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Investigation of Roll-to-Sheet Imprinting for the Fabrication of Thin-film Transistor Electrodes

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SUMMARY We applied a roll-to-sheet imprinting process to a large-scale substrate. Patterned ruthenium oxide (RuO_2) electrodes were fabricated on both glass and flexible substrates. The resistivity of the electrodes on a glass substrate was $3.5\times10^{-5}\,\Omega$ cm, which indicates that this technique is useful for the fabrication of thin-film transistor (TFT) electrodes.

key words: *Nano-rheology Printing, Oxide TFT, Printed Electronics, Printed TFT*

1. Introduction

In recent years, the demand for miniaturization of electronic devices has required greater device density. Photolithography is a conventional technology for fabricating electronic devices; however, it suffers drawbacks in terms of manufacturing costs and the complex nature of the process. As an alternative technique, imprinting methods are superior to photolithography in several aspects because these methods are simpler for smaller patterns and feature a considerably greater efficiency in terms of material consumption [1]–[3]. In particular, direct imprinting does not require the use of photoresists for patterning and is therefore attractive for the fabrication of electronic devices. We developed a new technology called "nano-rheology printing" [4], which is a direct imprinting method that differs from other direct imprinting techniques. In this process, when the gel film on the substrate reaches a certain temperature, it undergoes plastic flow. During processing, rheological pattern formation and condensation of the metal oxide concurrently occur as the result of viscoelastic transition of the gel film. The features of this technique include a very fine fabricated pattern and very low shrinkage after post-annealing.

2. Roll-to-sheet Imprinting System

Most imprinting systems are of the sheet-to-sheet type, which enables easy fabrication and good control of micro-to-nanoscale patterns. However, the sheet-to-sheet imprinting process, as shown in Fig. 1, cannot be utilized for patterning of large-scale substrates. Because sheet-to-sheet systems involve plane contact, large-scale equipment would be required to supply the necessary pressing force to apply the mold against the substrate.

Therefore, we developed a roll-to-sheet imprinting system, shown in Fig. 2. This system involves line contact; thus, the effective force is much smaller than that necessary in a plane contact system. Consequently, such a roll-to-sheet system is particularly effective for imprinting large substrates. This component can be expanded for use with

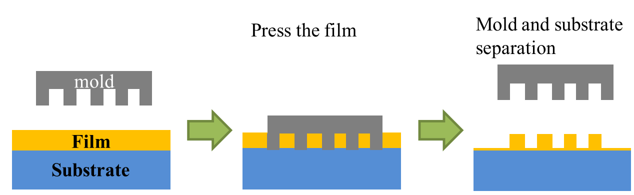
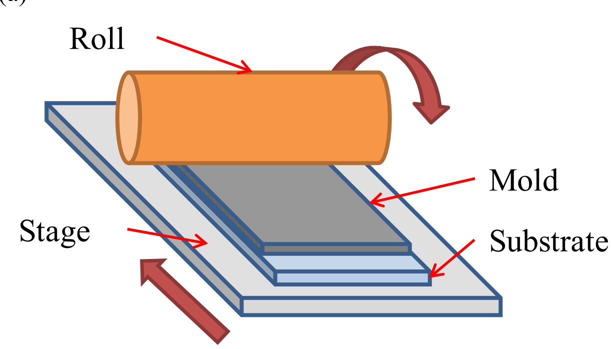


Fig. 1 Conventional sheet-to-sheet nanoimprinting system.

(a)



(b)

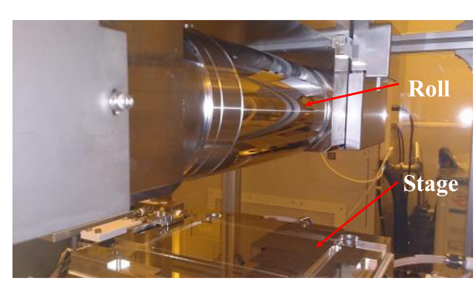


Fig. 2 Diagram (a) and photograph (b) of the roll-to-sheet imprinting system.

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larger substrates. In addition, the roll-to-sheet system can be employed with both rigid and flexible substrates. In this study, we demonstrate the patterning of a gel using our roll-to-sheet imprinting system, and we attempt to pattern RuO_2 electrodes for active matrix backplane TFTs using the developed roll-to-sheet imprinting system.

3. Experimental Details

3.1 Preparation of the RuO_2 Precursor Solution and the Substrate

A RuO_2 solution was prepared for the fabrication of thin-film electrodes [5]. The solution was synthesized by blending 0.35 mol/kg of Ru(III) nitrosylacetate (Alfa Aesar) in propionic acid (Kanto Chemical). The solution was stirred at 150°C for 30 min under ambient conditions and then cooled to room temperature and filtered. An organic polymer, polyvinylpyrrolidone (PVP) (Kanto Chemical), was added to the solution to serve as a stress relaxation agent during drying and calcination of the film. The PVP was added to the solution to a concentration of 1 wt%.

The glass substrate was Eagle XG glass ($200 \times 150 \times 0.7\,mm^3$). The flexible substrates were Kapton 500 V (DuPont), 125-μm-thick, which was taped onto the glass, and 15-μm-thick Pyre ML (I.S.T.), was coated onto the glass.

3.2 Preparation and Demold Treatment of Ni Mold

A nickel mold ($150\times120\times0.3\,mm^3$) with electrode lines was used in the experiments. The line width and the mold depth were 10 μm and 350 nm, respectively. The surfaces of the nickel mold were modified by a demolding treatment with HD-2100TH (Daikin) and via a rinse treatment using the dip-coating method with HD-TH (Daikin). After the rinse treatment, the mold was baked on a ceramic heater at 100°C for 5 min.

3.3 Fabrication Processes of RuO_2 Patterns

First, the RuO_2 solution was coated onto the glass substrate using a slit coater and was pre-annealed at 100°C for 5 min on a ceramic heater. Second, an anti-adhesion agent (HD-1100TH, Daikin) was formed by spin coating. Third, the substrate was placed on the stage in the roll-to-sheet imprinting system, and the RuO_2 gel electrode was patterned by the imprinting system. In this study, the pressure of patterning was approximately 13 MPa. Finally, the glass substrate was post-annealed with an infrared heating system at 500°C for 30 min under nitrogen. RuO_2 patterns were also prepared on a flexible substrate using this same procedure, except that the patterned substrate was post-annealed at 300°C.

The prepared RuO_2 patterns were observed with an optical microscope (Olympus MX-50) and an atomic force microscope (Keyence nanoscale hybrid microscope), and the film resistivity was measured with a resistivity meter (Mitsubishi Chemical Co., Loresta).

4. Results and Discussion

4.1 Thermofluid Analysis of the Roll-to-sheet System

Kaneda et al. reported that nano-rheology printing requires moderate temperatures between 150°C and 200°C to induce viscoelastic character in an indium tin oxide (ITO) gel film [4]. Their results show that imprinting systems depend on the rheological properties of the material pressed onto the substrate.

We first simulated the thermal conduction of the roll-to-sheet system using the Flow-3D thermofluid analysis software by calculating the dependence of the gel temperature on the roll temperature (Fig. 3). Figure 3(a) shows the difference between the actual temperatures of the gel and preset temperatures of the roll (150, 200, 250, and 300°C). The diagram of the calculation model is shown as Fig. 3(b). We found that the gel film required at least 6 s to reach a saturation temperature. In addition, the heated area was very narrow because of the poor thermal conduction that resulted from the small contact area between the roll and the sheet. We therefore used the slowest roll speed and the highest roll temperature possible with this system to effectively heat the

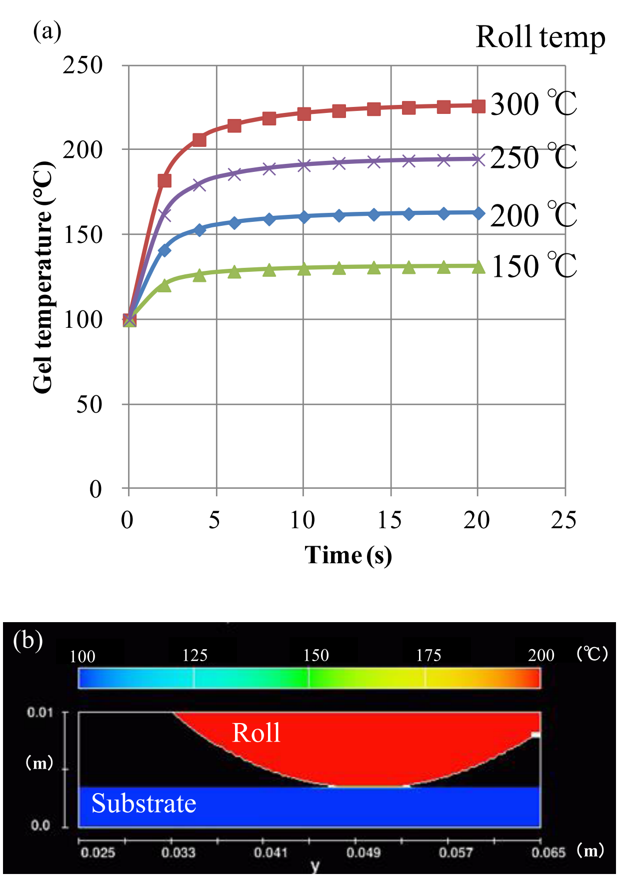

Fig. 3 Dependence of the gel temperature on the roll temperature (a) and a diagram of the temperatures (b).

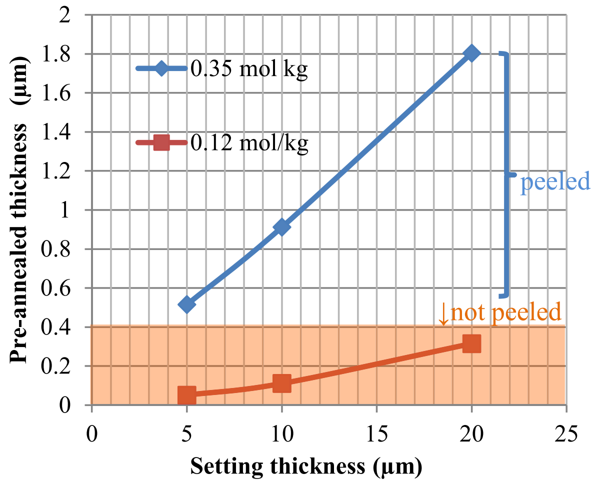

Fig. 4 Relationship between the pre-annealed thickness of the RuO_2 patterns and the selected slit-coat thickness setting.

Table 1 Pattern evaluation results determined by optical microscopy.

	220°C	230°C	240°C	250°C
0.01 mm/s	Good	Good	Good	Good
0.05 mm/s	Poor	Poor	Poor	Excellent
0.1 mm/s	Poor	Poor	Good	Poor
0.5 mm/s	Poor	Poor	Good	Poor

gel film.

4.2 Optimization of Film Thickness

First, we optimized the film thickness and peeling properties (adhesiveness) of the RuO_2 films on the glass substrates. Figure 4 shows a plot of the pre-annealed film thickness compared to the thickness setting of the slit coater. Peeling tests were performed under all process conditions, irrespective of any adjustment to the thickness setting. We assumed that the peeling was caused by internal stress of the films when they became excessively thick. Therefore, we diluted the RuO_2 precursor solution by a factor of three and reattempted the deposition. As a result, we confirmed that RuO_2 films prepared using the diluted solution did not peel.

4.3 Formation of Electrode Pattern on a Large-scale Substrate

We patterned RuO_2 electrodes using the roll-to-sheet direct imprinting method. Table 1 lists the quality of the electrode patterns, as observed via optical microscopy, for patterns prepared at four imprinting temperatures and at four distinct imprinting speeds at a pressure of 13 MPa. This pressure is the same as the sheet to sheet system.

In this table, “excellent” indicates a clearly observed pattern, whereas “good” means slightly distorted patterns, and “poor” indicates crumbled, cracked, or void patterns. The results in this table show the same tendency as those of the aforementioned simulation: better patterns were formed at high temperatures and at slower speeds.

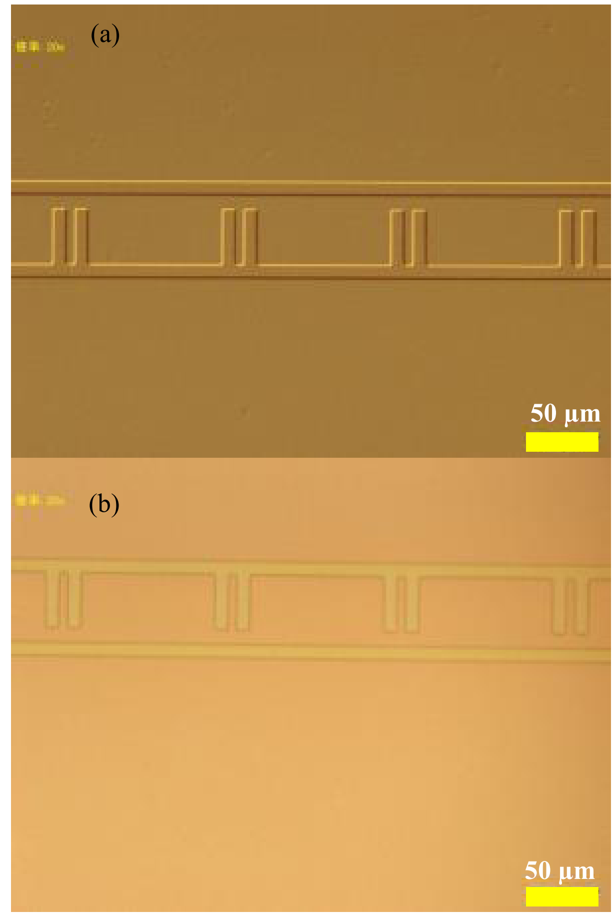

Fig. 5 Optical microscopy images of patterned RuO_2: a) 220°C, 0.05 mm/s; b) 250°C, 0.05 mm/s.

Figure 5(a) shows the RuO_2 pattern prepared at 220°C and 0.05 mm/s, and Fig. 5(b) shows the pattern prepared at 250°C and 0.05 mm/s. Although both patterns appear to be completely formed without any breaks, their AFM images (Fig. 6) revealed that the pattern shown in Fig. 5(b) was of good quality, whereas that shown in Fig. 5(a) was of relative poor quality. More specifically, the AFM in Fig. 6(a) clearly shows that the pattern was concave rather than the desired convex shape. In contrast, the AFM image of the pattern shown in Fig. 6(b) indicates that the desired convex pattern was obtained.

We speculated that this defect would occur as shown in Fig. 7. Figure 7(a) shows the pattern being peeled away and sticking to the mold, which would indicate a deficient separation treatment.

Figure 7(b) shows comparison of the non-contact area with the contact one between the mold and the gel. The temperature of the non-contact area is lower, leading to insufficient fluidity of the gel film in this area. In contrast, the temperature in the contact area is high enough to allow viscoelastic deformation. Consequently, filling gel into the cavity is insufficient, and only the edge patterns are formed, resulting in concave patterns. The resistivity of the film in Fig. 5(b) is $3.5 \times 10^{-5}\,\Omega\,\text{cm}$, which is sufficiently low for its

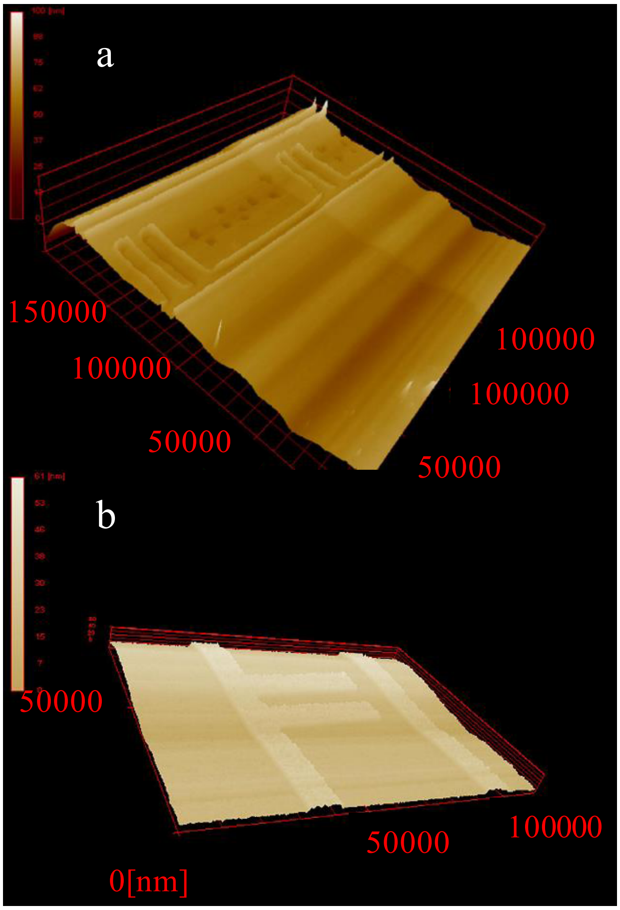

Fig. 6 AFM images of patterned RuO_2: a) 220°C, 0.05 mm/s; b) 250°C, 0.05 mm/s.

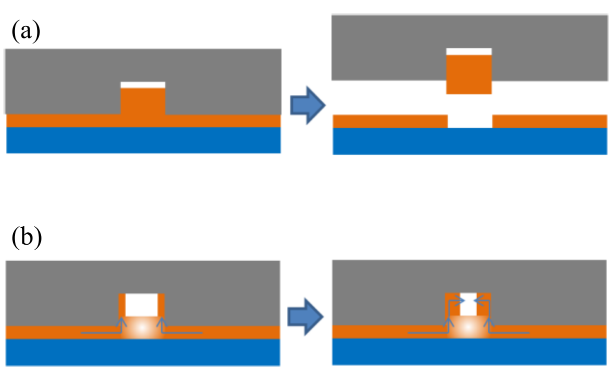

Fig. 7 Diagram of typical defects that occur during imprinting: a) sticking to the mold; b) insufficient filling into cavity.

application as an electrode for TFTs.

4.4 Formation of Electrode Pattern on a Flexible Substrate

Figure 8(a) shows an optical microscopy image of a RuO_2 pattern prepared on a flexible substrate. This flexible substrate was a polyimide film taped onto glass. We attempted to perform the imprinting under the same conditions used for glass substrates. However, the film cracked under almost all of the investigated conditions. During processing, a gel film on a flexible substrate is subject to much greater mechanical stress than a film on a glass substrate. Therefore, we doubled the amount of additives for stress relaxation in the RuO_2 solution, which resulted in good patterns without any kinds of cracks (Fig. 8(b)).

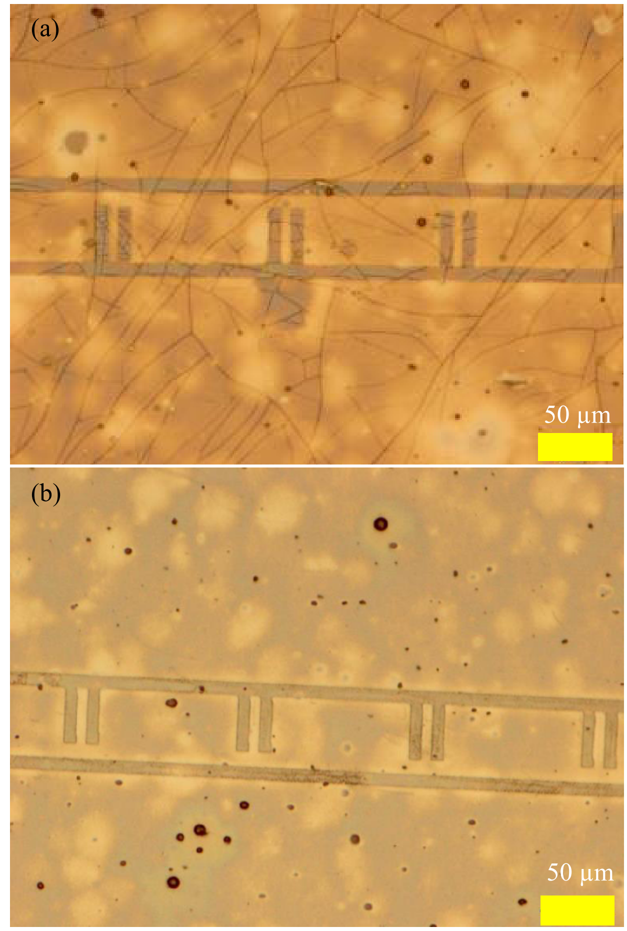

Fig. 8 Optical microscopy images of patterned RuO_2: a) 250°C, 0.05 mm/s without additive; b) 250°C, 0.05 mm/s with additive.

Next, we attempted to fabricate electrodes on coating-type flexible substrates because the surface of the previous film was too rough for it to be used in an electronic device. Figure 9 shows an optical microscopy image and an SEM image of a RuO_2 pattern prepared on a flexible substrate. Although the pattern was successfully fabricated on this substrate on glass, the resistivity of the pattern was slightly high (5.9×10^{-4} Ω cm) for it to be used as a TFT electrode. The high resistance of the RuO_2 film on the flexible substrate can be attributed to the greater amount of additive agent used in the solution to impart the RuO_2 gel film with greater stress resistance. Since the dependence of additive amount was not observed in glass substrate, it is considered that the resistivity difference was caused by the effect from flexible substrates. As previously noted, a gel film on a flexible substrate is subject to considerably greater mechanical stress during processing than a film on a glass substrate. However, by optimizing the annealing conditions to reduce stress and by adjusting the solution composition, we succeeded to fab-

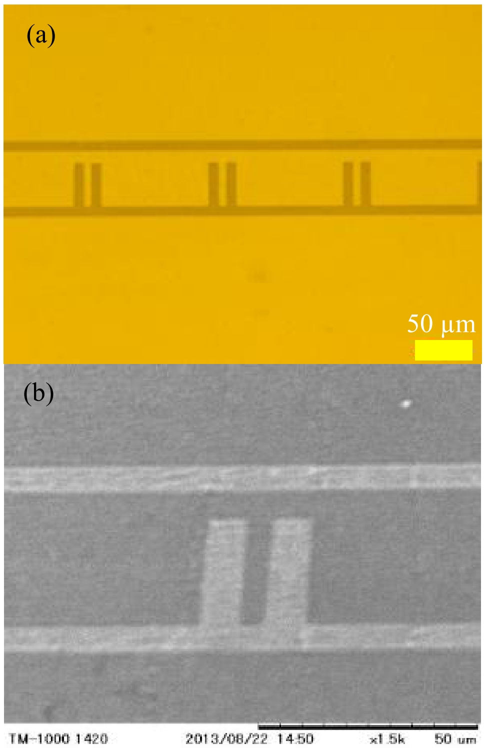

Fig. 9 RuO_2 patterned at 250°C and 0.05 mm/s on a flexible substrate: a) optical microscopy image; b) SEM image.

ricate a pattern with quality equivalent to that obtained for patterns on the glass substrate.

5. Conclusions

In this study, RuO_2 patterns were fabricated using a roll-to-sheet imprinting system. Patterns fabricated on a glass substrate were convex and exhibited a sufficiently low resistivity to enable their use as TFT electrodes. Similar to the case of the glass substrate, we successfully fabricated a clear pattern using a coating-type flexible substrate. The resistivities of the patterns fabricated on the flexible substrate were approximately one order of magnitude higher than those of the patterns fabricated on the glass substrate. Further improvement is required.

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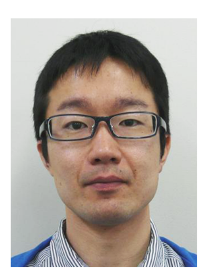

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