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Enhanced Permeability Property of Silicon Oxide Thin Films Deposited by Facing Target Sputtering System for OLED Application

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ABSTRACT
The thin silicon oxide (SiO_x) films were deposited by using the facing target sputtering(FTS) apparatus for the thin film passivation application of OLEDs. The deposition system was investigated under various process conditions such as the array of cathode magnets, oxygen concentration[$O_2/(Ar + O_2)$] during deposition, distance between two targets, and working pressure. The optimum conditions for FTS apparatus for the deposition of thin silicon oxide films are as follows: distances between target and substrate (T-S) as well as two targets (T-T) are 90 mm and 120 mm, respectively. Dense structured SiO_x film with maximum deposition rate is obtained under a gas pressure of 2 mTorr with an oxygen concentration of 3.3%. Under the optimum conditions, SiO_x thin films were grown with deposition rate of 25 nm/min by rf-power of 4.5 W/cm^2, which was remarkably enhanced as compared with a deposition rate(3–4 nm/min) of conventional sputtering system. The SiO_x thin film showed a very low water vapor transmission rate(WVTR) less than 3×10^{-2} $g/m^2/day$ compared to the conventional sputtering system.

KEYWORDS
SiO_x thin film; rf-sputtering; facing target sputtering; OLED passivation

Introduction

Transparent gas barrier coatings such as silicon oxide(SiO_x) and aluminum nitride(AlN_x) thin films on polymers have received much attention in industries for pharmaceutical, food, and beverage packing applications [1–2]. Another application of this technology, namely, for passivation of organic light-emitting display(OLED), also require a good barrier against inward permeation of water and oxygen[3–6] vapor to the OLEDs. Both vapors can oxidize the metalic cathode, which reduce the electron injection in the OLED and thereby drastically decreases its performance. Barrier films have been prepared by using the sputtering and plasma enhanced chemical vapor deposition (PECVD) techniques [6].

The conventional sputtering apparatus has a system in which the target and the substrate are facing each other, thus particles with high energy, such as γ-electrons, neutral argon atoms,

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and negative oxygen ions, collide with the substrate. When the gas barrier films are deposited on the organic layer of OLEDs by using a conventional sputtering technique, the bombardment of energetic particles during the sputtering process can damage the underlying organic layers [9]. Therefore, the three-polar sputtering and the magnetron sputtering techniques are widely used since they give excellent thin-film deposition and possess characteristics such as simplicity, high deposition rate, broad deposition area, and fewer shortcomings than the old bipolar sputtering technique [7–8].

In order to get a good passivation layer for the OLED devices, we fabicated a facing target sputtering(FTS) apparatus which can deposit a uniform SiO_x thin-films with low damage and have high sputtering yield by forming a high density plasma in the electrical discharge space [10–13].

Although the FTS apparatus has many advantages for the growth of various thin films, the process control characteristics are not well known. We examined the optimum conditions of the FTS apparatus for the deposition of the silicon oxide films for application to thin film passivation for OLEDs by assessing the growth rate, optical, structural characteristics, uniformity, and composition of thin films deposited.

The reulting SiO_x thin films were studied from the view point of the surface uniformity, the films density, and the rate of permeation of water vapor while comparing with those SiO_x thin films prepared by the conventional sputtering system.

Experimental details

The FTS apparatus used for the experiment is shown in Fig. 1(a). Two circular targets with a diameter of 3 inch are located horizontally facing with each other. Nd alloy permanent magnets of 4700 Gauss for plasma-confining magnetic field were mounted to the back of the targets, which was adjusted by variation of the distance between both targets (T-T). In order to control the heat of the system caused by the ion bombardment of the cathode, we used cooling water.

Process characteristics of the FTS apparatus are investigated under various sputtering conditions, such as arrays of the cathode magnet, variations of the distance between both targets(T-T), and the distance between the target and the substrate (T-S), as shown in Fig. 1(b). Slide glass substrates with a size of 25 × 25 mm^2 were cleaned sequentially by using distilled water, acetone, and alcohol, after which they were placed vertically to between the facing targets, as shown in Fig. 1(b).

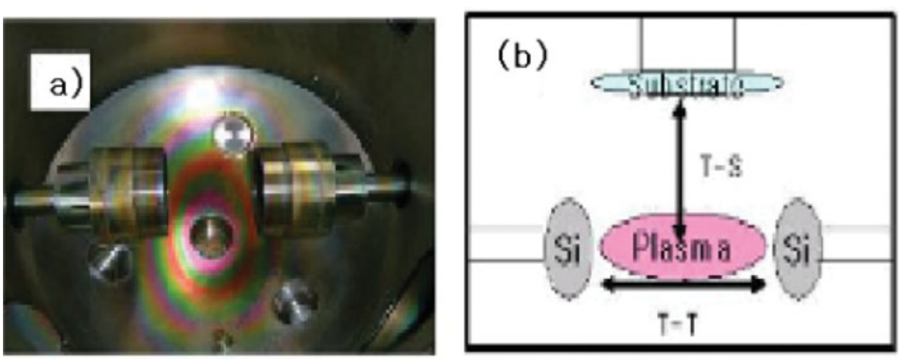

Figure 1. (a) Picture of the facing 3-inch circular cathods in the chamber of the FTS apparatus. (b) Schematic diagram for the distance between two targets (T-T) and the distance between the target and the substrate (T-S).

On the other hand, the SiO_x films were coated on the polyethylene naphthalate(PEN) substrates with a size of $50 \times 50\ mm^2$ for measurement a water vapor transmission rate (WVTR).

The depositions were carried out under various gas pressures by using two Si targets (99.99%) with a diameter of 3 inch. In a deposition of SiO_x films, as an active gas and a reactive gas a mixed $Ar + O_2$ gas was introduced during deposition, where oxygen concentration $[O_2/(Ar + O_2)]$ varied from 1% to 10%.

To find the optimum conditions of our FTS apparatus for the growth of the silicon oxide films, SiO_x films were prepared under various working pressures form 1 mTorr to 10 mTorr, and facings between two targets, but the distance between T-S is fixed by 90 mm for all depositions.

The substrate temperature changes as a function of the deposition time were measured by using thermal tape(TMC Co.) to estimate the temperature at which deposition free of thermal damage occurred. The film thickness was measured by using α-step profiler. The optical transmission spectra of the deposited films were measured in the wavelength range from 200 nm to 900 nm by using a UV-Vis spectrophotometer(Shimadzu Co). The surface morphology and cross section images were observed by using Atomic Forced Microscope(AFM: Digital Instrument Co.) and Scanning electron microscope(SEM: Hitachi Co.), respectively. The composition ratios were analyzed by using Energy Disperse x-ray spectroscope (EDS: JEOL Co.). In order to estimate the water vapor permeability of SiO_x films, their water vapor transmission rate (WVTR) were measured for 36 hour under a relative humidity of 100% and N_2 gas flow rate of 9.8 sccm by using Permatran W3/31(MOCON Co.).

Results and discussion

Three types of arrays of permanent magnets, such as a reverse array(NSN:NSN), a forward array(NSN:SNS), and two polar forward arrays(NNN:SSS), are used in the FTS system, as shown in Fig. 2. The plasma shapes formed for each arrangement are also represented on the down sides of the figures. In the case of the reverse array, where the same magnet poles

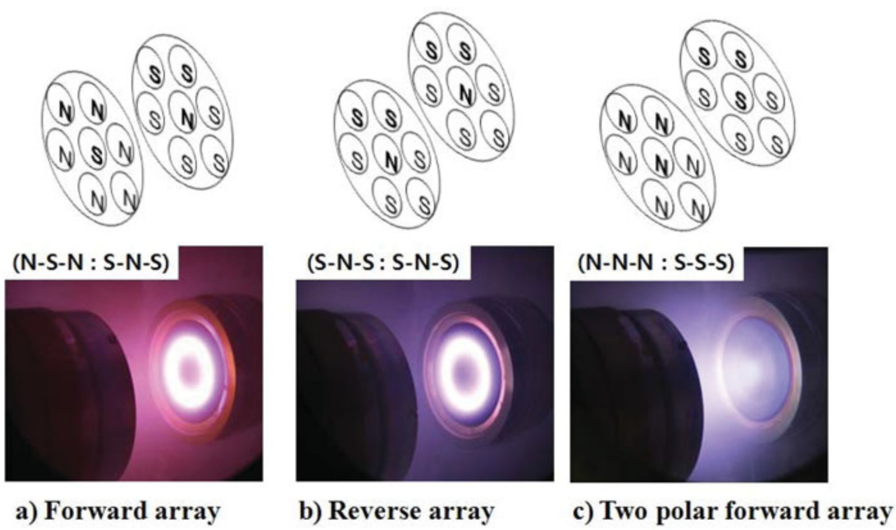

Figure 2. (a) Forward array (NSN : SNS), (b) reverse array (SNS : SNS), and (c) one polar forward array (NNN: SSS) in the arrangements of permanent magnets facing each other and the plasma shapes corresponding to each array.

are facing each other, as shown Fig. 2(a), a symmetrical plasma between the both targets is formed; however, since the plasma is dispersed in all direction, the plasma density is found to be weakend as compared with that formed in the forward array of Fig. 2(b).

Since the dispersed plasma moves toward the substrate, the high-energy ions in the plasma are expected to seriously damage the substrate. it was practically confirmed that high-quality films are unlikely to be obtained when using in a reverse array of magnet Furthermore, in the reverse arrangement, the substrate temperature is also expected to be increased due to the bombardment of high-energy particles. In our experiment, it was practically confirmed that high-quality films are unlikely to be obtained when using in a reverse array of magnet due to the dispersion of the γ-electrons generated between the facing target, and that the substrate temperature increased up to 120 °C during deposition for 20 minute, may be caused by bombardment of energetic particles. In contrast, high deposition rate and low temperature sputtering can be achieved in the forward array where the opposite magnetic poles are facing each other, because a symmetrical plasma without any dispersion is formed between the facing targets. High-deposition-rate and low-temperature sputtering can be achieved. In this case, the substrate is located away from the plasma, thin-films with a plasma-free state can be deposited.

Furthermore, ionization of the gas at a low working pressure is promoted, resulting in a high density plasma due to the round-screw-moving high-speed γ-electrons between the arrays of the two targets.

Additionally, the FTS system inserts a plasma-arresting magnetic field in a direction parallel to the center axis of both targets; therefore, more γ-electrons are restrained in the forward array as compared with the reverse array and the two polar forward array.

Subsequently, more γ-electrons generate more secondary electrons, which in turn increase the ionization of particles within the plasma, thus resulting in a decrease in the discharge voltage.

On the other hand, in the case of Fig. 2(c), the thin-film is hardly formed because the plasma is dispersed in all directions, in particular, the plasma density formed in the erosion area on the target is the most weak among the three types of arrangement. The weakened plasma density affects deposition rate of the sputtered films.

Fig. 3(a) shows the film thickness as a function of the facing between T-T for SiO_2 films prepared under different arrangements of the cathode magnets, where T-S was 90 mm and an applied rf-power and an introduced oxygen concentration during deposition were 200 W and 10%, respectively.

It is shown that the deposition rate is larger in the order of the forward array, the reverse array, and the two polar forward array. Thus it was found that the plasma density greatly affect the film growth in the sputtering process.

The maximum deposition rates are obtained when the facing between T-T is 120 mm for the forward and reverse arrays. While in the two polar forward array, since the deposition ratio is too low, the thin-film is hardly formed.

In view of the above results for further investigation, all SiO_x films were prepared using the forward array configuration.

In Fig. 3(b), we shows the deposition rate of SiO_2 films as a function of working pressure, where T-S and T-T were 90 mm and 120 mm, respectively and the applied rf-power and the introduced oxygen concentration during deposition were 200 W and 3.3%, respectively.

The deposition rate is the largest at working pressure of 2 mtorr over 2 mtorr, the deposition rate remarkably decreases with increasing working pressure. As the working pressure increases, the adatoms sputtered from the target are more likely to collide with the sputter gas

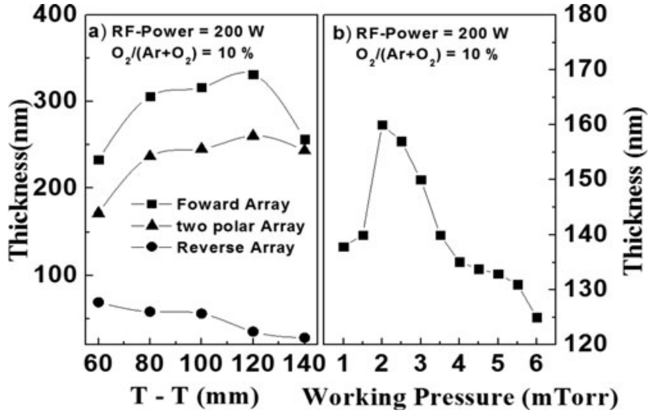

Figure 3. (a) Film thickness as a function of the facing between T-T for SiO_2 films prepared under different arrangements of the cathode magnets and (b) the deposition rate of SiO_2 films as a function of working pressure.

molecules, resulting in the reduction in the number of adatom that reach the substrate, thus inducing the decrease of deposition rate.

Figure 4(a) shows the film thickness as a function of oxygen concentration introduced during deposition for SiO_x films prepared under a working pressure of 2 mTorr, where T-T and rf-power were 120 mm and 200 W, respectively.

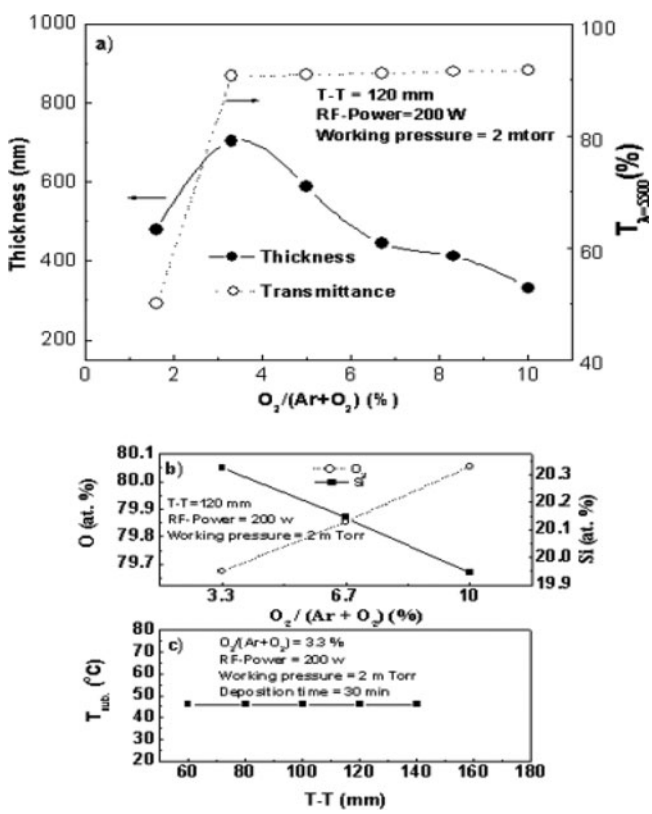

Figure 4. (a) The deposition rate, (b) the film thickness as functions of oxygen concentration introduced during deposition for SiO_2 films prepared under working pressure of 2 mtorr and (c) the substrate temperature as a function of distance between facing two target.

To evaluate their transparency, the optical transmittances at a specific wavelength of 550 nm, $T_{\lambda=550}$ are also shown. The films deposited at oxygen concentration less than 2% shows a very poor transmittance below 50%, while the films prepared at oxygen concentration more than 3.3% are very transparent with the optical transmittance over 90%, where the optical transmittance somewhat increases with increasing oxygen concentration. However, The maximum thickness is obtained at oxygen concentration of 3.3% and over 3.3%, the thickness decreases with increasing oxygen concentration.

Therefore, it can be explained that the optical transmittance increase with oxygen concentration, as shown in Fig. 4(a) is caused by decrease of the film thickness.

In Fig. 4(b), we show the ratio of compositions consisting the film as a function of oxygen concentration introduced during deposition for SiO_x films prepared under a gas pressure of 2 mTorr, where T-T and applied rf-power were 120 mm and 200 W, respectively. the oxygen content contained into the films gradually increases with increasing oxygen concentration introduced during deposition, while Si component gradually decreases with increasing oxygen concentration, which means that our FTS is a reliable equipment for the growth of oxide films, where the compositional ratios of films were measured by using an EDS.

In Fig. 4(c), the substrate temperature after the deposition of 200 nm thick film (deposition time of 30 min) is plotted as a function of the T-T distance. It is shown that the substrate temperature is maintained at a temperature below 60°C regardless of T-T distance. This result guarantees that the FTS system can achieve a low temperature deposition free of the thermal damage caused by the plasma.

Figure 5(a) shows AFM images of 200 nm thick SiO_x films prepared by (a) the FTS and (b) the conventional sputtering system (CSS). The root-mean-square surface roughness of the FTS-SiO_x film was 1.34 nm, which was much less than that of the CSS-SiO_x film (3.21 nm). On the other hand, it was further observed from the field-emission scanning electron microscopy(FE-SEM) images(Fig 5 c and d) for the cross-sections of both films that the

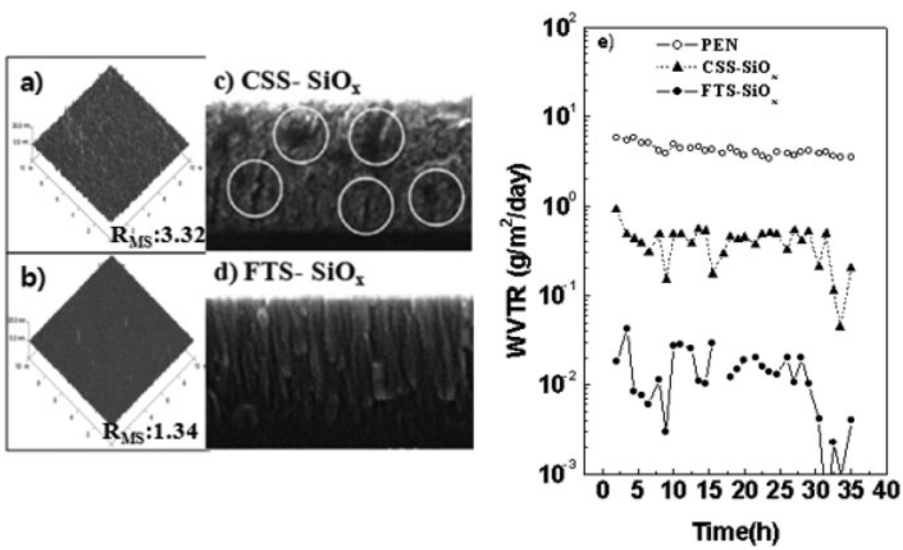

Figure 5. (a) - (d) The film thickness at center and edge of the substrate and (e) thickness uniformity as functions of working pressure for films deposited on glass substrates with a size of 25 × 25 cm^2 under various gas pressures with an oxygen concentration of 3.3%.

CSS-SiO_x film possesses a random structure with relatively large pores (cylindrical and spherical shapes) (see the circles), whereas the FTS - SiO_x film consists of a columnar structure with densely packed narrow pores.

Such a structural difference between the FTS-films and the CSS-films may be attributed to the differences in the ion-flux energy, the deposition rate, and the adatom mobility and the resulting surface diffusion during the film growth. Since the conventional sputter apparatus has a system of the target and the substrate facing with each other, the particles with high energy such as γ-electrons, neutral Ar particles, and negative oxygen ions collide with the substrate. It is generally considered that the bombardment of the growing surface with energetic particles suppresses the surface migration of sputtered adatoms during the conventional sputtering process, which results in low-density films with rough surface. In contrast, FTS apparatus is a plasma-free sputter method in which the substrate is located apart from plasma, which enhances the surface migration of the adatoms in the sputtering process, thus inducing a smooth surface and a higher packing density.

Since these pores become the main pathway of the water vapor permeation, such a structural difference will also affect the ability of the water permeability.

For measurement of WVTR, both films were prepared on PEN substrates and their permeability was compared with each other.

The Fig. 5(e) shows the WVTR graph of 200-nm-thick SiO_x films deposited on PEN substrates with a size of 50×50 mm^2 by using the FTS system and the CSS. For comparison, that of bare PEN is also shown. The bare PEN shows WVTR of 1–3 g/m^2/day. However, The PEN coated with FTS - SiO_2 film shows WVTR less than 3×10^{-2} g/m^2/day, which was much less than that of the PEN coated with CSS-SiO_2 that shows WVTR more than 10^{-1} g/m^2/day.

We, therefore, suggest that the FTS is an excellent thin-film-deposition system that possesses characteristics such as a high deposition rate, a broad deposition area, a low-temperature deposition, and a capability to fabricate high-quality silicon oxide films with a dense micro-structure.

Conclusion

In this study, the silicon oxide thin films were deposited on the PEN films by using the FTS apparatus for application to thin film passivation system in OLED devices. The optimum conditions for FTS apparatus for the deposition of thin silicon oxide films were investigated by varying the process conditions such as the array of cathode magnets, oxygen concentration $[O_2/(Ar + O_2)]$ during deposition, spacing between two targets, and working pressure.

The optimum conditions for the deposition of the silicon oxide thin film using FTS apparatus are as follows: T-S and T-T are 90 mm and 120 mm, respectively and the maximum deposition rate is obtained under a gas pressure of 2 mTorr with an oxygen concentration of 3.3%. Under this conditions, the SiO_x thin film was grown with a deposition rate of 25 nm/min at rf-power of 4.5W/cm^2, which was remarkably enhanced as compared with a deposition rate(3–4 nm/min) of the conventional sputtering system. It was also found that SiO_x film grown by FTS had more dense microstructure than the film grown by the conventional sputtering, which could result in a better protection against the permeation of water and oxygen vapor in the for thin film passivation layers of OLEDs.

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