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Fabrication of Planarized Stainless Steel Foil for Flexible Substrate

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Abstract

The surface of stainless steel foil was covered with a film composed of an organically modified siloxane network in order to furnish the foil with planarization and electric insulation. A coating solution to form the film was designed to be dried and cured for a short treatment-time, leading to the fabrication of roll-to-roll planarized stainless steel foil. No degradation of OLED (organic light emitting diode) was observed by the outgas from the planarization film. Planarized stainless steel foil could withstand patterning processes of the electrode including photolithography and etching. Successful demonstration of flexible OLED on the planarized stainless steel foil suggests the capability of the foil as a flexible substrate.

1. Introduction

Today, with portable terminal equipment as represented by smartphones having become widespread, terminal equipment including display devices that are unbreakable even when dropped, rolled portable E-books, and multi-functional watches bendable like a wrist band are attracting attention as that of next-generation. Furthermore, king-sized electronic sign boards for stations and commercial facilities, thin film type solar batteries installable on the wall of a building, curved screen type TVs and illuminations are expected as the new type electronics equipment. To realize such displays and the thin film solar batteries, electronic devices are required to be fabricated not on the conventional glass substrate but on a thin and light flexible substrate.

Fabrication of a device on a flexible substrate embraces the possibilities of not only creating new products, but also the capability of producing devices at low cost. Currently, devices are fabricated on glass substrates in vacuum deposition equipment. In the meantime, study on the fabrication of devices by the roll to roll method is under way, wherein such device constituting elements such as electrode paste and organic semiconductor layers are printed in succession on a flexible substrate uncoiled from a roll and coiled to a roll. Continuous fabrication of devices on flexible substrates by means of a printing method without using vacuum equipment can realize drastic cost reduction.

Flexible substrates are thus promising, and three types of material are listed as candidate materials. They are thin sheet glass, plastic film and metal foil. The thin sheet glass is about 50–100μm thick and can be coiled to a roll. Although the glass material has been used plentifully for the fabrication of devices, the material is fragile and vulnerable in handling. The plastic film is light and soft. However, it is inferior in heat resistance and in the function as a gas barrier. Although heat-resistant, the metal foil is disadvantageous in that it has a rough surface and electric conductivity. Presently, there are no materials decisively suited to flexible substrates, and development efforts are being made for the respective material.

We are developing a stainless steel foil that is excellent in heat resistance and chemical resistance with a planarized surface and electric insulation by coating the surface with a film.[1)] To effectively utilize the heat resistance of a stainless steel foil, a film consisting of inorganic-organic hybrid material equipped with the heat resistance of inorganic material and the flexibility of organic material is formed.[2)] This article reports the stainless steel foil coated with the developed planarizing film, and the trial manufacturing of a flexible OLED (organic light emitting diode) device employing the developed foil. Trial fabrication of the OLED device by the roll to roll method was also conducted, and it showed that the coiled roll stain-

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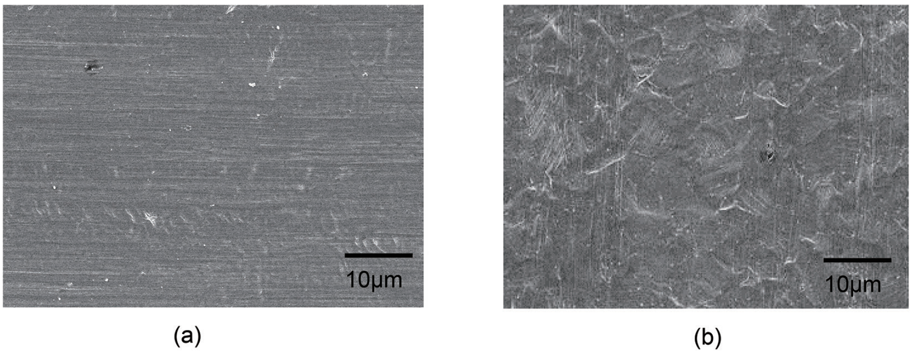

Fig. 1 SEM photographs of stainless steel foils
(a) NSSC190SB, (b) SUS304MW

less steel foil coated with a planarizing film is applicable as a material to the future manufacturing of devices using the roll to roll method, the result of which is also introduced.

2. Stainless Steel Foil

The super-bright-finished NSSC190SB ferritic stainless steel and the milk-white-finished austenitic stainless steel of SUS304MW produced by Nippon Steel & Sumikin Materials Co., Ltd. were used. **Figure 1** shows the photos of the surfaces of the two stainless steel foils observed by SEM (scanning electron microscope). On the SB-finished stainless steel foil surface, streaks running in the direction of rolling in parallel are clearly observable, and on the MW-finished stainless steel foil surface, undulation is observable in the entire field of view. The thickness of both the used foils is 50μm. A stainless steel foil coated with an undercoating film to enhance the adhesivity of the planarizing film was also used. To date, the formation of a planarizing film, trial fabrication of an OLED device and light emission have been confirmed on both substrates of NSSC-190SB and SUS304MW regardless of whether the undercoating film is present or not.

3. Planarizing Film

3.1 Coating solution

There exists fine ruggedness of a number of rolled-in streaks on the surface of the stainless steel foil. Since the thickness of each layer constituting an electronics device is of nanometer order, in order to deposit each film layer without it being broken, the surface of the stainless steel foil needs to be planarized to the level of a glass substrate. Additionally, as schematically illustrated in **Fig. 2**, in order to produce a planarized stainless steel foil coiled to a roll by the roll to roll method, the planarizing film needs to be dried and cured within a very short time. Furthermore, flexibility that allows coiling to a roll and heat resistance to withstand the temperature rise in fabricating a device are also required for the film.

A coating solution that meets such requirements was designed. Firstly, organoalkoxysilane was hydrolyzed in an organic solvent, and a precursor of high molecular weight was produced by forming the siloxane bond of Si-O-Si through dehydration condensation. By optimizing the combination of catalysts and the synthesis condition, the structure and the molecular weight of the precursor were controlled. The coating solution that contains the precursor was coated on the surface of the stainless steel foil, and dried and cured. Then, the inorganic-organic hybrid planarizing film of the siloxane network that is modified with organic groups as shown in **Fig. 3** was obtained. The solution was coated on a 110 mm square stainless steel foil by the spin coating method and was cured in a clean oven, and a planarized stainless steel foil was produced. The planarized stainless steel foil roll was produced by coating either with a gravure as shown in Fig. 2, or by the slit coating method, and by continuously drying and curing. In either coating method, coating was controlled so that a film 3–4μm thick is formed after curing. **Figure 4** shows the photograph of a planarized stainless steel foil roll. So far, a roll of the planarized stainless steel foil of up to 430 mm wide and 200 m long has been produced.

3.2 Characteristics of film

Figure 5 shows a SEM photograph of the stainless steel foil of NSSC190SB planarized by the spin coating method. Streaks and ruggedness on the surface of the stainless steel foil surfaces as observed in Fig. 1 have disappeared and the stainless steel surface has been planarized. Planarization is also confirmed on the AFM (atomic force microscopy) image taken for microscopic observation in **Fig. 6**. In terms of surface roughness before and after the formation of planarizing film, Rmax was reduced from 78.2 nm to 8.9 nm, and

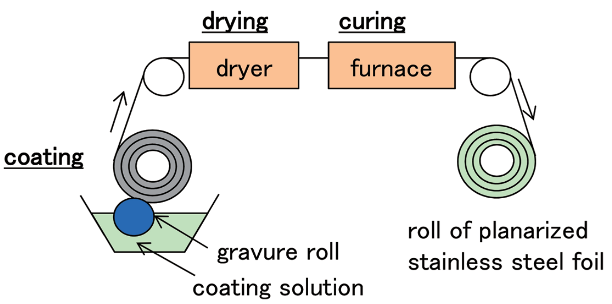

Fig. 2 Fabrication of planarized stainless steel foil by roll-to-roll process

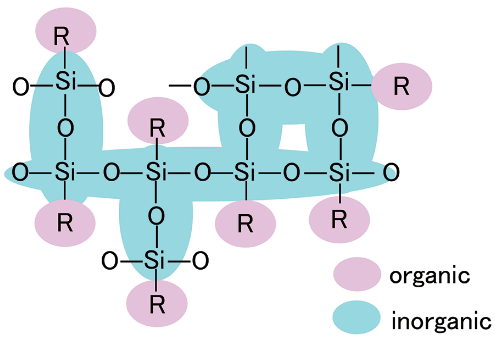

Fig. 3 Schematic of molecular structure of inorganic-organic hybrid

Ra, from 6.2 nm to 0.6 nm. The value of Ra is equal to that of a glass substrate.

To examine whether the stainless steel foil surface has been insulated by the planarization, nine 10 mm square electrodes were placed on the planarizing film and a voltage of 100 was applied across the electrodes and the stainless steel foil. The leak currents measured at the nine locations on the sample with the planarizing film 3.5 μm in thickness were all in the order of around 1E-6A/m^2, and sufficient insulation has been confirmed. Although the insulation depends on the thickness of the planarizing film, with film thickness over about 3 μm, insulation is secured regardless of the type of stainless steel foil, coating method, and with or without undercoating film.

Outgas from the film and the generated moisture in particular are anticipated to deteriorate electronics devices. To estimate the deterioration due to moisture, a method of measuring the shrinkage rate of the light emitting area of an OLED device at its edge has been developed.[3] At the stage of encapsulating with glass an OLED device with the light emitting area of 2 mm square fabricated on a glass substrate, samples as shown in **Fig. 7** were prepared. Two samples were encapsulated with the inserted chips of planarized stainless steel foil, and another one as a reference sample was encapsulated without the insertion of the chip. Two planarized stainless steel foil

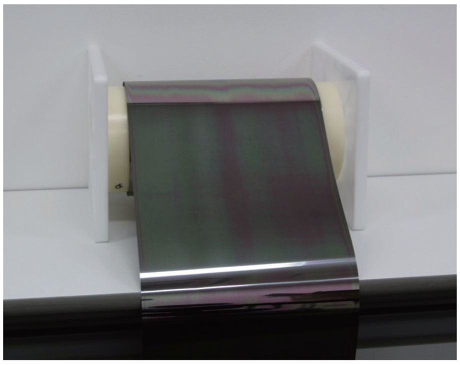

Fig. 4 Planarized stainless steel foil roll with the width of 300 mm

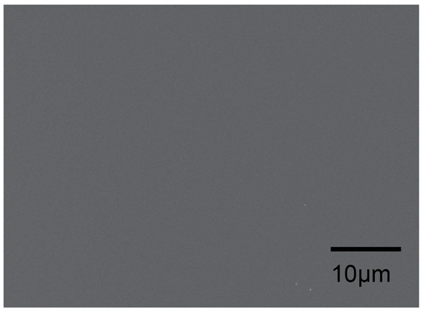

Fig. 5 SEM photograph of NSSC190SB after planarization

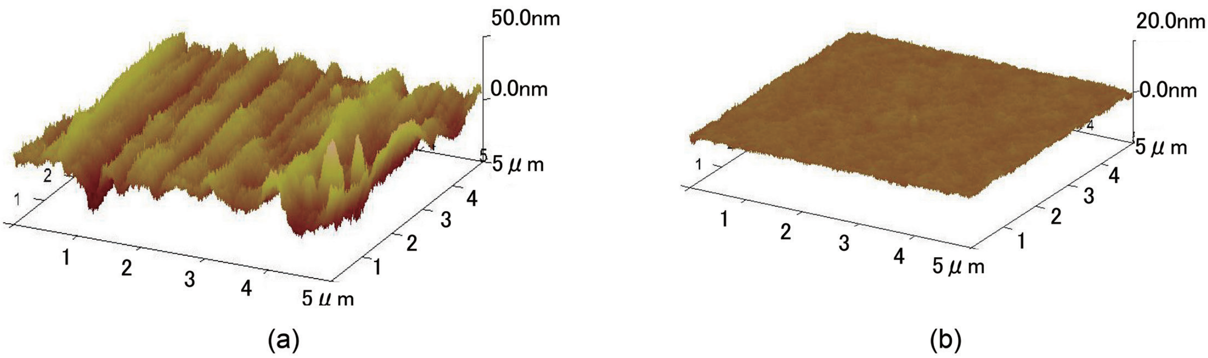

Fig. 6 AFM images of NSSC190SB
(a) Before and (b) After planarization

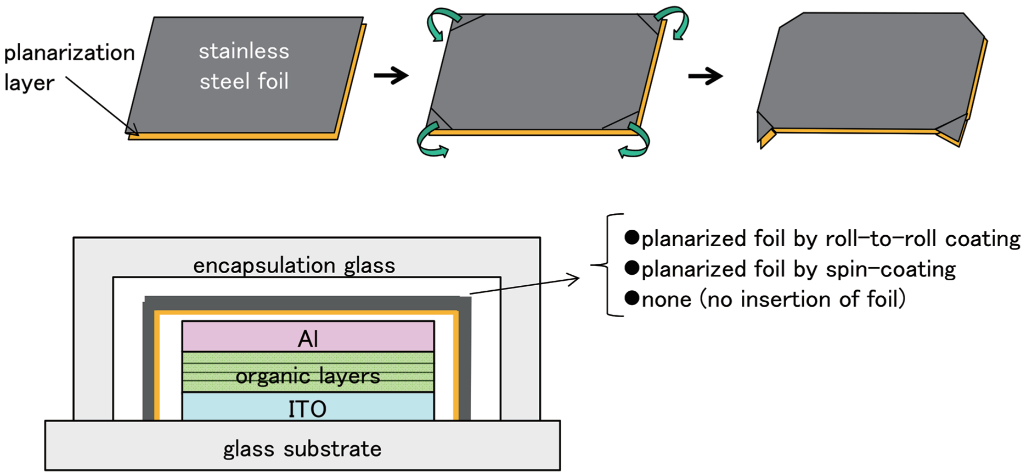

Fig. 7 Sample preparation method for evaluating out gas

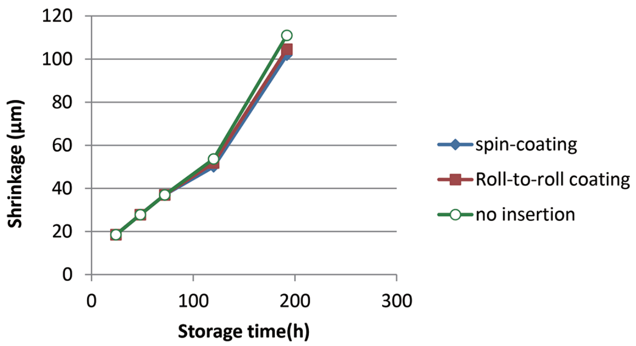

Fig. 8 Shrinkage rate of light emitting area

chips, one spin-coated and another coated by the roll to roll method, were washed by water, then treated with UV ozone for 6 minutes at 120°C, and then inserted for capsulation, respectively. The water washing and the UV ozone treatment condition is one of the typical conditions for fabricating devices on planarized stainless steel foils. The OLED device was stored at 85°C and the shrinkage width of the light emitting area on the Al electrode side was examined at a constant time interval.

As shown in **Fig. 8**, no difference in the rate of shrinkage of the light emitting area is observed among the devices inserted with the spin-coated planarized stainless steel foil chip, inserted with the one coated by the roll to roll method, and the one without the planarized stainless steel foil chip. The planarized stainless steel foil coated by the roll to roll method and the spin-coated one have the same degree of outgas rate, and they are also the same as that of the reference sample without insertion thereof. This indicates that, when fabricating OLED devices after washing and treating planarized stainless steel foils with UV ozone, the possibility of the outgas of either of the spin-coated stainless steel foil or of the roll-coated stainless steel foil exerting harmful effects on devices is low.

4. Trial Fabrication of OLED Device

A stainless steel foil planarized by the spin-coating method was plastered to a glass substrate via a slightly adhesive sheet and rinsed, and the patterning of the lower electrode of an OLED device and the deposition of organic layers thereon were conducted in the same process as the one applied to the fabrication on a glass substrate. The schematic process of the fabricating OLED device is shown in **Fig. 9**. IZO (indium zinc oxide) (10 nm)/Ag alloy (100 nm)/IZO (10 nm) was deposited by sputter-deposition to form the lower electrode. Then a photoresist was coated, photographically exposed, and the patterning of the photoresist was conducted by alkaline development. The lower electrode was masked by the patterned photoresist and etched with a mixed acid. The photoresist was removed with an organic alkali and the lower electrode with a desired pattern was obtained.

On the lower electrode, a plurality of organic layers including an emitting layer, and the upper electrode of Ag were coated by vapor deposition. After being vacuum-laminated with a flexible encapsulating film, the planarized stainless steel foil was peeled off from the glass substrate. As the organic layers were thin and placed between the planarized stainless steel foil and the encapsulating film, this device was flexible. **Figure 10** shows a photograph of the OLED device glued onto a cylinder 80 mm in diameter and lit under the curved state. No defects were observed on the light-emitting area and the OLED device exhibited excellent light emission.

Through this trial fabrication, it was verified that the planarized stainless steel foil can be processed trouble free through photolithography and the etching process, and can be the substrate for fabricating flexible devices. As the flexible substrate consisted of the

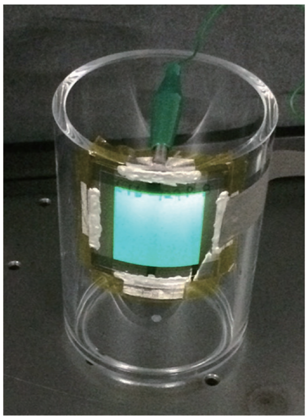

Fig. 10 Photograph of flexible OLED device (light emitting area: 32 mm square)

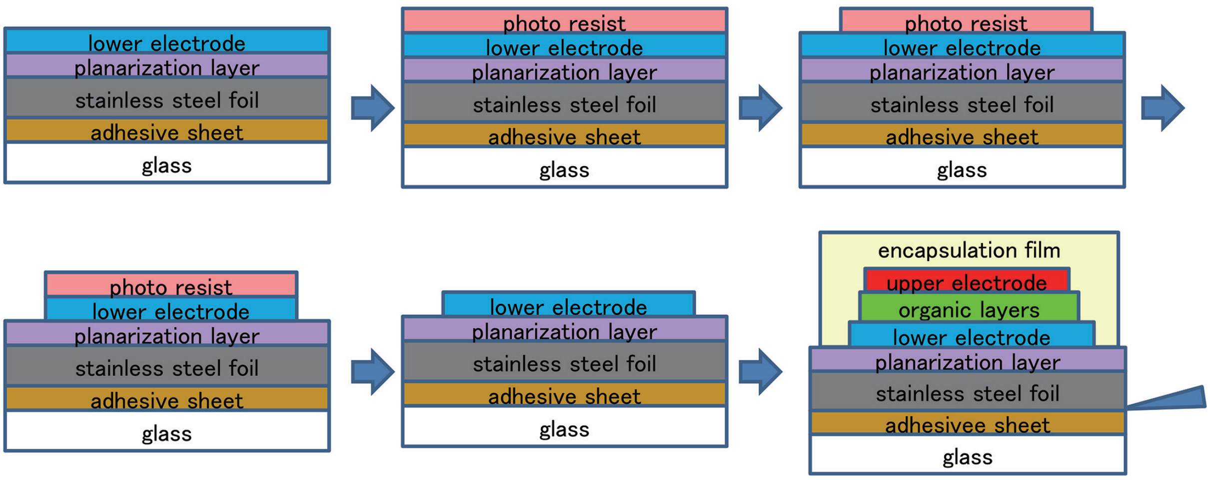

Fig. 9 Fabrication process of flexible OLED device

stainless steel foil combined with the planarizing film of the siloxane network, both excellent in chemical resistance, high chemical resistance is considered to have been exhibited. Additionally, the organic groups modifying the siloxane network provide the planarizing film with flexibility, and are considered to contribute to the fabrication of excellent flexible OELD devices.

5. Study on Trial Fabrication of Device by Roll to Roll Method

5.1 Trial fabrication of roll of substrate provided with lower electrode

By using the roll to roll deposition equipment of Kobe Steel, Ltd., sputter deposition of Ag (100 nm)/ITO (indium tin oxide) (20 nm) was applied thoroughly to a planarized stainless steel foil roll 300 mm wide.

Figure 11 shows the outline of the equipment. A planarized stainless steel foil roll is uncoiled and Ag and ITO are deposited continuously on the stainless steel foil on the rotating drum, and coiled to a roll. Input electrical power, the roll transfer speed and the drum temperature were controlled to suppress the deformation of the stainless steel foil caused due to the heat generated by the sputter deposition. On the stainless steel foil with continuously deposited Ag and ITO, an etching paste was screen-printed by the roll to roll screen printer of Seria Engineering, Inc., and then heat-treated. Unnecessary parts were washed off with water by the roll to roll cleaning equipment of FEBACS Co., Ltd. and a roll of planarized stainless steel foil with a patterned lower electrode was obtained. All the three roll to roll equipment types used are owned by the Yamagata University Innovation Center for Organic Electronics. **Figure 12** shows a photograph of the roll with the lower electrode that is deposited by this method. The width of the stainless steel foil is 300 mm.

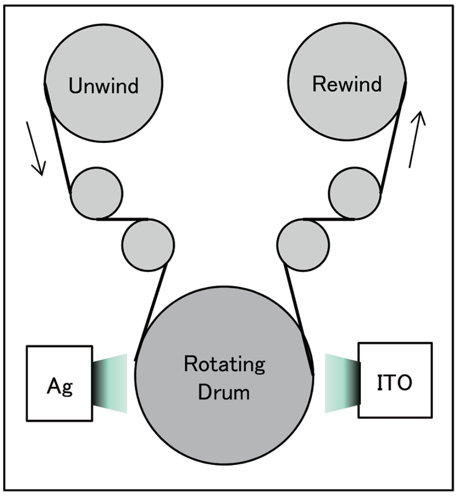

Fig. 11 Roll-to-roll deposition equipment

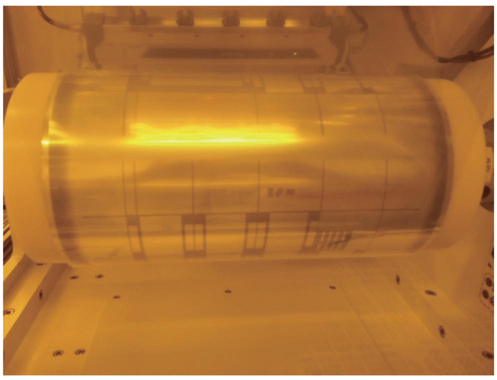

Fig. 12 Planarized stainless steel foil roll with lower electrode (width of the roll: 300 mm)

In future, fabrication of OLED devices by the roll to roll method using a roll with the lower electrode deposited in this way will become possible. It is also possible to fabricate a device on a sheet properly cut-out from a roll and glued to a supporting substrate by the same process as that currently applied to the device on the glass substrate as stated in the above section.

5.2 Trial fabrication of OLED device by roll to roll method

The Fraunhofer Institute for Organic Electronics, Electron Beam and Plasma Technology FEP owns the equipment and the technologies for fabricating OLED devices on various flexible substrates by the roll to roll method.[4)] The Fraunhofer Institute has also succeeded in fabricating an OLED device on a planarized stainless steel foil as shown in **Fig. 13**. Although problems like non-uniformity in light emission exist, the success suggests its feasibility as a flexible substrate.

6. Conclusion

A planarized stainless steel foil has been developed by coating the surface of a stainless steel foil with a film consisting of the siloxane network modified with organic groups. This film provides planarization and electrical insulation onto the surface of a stainless steel foil without impairing the heat resistance and the chemical resistance of the stainless steel foil. The coating solution used for forming the film is designed so as to allow drying and curing within a short period of time, and not only the planarized stainless steel foil in the form of the sheet coated by the spin coating method, but also the planarized stainless steel foil in the form of a roll coated by the roll to roll method have also been obtained.

Applicability of the planarized stainless steel foil to a flexible substrate was examined through the trial fabrication of an OELD device. On a planarized stainless steel foil sheet, a lower electrode of the OELD device has been successfully produced by the photolithography and the etching process used in fabricating a thin film device on a glass substrate. Organic layers were deposited thereon, laminated by an encapsulating film, and the flexible OELD device could be lit.

A roll of planarized stainless steel foil provided with a patterned lower electrode thereon by the roll to roll method was produced.

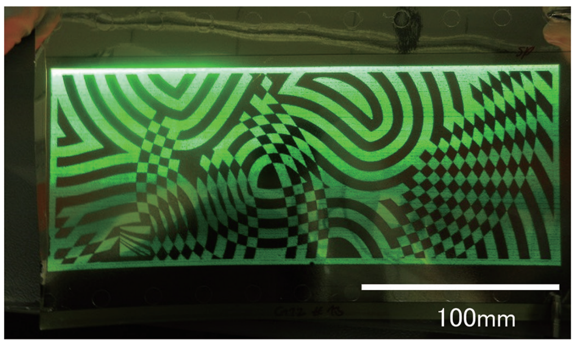

Fig. 13 Photograph of OLED device fabricated by roll-to-roll process

Furthermore, although insufficient in uniformity on the light emission area, the trial fabrication of an OELD device by the roll to roll method was successful.

The results of the trial fabrication have proven that the planarized stainless steel foil is a prospective material as a flexible device substrate for OELD devices, displays, solar batteries and so forth. In the field of flexible devices, to promote practical applications, aggressive technical developments both in the material and fabrication process are in progress. We are determined to continue to promote developments so that the planarized stainless steel foils are recognized as a flexible substrate.

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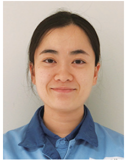

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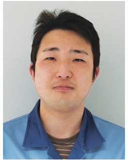

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