Metallic Antireflection Structures Made from Silver Ink by a Liquid Transfer Imprint Lithography Technique

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Solar power can become a major source of energy that is beneficial to the environment. However, the front surfaces of solar cells have a reflectance greater than 30%, resulting in low energy-conversion efficiencies. The light-absorption performance of solar cells can be improved by using antireflection structures (ARSs), which are effective in ensuring efficient absorption of light. Liquid transfer imprint lithography (LTIL) is a promising method for producing thin films under atmospheric conditions. In addition, it is possible to obtain thin and uniform films using a roller regardless of the viscosity of the liquid. We succeeded in forming metallic ARSs by using silver ink and a LTIL process. Metallic ARSs without a residual layer were produced at a roll pressure of 40 MPa in the first LTIL cycle, thereby improving its reflectance. Furthermore, reflection from the metallic ARSs with a high aspect ratio showed intense plasmon peaks around a wavelength of 560 nm, exhibiting a green color on the surface. Consequently, our process is suitable for fabricating metallic ARSs by using high-viscosity materials such as silver ink.

Keywords: Antireflection structure, Liquid transfer imprint lithography, Silver ink, Roll press, Solar cell

1. Introduction

Solar power is a potential energy source that is beneficial to the environment [1,2]. However, the front surfaces of solar cells have a high reflectance of more than 30%, resulting in low energy-conversion efficiencies [3]. Improving the energy-conversion efficiency is a key factor in producing better solar cells. To improve the light-absorption efficiencies of solar cells, their surfaces can be coated with antireflection structures (ARSs) [4-7]. In addition, light management by reflection control and light trapping utilizing plasmons in metallic nanopatterns have also been investigated [4,8,9].

Fabrication of metallic nanostructures, such as ARSs, is an important factor in developing solar-consuming [10,11]. Thus, a print-type process is needed to improve throughput and to reduce the cost of fabrication. In our previous study, we reported that metallic nanostructures could be transferred under atmospheric conditions using silver ink [11]. This enables the materials to be deposited as metal layers under ambient conditions. However, it is difficult to produce thin films using the silver ink process because the coating thickness is controlled by the viscosity of the material, and silver ink has a high viscosity of more than 1 Pa·s.

Liquid transfer imprint lithography (LTIL) is a promising method for producing thin films under atmospheric conditions [12-14] because LTIL can reduce thickness of the residual layer of silver ink in the mold in the liquid phase [11,15]. In addition, by using a roller [15,16], it is possible to obtain thin and uniform films regardless of the viscosity of the liquid. In this study, we fabricated metallic ARSs using silver ink and the LTIL process with a roll press.

2. Experimental

The master mold for the ARSs was machined from glassy carbon (GC, Tokai Carbon Co., Ltd., Tokyo) with a beam of oxygen ions from an EIG-20ER ion-beam apparatus (Elionix Inc., Tokyo)
equipped with an electron-cyclotron-resonance-type ion source [17,18]. The machining conditions is shown in Table 1.

Table 1. Machining condition of GC master mold

|                  | Mold A       | Mold B       |
|------------------|--------------|--------------|
| Substrate        | Grassy carbon (GC) |              |
| Gas              | O₂           |              |
| Accelerating voltage | 530 V | 400 V        |
| Machining time   | 60 min       | 90 min       |

The GC master molds underwent a release treatment is illustrated in Fig. 1.

Fig. 1. Release treatment of the mold.

A 30-nm-thick chromium intermediate metal layer was deposited onto the GC master molds using a heated vacuum-evaporation system (VPC-260F; ULVAC KIKO, Inc., Saito city). Subsequently, the chromium layer was converted into Cr₂O₃ by reaction with oxygen upon exposure to air for 1 h [19,20]. The presence of the Cr₂O₃ layer improved the effectiveness of subsequent treatment with a fluorinated silane coupling agent (Optool DSX; Daikin Industries, Ltd., Osaka), which was applied to the chromium-plated mold [21]. The molds were immersed in the liquid release treatment agent for 1 h, kept in a container with the vapor phase of the treatment agent for 12 h, baked at 120 °C for 5 min, and immersed in the fluorinated solvent NOVEC 7300 (3M Japan Ltd., Tokyo) for 1 min.

Figure 2 illustrates the fabrication process of the replica molds.

Fig. 2. Fabrication of the replica mold.

First, the UV-curable resin (PARQUIT OEX-028-X433-3, hereafter X433-3; AUTEX Co., Ltd., Tokyo) was placed on two types of GC master molds [22]. Subsequently, the resin layer was covered with a polyester film (Cosmoshine A4300; Toyobo Co. Ltd., Osaka) and pressed at 0.3 MPa, which was cured using UV irradiation. After the UV-curable resin had cured, the polyester film was released from the GC master molds. The release treatment was the same as that for the GC master mold. The replica mold imprinted from the GC master molds GC A and GC B is referred to as REP A and REP B, respectively.

Figure 3 is a schematic representation of this process.

Fig. 3. Schematic of LTIL with roll-press method.

First, the silver ink (T10Z-A02; Dowa Electronics Materials Co., Ltd., Tokyo) was placed on the replica mold. The layer of silver ink was then pressed with a polyester-film-coated roller (40 MPa, 1.6 mm/s) to form a thin and uniform film. The film was released, removing excess ink from the replica mold. The replica mold with the silver ink was then baked at 120 °C for 5 min. Next, the ARS consisting of the remaining silver ink was transferred from the replica mold using a UV-NIL (ultraviolet nanoimprint lithography) process with a UV-curable resin (PAK-02; Toyo Gosei Co. Ltd., Tokyo).

We examined the relationship between the number of repetitions of LTIL and the properties of the ARSs and the residual layer of silver ink. We also evaluated the thickness of the residual layer and the reflectance of the ARSs for various roll pressures. The metallic ARSs and the residual layers were observed by scanning electron microscopy (SEM; ERA-8800FE, Elionix Co., Tokyo). The optical properties were evaluated using UV-visible-IR spectrophotometry (Solidspec-3700: Shimazu Corp.).

Since this spectrophotometer is equipped with an integrating sphere, a highly accurate evaluation of the optical properties is possible. In these experiments, the total light reflection and diffuse
reflection were measured at an angle of incidence of 8°.

3. Results and discussion

Figure 4 shows the surface [Fig. 4(a)] and cross-sectional [Fig. 4(b)] SEM images of the GC master mold (GC A).

Fig. 4. SEM images of the GC master mold (GC A): (a) surface and (b) cross section.

The ARSs of the GC master mold (GC A) had a pitch of 70 nm, diameter of 40 nm, and a height of 830 nm, which were the average of 100 points measured from the SEM images. In addition, the aspect ratio (height/diameter) of these ARSs was 20.8.

Figure 5 shows the surface [Fig. 5(a)] and cross-sectional SEM [Fig. 5(b)] images of the replica mold (REP A).

Fig. 5. SEM images of the replica mold (REP A): (a) surface and (b) cross section.

The ARSs of the replica mold (REP A) had a pitch of 130 nm, diameter of 60 nm, height of 590 nm, and an aspect ratio of 9.8 [Figs. 5(a) and 5(b)]. The measurement and method of calculation manner were the same as that for the GC master mold.

Figure 6 shows the metallic ARSs transferred from the GC master (GC A) and the replica mold (REP A).

Metallic ARSs were not obtained from the GC master mold because silver ink could not be filled into the ARSs with a narrow pitch of less than 100 nm [Fig. 6(a)]. However, when using the replica mold, needle-like metallic ARSs were successfully fabricated using the silver ink [Fig. 6(b)]. Thus, it was easy to fill in the ARSs with high-viscosity silver ink by extending the pitch of the needle shape, which enabled formation of complex structures like the ARSs. In addition, it was easy to fabricate replica molds from the GC master mold using UV-NIL and the GC master mold could be prevented from breaking by contact damage.

Figure 7 shows the metallic ARSs produced from the replica mold (REP A) by using a planar press [Fig. 7(a)] and a roll press [Fig. 7(b)].

Fig. 7. Silver ink ARSs produced by (a) the planar-press method (0.5 MPa) and (b) the roll-press method (40 MPa).

The pressure of planar-press method was 0.5 MPa. The roll-press method is, therefore, suitable for removing residual layers of silver ink.

Figure 8 shows the relationship between the number of LTIL repetitions and the properties of the metallic ARSs.

In the first LTIL cycle, the height of the metallic ARSs was 350 nm [Fig. 8(a)], whereas in
the second LTIL cycle, it was 190 nm [Fig. 8(b)]. This shows that silver ink at the bottom of the ARSs was removed in the repeated LTIL cycles. It also confirmed that the properties of the metallic ARSs deteriorated with repeated LTIL cycles. Figures 9(b)–(e) show the SEM cross-sectional images of the silver layers with the metallic ARSs for various roll pressures; Figure 9(f) is a SEM image of the surface of the replica mold after an imprint at 50 MPa.

For a film with a planar surface that does not undergo the LTIL process, the thickness of the silver ink layer was 7.0 μm [Fig. 9(a)]. Figures 9(b)–(e) show that a thin layer of silver ink with the ARSs having a uniform thickness of < 1.5 μm was obtained by the LTIL process by using the roll press. In particular, a silver ink ARS without a residual layer was obtained at a roll pressure of 40 MPa. The thickness of the silver ink layer with the ARSs tended to decrease upon increasing the roll pressure.

Figure 10 shows the reflectance of the ARSs fabricated from silver ink at various roll pressures. Figure 10 shows that light with a wavelength of around 300–400 nm (blue color) was absorbed by the silver ink because of the presence of silver plasmons. The silver ink ARSs without a residual layer, produced by the LTIL process with a roll press, showed a reflectance of about 10% at a wavelength of around 500 nm. This confirmed that the metallic ARSs with the thinner silver ink layer showed a better efficiency than the thicker silver ink layer. However, Figure 10 also shows that a low reflectance requires not only a thin layer of silver ink, but also forming the high quality of needle-like ARSs.

However, these metallic ARSs with weak plasmon peaks are not suitable for application in plasmon devices. Thus, the metallic ARSs were fabricated from another mold (GC B and REP B) with a higher aspect ratio. Figure 11 shows the SEM images of the GC master mold [Fig. 11(a)] and the replica mold with a higher aspect ratio, fabricated from the GC master mold by using UV-NIL [Fig. 11(b)].

![Fig. 9. Cross-sectional SEM images of: a layer of silver ink on a planar surface (a); silver ink ARSs produced by LTIL at pressures of 25 MPa (b), 30 MPa (c), 40 MPa (d), and 50 MPa (e); and the mold surface after the 50 MPa imprint (f).](image1)

![Fig. 10. Reflectance of the planar surface and of silver ink ARSs produced by LTIL at various roll pressures.](image2)

![Fig. 11. SEM images of (a) the master mold (GC B) and (b) the replica mold (REP B) with higher aspect ratio.](image3)

However, the quality of the metallic ARSs deteriorated at a roll pressure of 50 MPa because the excessive pressure broke the replica mold, which is composed of epoxy resin [Fig. 9(f)]. Figure 10 shows the reflectance of the ARSs fabricated from silver ink at various roll pressures.
respectively [Figs. 11(a) and 11(b)]. This replica mold was used for imprinting the high aspect ratio metallic ARSs.

Figure 12 (a) shows the metallic ARSs with a height of 270 nm and an aspect ratio of 3.4, which were fabricated from the replica mold [REP A, see Figs. 5]. And Fig. 12 (b) shows the metallic ARSs with a height of 540 nm and an aspect ratio of 6.8, which were fabricated from the high aspect replica mold [REP B, see Fig. 11(b)].

![Fig. 12. SEM images of the metallic ARSs transferred from a replica mold with an aspect ratio of (a) 9.8 and (b) 15.7.](image)

In other words, the aspect ratio of the high aspect ratio metallic ARSs [Fig.12 (b)] was twice that of the low aspect ratio ARSs [Fig.12 (a)]. The metallic ARS with an aspect ratio of 3.4 showed no plasmon peaks, whereas those with an aspect ratio of 6.8 showed plasmon resonance around a wavelength of 560 nm [Figs.13 (a)]. Figure 13(b) shows the diffuse reflectance and the surface color of the metallic ARSs.

![Fig. 13. Optical properties of the metallic ARSs with aspect ratios of 3.4 and 6.8: (a) reflectance and (b) diffuse reflectance.](image)

ARSs with an aspect ratio of 3.4 showed weak peaks around a wavelength of 720 nm and a yellow-orange color was observed on the surface of the metallic ARSs. On other hand, an aspect ratio of 6.8 gave rise to intense peaks around a wavelength of 560 nm, showing a green color.

4. Conclusion

We have successfully fabricated metallic ARSs using silver ink and the LTIL process with a roll press under atmospheric conditions. In addition, it was easy to fill in the ARSs with high-viscosity silver ink by extending the pitch of the needle shape, which enabled formation of complex structures like the ARSs. The process eliminates residual layers of silver ink and it produces thin and uniform films. However, a second cycle of LTIL or excessive roll pressures caused deterioration of the ARSs. A metallic ARS without a residual layer was produced at a roll pressure of 40 MPa in the first LTIL cycle, and this ARS showed a reduced reflectance.

The metallic ARSs with low aspect ratio showed no plasmon peaks, whereas those with a high aspect ratio showed plasmon resonance around a wavelength of 560 nm. Furthermore, diffuse reflection of the metallic ARSs with an aspect ratio of 6.8 showed intense peaks around a wavelength of 560 nm, and a green color was observed on the surface. Our non-vacuum process using a roll press can eliminate residual layers of high-viscosity materials like silver ink. Furthermore, it is possible to remove the residual layer regardless of the viscosity of the liquid. Therefore, our process is suitable for fabricating metallic ARSs using silver ink.

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