports, the best data were obtained from a moth-eye structure using silica particles, which could withstand a scratch test 10 times at a load of 200 g/cm^2 with grade 0000 superfine steel wool, and its reflectance was less than 0.5% [6]. In addition, a report on the antifouling property [9] showed water and oil repellency by an antifouling coating on nanostructures like a moth-eye structure, and the reflectance was 4% or less. However, no report has stated that an ARS film has both scratch resistance and antifouling properties. Therefore, for any practical application of an ARS film, their abrasion resistance and antifouling effect are key factors.

Hence, a UV-curable epoxy resin was developed with antifouling properties [10] and high hardness. However, because the developed epoxy resin has a high adhesive strength, the ARS films were fabricated by the partial-filling technique, where partial filling refers to an incomplete filling ratio of resin [11–14]. Thus, in this study, ARS films were fabricated by means of partial-filling UV-NIL using a UV-curable resin exhibiting antifouling properties and high hardness.

Abbreviations: ARS, antireflective structure; UV-NIL, ultraviolet nanoimprint lithography

* Corresponding author.
E-mail address: junt@te.noda.tus.ac.jp (J. Taniguchi).

https://doi.org/10.1016/j.mee.2018.04.017
Received 12 March 2018; Accepted 20 April 2018
Available online 02 June 2018
0167-9317/

2. Material and methods

2.1. ARS mold fabrication

In our technique, glassy carbon (GC; Tokai Carbon Co., Ltd., Japan) was used as a master mold, and we fabricated the ARS GC mold by etching mirror-finished GC with an oxygen ion beam from an EIS-210ER ion-beam apparatus (Elionix Inc., Japan) equipped with an electron cyclotron resonance-type ion source [15,16]. The size of the ARS GC mold was 20 mm square. The processing conditions were an ion-beam acceleration voltage of 400 V and an oxygen gas flow rate of 3.0 sccm with an irradiation period of 30 min at room temperature. The fabricated ARS GC mold of the surface was deposited on a 30-nm-thick chromium layer by using a resistively heated vacuum-evaporation system (VPC-260F; ULVAC KIKO, Inc., Japan). The chromium layer was subsequently converted into Cr_2O_3 by reaction with oxygen upon exposure to air [17,18]. The presence of the chromium oxide layer improved the effectiveness of the subsequent treatment with a fluorinated silane coupling agent (Optool DSX; Daikin Industries, Ltd., Japan) coated on the ARS GC mold [11]. The coating conditions were a dipping time of 60 min and baking at 120 °C for 5 min [19].

2.2. Tough and antifouling ARS film fabrication

ARS films were fabricated using two types of UV-curable resins which exhibited an antifouling effect and a different hardness. These UV-curable resins were the conventional resin (JST-FD-52-4K-33; Autex Co., Ltd., Tokyo) [20] and the newly developed hard resin. The newly developed hard resin had a pencil hardness of 9 H, which was a much higher hardness than the conventional resin. The fluorinated component of the two types of resins segregates at the surface of the cured resin after heat treatment and imparts an antifouling property to the surface of the resin [10]. Fig. 1 shows the fabrication process of the ARS film using partial filling. To obtain the ARS film, a UV-curable resin was placed on the GC mold, which was then covered with a polyester film (Cosmoshine A4300; Toyobo Co., Ltd., Japan), and UV light was irradiated through the polyester film. The UV dose was 10 J/cm^2. In addition, the UV-curable resin was cured while heating at 70 °C to improve the hardness. After solidification of the UV-curable resin, the polyester film was peeled from the GC mold. Moreover, to produce an antifouling effect at the resin surface, baking of the replicated ARS film was carried out at 100 °C for 30 min.

2.3. Wiping test for the antifouling effect of the ARS film

For any practical applications of the ARS film, their abrasion resistance and antifouling effect are key factors.

First, the wiping test with a colored artificial fingerprint was carried out to investigate the antifouling effect of the ARS film. The red colored artificial fingerprint liquid (0.5 μL; Autex Co., Ltd., Japan, JIS K2246 compliant) was dropped onto the mold, and was wiped off with 20 wipes using a Kimwipe S-200 (Nippon Paper Crecia Co., Ltd., Japan). After wiping, the remaining dirt on the ARS film was removed by pouring water containing ethanol 30 vol%.

2.4. Scratch test for the toughness of the ARS film

The scratch test with steel wool was carried out to investigate the toughness of the ARS film. The scratch test was carried out using superfine grade 0000 steel wool. In addition, the scratch test consisted of rubbing the surface of the ARS films for 10 cycles with an applied load of 250 g/cm^2.

Next, the wiping test was carried out to investigate the antifouling effect of the ARS film after rubbing. The red colored artificial fingerprint liquid (0.5 μL) was dropped on the mold, and was wiped off once with a Kimwipe.

After the scratch and wiping tests, the absorbance of the ARS films were measured using a UV–Vis-IR spectrophotometer in the spectral range of 300–800 nm at an angle of incidence of 5° (Solidspec-3700; Shimadzu Co., Japan). These ARS films were also observed using a scanning electron microscope (SEM; ERA-8800FE, Elionix Co., Japan).

3. Results and discussion

3.1. Fabrication of the ARS film with UV-NIL

3.1.1. ARS GC mold fabrication

Fig. 2(a) shows the top view and the view when tilted by 75° of the ARS GC mold used as the master mold. The ARS needle diameter, needle pitch, and height of the master ARS mold were 37, 78, and 990 nm, respectively. The reflectance of the ARS GC mold was approximately 0.3% at visible-light wavelengths [Fig. 2(b)].

3.1.2. Properties of UV-cured resin

The newly developed hard resin was a cationically curable multifunctional epoxy resin that uses a sulfonium salt as an initiator. Since these resins consist of a blend of a cationically polymerizable UV-curable resin and an epoxy-modified fluorinated resin, they are extremely hard resins.

The properties of the newly developed hard resin were a viscosity of 60–150 (23 °C·cps), pencil hardness of 9 H, and Young's modulus of 1305 MPa. In general, an epoxy resin is hard and its elastic modulus is high [21–23]. However, this hard resin has the property of not breaking even if it is bent because its modulus of elasticity is low.

3.1.3. ARS film fabrication with UV-NIL

Fig. 3 shows the 75° tilted views and the top view of the ARS film fabricated with UV-NIL.

The height of the ARS film in Fig. 3(a) was 500 nm and the height of the ARS film in Fig. 3(b) was 530 nm. The height of the ARS film was lower than the height of the ARS GC mold, which confirmed a partial filling. Partial filling facilitates release of the film from the ARS mold because of the small surface area of the adhesion resin, which consequently increases its lifetime. In addition, we conducted the scratch test for the moth-eye structure, because very sharp needles, which result from complete filling, are not suitable for the scratch test because we

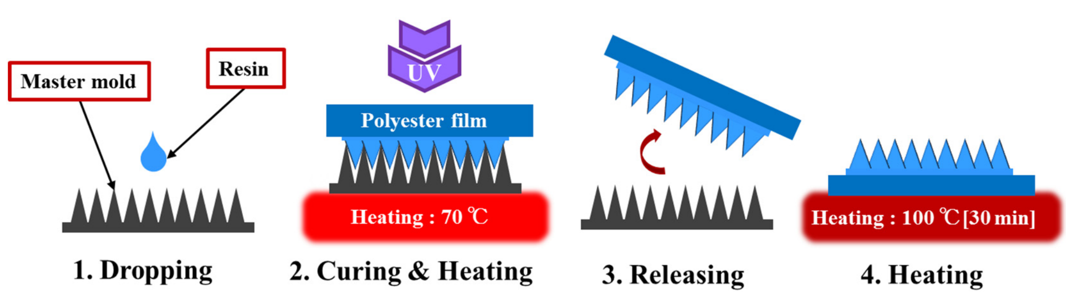

Fig. 1. Repeated fabrication of the ARS film.