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Fabrication and evaluation of oxygen and humidity penetration prevention film

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The plastic sheet is used as the substrate of the flexible organic electroluminescence device (OELD). Though oxygen and humidity penetrate through the plastic sheet and damage the organic light-emitting layer, the life span and the luminescence of the OELD decrease. In this study, SiO_2 thin film was fabricated by the sol-gel method that decreases oxygen and the humidity that penetrate through the plastic substrate. The poly(allylaminehydrochloride) (PAH) / Poly(acrylicacid) (PAA) buffer layer fabricated by layer-by-layer sequential adsorption process was found to increase the adhesiveness between the plastic substrate and SiO_2 penetration prevention coating film, and to prevent abruption. Polyethyleneoxide (PEO) or methyltriethoxysilane (MTES) was mixed into the SiO_2 thin film using tetramethoxysilane (TEOS) to prevent the crack. The coating film mixed organic substance alleviate the force derive from the thermal expansion of the plastic substrate by heating treatment. The surface sol-gel method was applied to bridge the pore of coating film, and enhance oxygen humidity prevention. There was no abruption and crack on the fabricated using MTES, and showed oxygen and humidity penetration prevention.

Key words: sol-gel layer-by-layer sequential adsorption process, organic EL device, penetration prevention film

1. INTRODUCTION

The sol-gel method that uses hydrolysis and polycondensation reaction of metal-alkoxide is useful in the way that low temperature synthesis, coat a large substrate, and so on. [1,2,3,4] The surface sol-gel method that separated hydrolysis and polycondensation reaction makes it possible that growth in increments of one molecule, and control nano order film growth.

OELD have many advantages, low voltage drive, light weight, and flexible [5,6,7]. Since OELD is thin, flexible device can be fabricated on the plastic substrate. However, oxygen and humidity penetrate through the substrate, and damage the organic luminescence layer. Therefore the penetrated gases invite undesirable affect such as dark spot, life span and luminescence decrease.

In this study, the SiO_2 penetration prevention coating film was fabricated on the plastic substrate (PET film) by sol-gel method. The PET film and coating film were incompatible, therefore abruption occurred. In order to increase adhesion properties and prevent abruption, polyelectrolyte layer-by-layer sequential adsorption process was applied [8,9]. At the same time, the crack derived the difference of the thermal expansion was occurred. To prevent the , cracking, PEO and MTES was added into TEOS solution. The existence of PEO or MTES award coating film to alleviation against the force of the thermal expansion. The surface sol-gel method was performed to enhance penetration prevention.

The surface of the coating film was observed by scanning electron microscope and atomic force microscope. And the oxygen and humidity penetration was measured.

2. EXPERIMENTAL DETAIL

A structural formula of substance is shown in Fig.1. TEOS, TMOS, MTES was purchased from Shinetsu Silicone. Poly(allylaminehydrochloride) (mol. Wt. 70,000), and poly(acrylicacid) (mol. wt. 90.000) were purchased from Polyscience and Aldrich respectively. Polyethyleneoxide (mol. Wt. 6,000) was purchased by Wako.

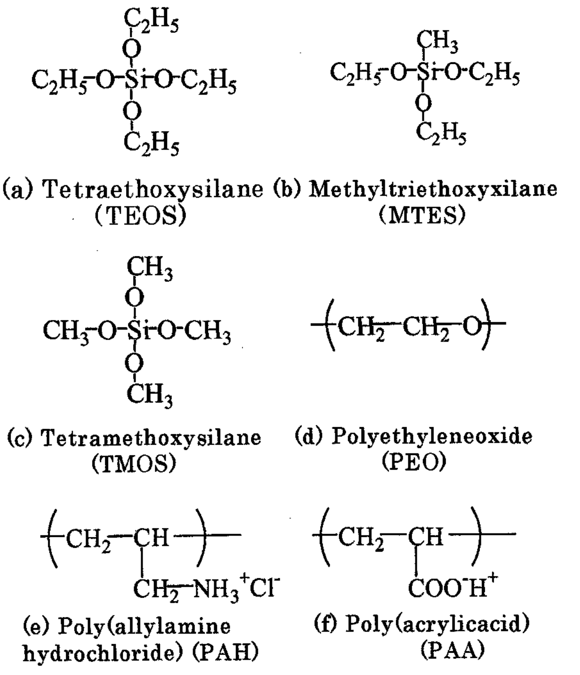


Fig.1 A structural formula

2.1 Substrate preparation

The PET film was used as the substrate. PET substrate was cleaned by ozone for 2 hours. In order to improve the adhesiveness of between the PET and the coating film by sol-gel method, pretreatment by the polyelectrolyte layer-by-layer sequential adsorption process was carried out and PAH/PAA buffer layer was fabricated.

As shown in Fig.2, the layer-by-layer sequential adsorption is the method that the polymer film was deposited by electrostatic attraction during the immersion of the substrate into a negative charged polymer (polycation) and a positive charged polymer (polyanion) alternately.

PAH (ph3.5、10^{-2} M) and PAA (ph3.5、10^{-2} M) were used as polycation and polyanion respectively. The dipping procedures consisted of 8 steps; PAH solution 180 sec, water rinse 60 sec three times each 60 sec, PAA solution 180 sec, water rinse each 60 sec three times. These procedures were executed 4cycle by using the automatic dipping machine (NIPPON LASER & ELECTRONICS), which controlled the dipping time with a personal computer. At the same time, PAH/PAA absorption was monitored by the quarts crystal microbalance (QCM) method. The top of buffer layer was PAA. Afterward the substrate was thermal treatment at 150℃ for 3 hours under vacuum.

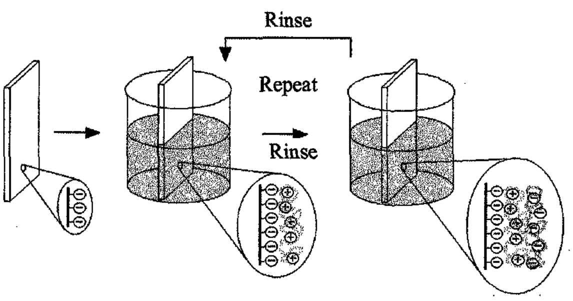


Fig2. Schematic illustration of the polyelectrolyte layer-by-layer sequential adsorption process

2.2 Fabrication of coating film by sol-gel method

Metal-oxide (SiO_2, TiO_2, Al_2O_3 etc.) is obtained from the sol-gel method make use of hydrolysis and polycondensation of metal-alkoxide. And metal-alkoxide film was easily fabricated by combining with diping method or spin-casting process.

Hydrolysis ;

$$\text{-M-O-R} + H_2O \rightarrow \text{-M-OH} + \text{ROH}$$

Polycondensation ;

$$\text{-M-OH} + \text{HO-M-} \rightarrow \text{-M-O-M-} + H_2O$$

$$\text{-M-OH} + \text{R-O-M-} \rightarrow \text{-M-O-M-} + \text{ROH}$$

As shown in Fig.3, by the surface sol-gel method that separated hydrolysis and polycondensation, metal-oxide grows in increments of metal-alkoxide molecules.

The SiO_2 penetration prevention coating film was fabricated by sol-gel method using TEOS solution introduced PEO or MTES, and pore of coating film was bridged by surface sol-gel method to enhance penetration protection.

First of all, following molar rate three kinds of solution was prepared.

(1). TEOS : C_2H_5OH : H_2O : HCl
 = 1 : 6.81 : 11 : 0. 07
(2). PEO mixed to the solution (1)
(3). MTES mixed to the solution (2)

To preventing the cracking, PEO or MTES was mixed into solution. The prepared solution was stirred for 24 hours.

These solution were spin-cast onto pretreated PET substrate at 1500rpm at relative humidity 45%, and thermal treatment at 150℃ for 3 hours. Afterward, substrate was performed surface sol-gel method by immersed into TEOS methanol solution (50vol.%) for 3 min, methanol rinse 1 min, water 3min, methanol rinse, and thermal treatment at 150℃ for 3 hours. By this means the coating film was fabricated.

The surface of the coating film was observed by the scanning electron microscope (SEM, PHILIPS XL30) and atomic force microscope (AFM, nanoscope Ⅲa, Digital Instruments). The thickness of the coating film was measured by the DekTak.

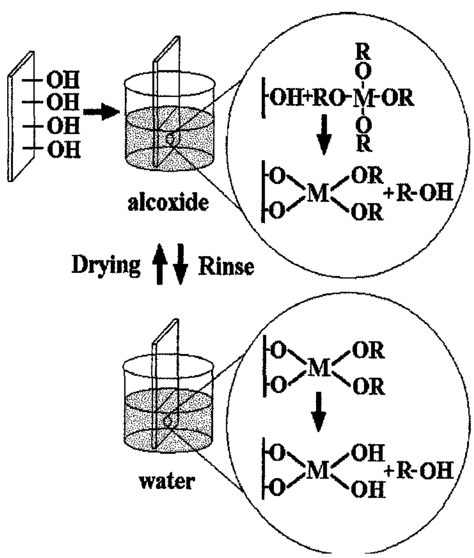


Fig3. Schematic illustration of the surface sol-gel method

2.3 Oxygen・humidity penetration measurement

Oxygen and humidity penetration prevention of the fabricated coating film was measured by the system shown in fig.4. By the way, this measurement was carried out about film (3) because of best quality of three kinds of solution. The mixed gas was oxygen concentration 99.4%, absolute humidity 18.7g/m^3. Initial condition of measuring room (fig.4) was oxygen 20.9%, absolute humidity approximately 8g/m^3,and temperature was kept at approximately 20℃. For the sake of comparison, a slide glass was measured.

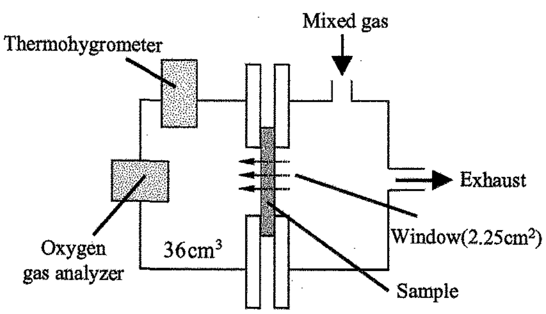


Fig.4 The penetration measurement system

3.RESULT AND DISCUSSION

3.1 Effect of PAH/PAA buffer layer

Frequency shift of QCM was shown in Fig.5. Frequency shift showed liner increase, the growth of PAH/PAA was confirmed. The effect of PAH/PAA buffer layer was shown in Fig.6. These shown coating films were fabricated by solution (3). The coating film without buffer layer (Fig.6(a)) has abruption derived from the poor of adhesion between the PET substrate and coating film On the other hand the coating film with buffer layer (Fig.6(b)), abruption was not

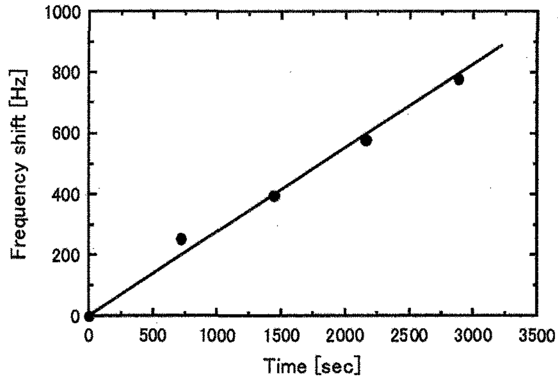
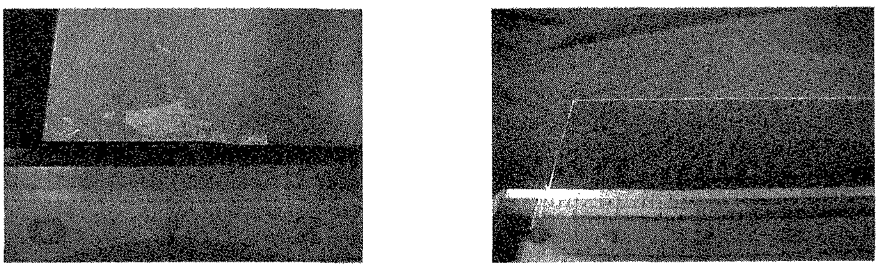
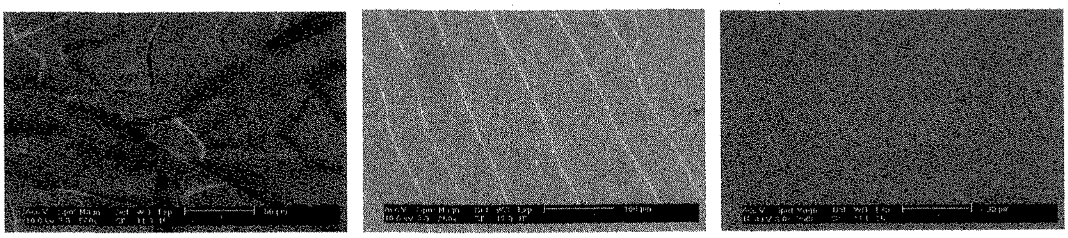


Fig.5 QCM characteristic



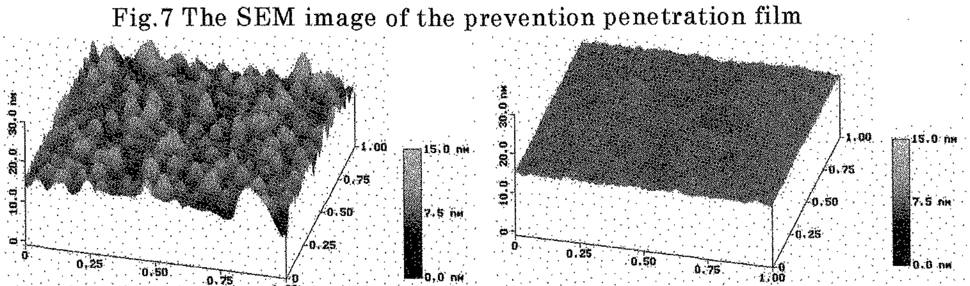
(a) Without PAH/PAA (b) With PAA/PAH

Fig6. The prevention abruption effect of PAH/PAA buffer layer



(a) Film(1) (TEOS) (b) Film(2) (PEO mixed) (c) Film (3) (MTES mixed)

Fig.7 The SEM image of the prevention penetration film



(a) PET substrate (b) Prevention penetration film derived from MTES solution

Fig.8 The AFM image of the substrate and the penetration film observed. carboxyl group of PAA and hydroxyl group of silicone-alkoxide bonded as CO-O-Si.

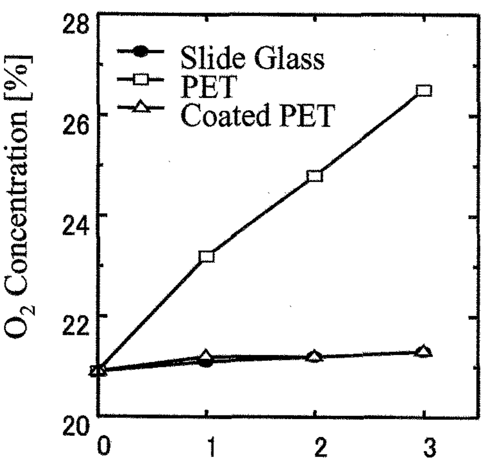
3.2 Quarity of the coating film

The thickness of all coating film was 450nm.

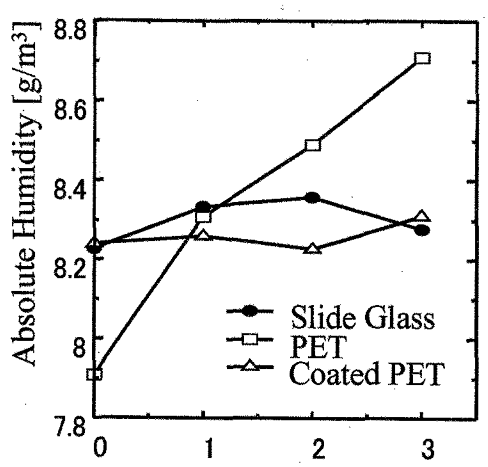
SEM image of the coating film were showed in Fig.7. The film (1) (Fig.7(a)) was irresistible against the force of thermal expansion of the plastic substrate, so crack occurred. The film (2) (Fig.7(b)) constricted occurrence of crack in some degree, however not enough. The film (3) (Fig.7(c)) has no crack and flat surface.

The film (1) consists of -Si-O- network, and this network has no degree of freedom. Therefore it is thought that coating film could not alleviate the force, crack occurred. It is thought that the film (2) consists of -Si-O- network and PEG writhen structure. PEG can absorb force of thermal expansion of substrate, however, -Si-O- network and PEG do not bond directly, so strength of the film is lack something. In consequence, the crack was generated. The -Si-O- network of film (3) has methyl group derived form MTES. This methyl group is terminal of -Si-O- network, and dose not bond other Si. Since the film has flexibility at this terminal, it is thought that the force of heat expansion of the substrate can be alleviated and occurrence of a crack is prevented.

AFM image of the film (3) was shown Fig.8. The height of unevenness of the PET film is about 15nm (Fig.8(a)), on the other hand the coating film of that is 3nm(Fig.8(b)). The coating film bridged the substrate unevenness, and is very flat surface. That is favorable for OELD on coating film.



(a) Oxygen Penetration



(b)Humidity Penetration

Fig.9 The preventively of oxygen and humidity penetration of coating film

3.3 Penetration prevention of the coating film

The result of oxygen and humidity penetration measurement was shown in Fig.9. As against the PET substrate (□), the shift of oxygen and humidity of the coated PET (△) was less. For the sake of comparison, that of slide glass (●) was also shown. The fabricated coating film had oxygen and humidity penetration prevention form fig.8. This result suggested that the pore of coating film is very low.

4.CONCLUSION

The SiO_2 Oxygen and humidity penetration prevention coating film on the PET substrate was fabricated by means of sol-gel method. The polyelectrolyte layer-by-layer sequential adsorption method was applied to fabricate the buffer layer that increases adhesion between the substrate and coating film. It was attempted that prevent occurrence of crack by PEO or MTES mixed into TEOS solution. The coating film mixed MTES was crack free and very flat. The fabricated coating film showed oxygen and humidity penetration prevention.

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