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High Temperature Tolerant Barrier Film with Stacking Barrier Layers by Sputtering and ALD

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ABSTRACT

High gas barrier layers were developed by alternated depositions of Si_3N_4 layer by sputtering and Al_2O_3 layer by ALD on simultaneously biaxially stretched polyetheretherketone (PEEK) film with high temperature tolerance.

The developed stacking layers with Si_3N_4 and Al_2O_3 achieved high gas barrier ability with WVTR of the order of 10^{-5}g/m^2/day.

1 INTRODUCTION

High gas barrier films are key components for flexible organic electronics devices such as OLEDs (organic light emitting diodes), OPVs (Organic Photovoltaics), OTFTs (Organic Thin Film Transistors), etc., which are inducing drastic changes in various applications in not only displays and lighting but also fields of healthcare, wearable, robots, etc. In these devices, high gas barrier ability is essentially required. For example, flexible OLEDs are said to require WVTR (Water Vapor Transmission Rate) values with the order of 10^{-5}g/m^2/day or lower.

The most common methods for achieving high gas barrier property seems to be PE-CVD (Plasma Enhanced Chemical Vapor Deposition) [1-3], while various wet processes have also been studied [4-6]. However, there are issues in productions using PE-CVDs because PE-CVD equipment are expensive, and the process speed is not so fast.

On the other hand, one of alternative methods with excellent productivity seems to be sputtering. However, it is well known that the film quality fabricated by sputtering is not as good as those by PE-CVD because of poor density, presence of defect and pinholes, etc. To solve this issue, the required thickness of the sputtering barrier layers tends to be thick, tending to induce mechanical stress and to reduce the productivity.

Based on such background, this study developed stacking barrier layers, using sputtering and ALD (Atomic Layer Deposition). It is well known that ALDs give excellent defect coverage [7]. Therefore, if ALD layers can cover defects and pinhole of layers deposited by sputtering, the combination of sputtering and ALD can be an alternative candidate instead of PE-CVDs.

In addition, this study utilized EXPEEK® films [8] fabricated by KURABO INDUSTRIES LTD. EXPEEK is a simultaneously biaxially stretched PEEK film. Fig. 1 shows the fundamental moiety of PEEK. By applying biaxially stretching treatment, EXPEEK film has such advantages as high temperature tolerance with Tg of about 300℃, excellent solvent tolerance, excellent transparency, low thermal shrinkage, etc., which are often required in OLED production processes. In particular, the high temperature tolerance is a superior merit because actual fabrication processes of OLEDs tend to require higher temperature than 200℃ for achieving suitable performance and lifetime, while such common flexible films as PET (Polyethylene Terephthalate), PEN (Polyethylene Naphthalate), etc. have lower temperature tolerance than 200℃.

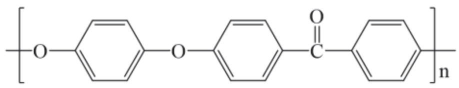


Fig. 1 Fundamental moiety of PEEK.

In this study, plural stacking layers with Si_3N_4 by sputtering and Al_2O_3 by ALD layers were deposited on high temperature tolerant EXPEEK films, achieving high gas barrier ability with WVTR of the order of 10^{-5}g/m^2/day. In addition, flexible OLED devices were fabricated on the developed high gas barrier EXPEEK films.

2 EXPERIMENT

2.1 EXPEEK film

The flexible film used in this study is EXPEEK with the film thickness of 50μm as shown in Fig. 2.

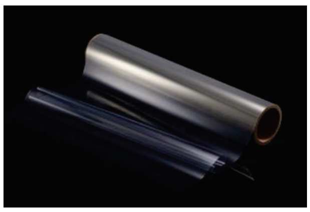


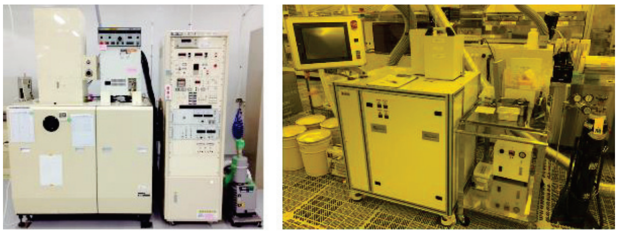
Fig. 2. EXPEEK of KURABO INDUSTRIES LTD.

2.2 Sputtering and ALD

The sputtering and ALD equipment used in this study are shown in Fig. 3.

The sputtering equipment is Tokki's model SPK-503, which is a typical flat plate type magnetron sputtering system. The deposition direction is facedown. The target is Si_3N_4. RF power is 500W. The vacuum level is 0.2~0.3Pa. The flow gas is Ar with the flow rate of 1-3 sccm. The substrate temperature under sputtering is not controlled.

The ALD equipment is made by SUGA CO., Ltd., in which the deposition direction is facedown. The precursor is trimethylaluminum (TMA). The oxidizing agent is ozone (O_3). The carrier gas is N_2. The substrate temperature is 100°C. For depositing Al_2O_3 layer with the thickness of 45nm, 550 cycles with the unit cycle of 20 sec. is required.



Sputtering ALD

Fig. 3. The equipment for depositing barrier layers.

2.3 Ca corrosion method

The barrier properties were evaluated by Ca corrosion method [9,10]. Examples of the devices are shown in Fig. 4, accompanying with the schematic illustration of the cross section. The deposited Ca layer is damaged by penetrations of water through the barrier layers under 40°C/90%RH condition as an accelerating evaluation as shown in Fig. 5. In each barrier layer, four samples were fabricated and evaluated for considering experimental error. When the increasing rate in the damaged area under a certain period is almost constant, WVTR values are calculated from the increasing rate of the damaged area with binarization modification.

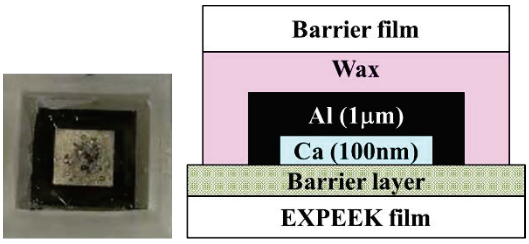


Fig. 4. An example of Ca corrosion device and the schematic illustration of the cross section.

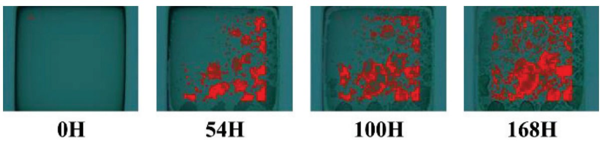


Fig. 5. Examples of degradation of Ca corrosion devices under 40°C/90%RH. The pictures are modified by binarization for calculating the ratio of damaged (red) and undamaged Ca areas.

3 RESULTS and DISCUSSUIN

3.1 Base Films

As base films this study uses EXPEEK films which are a biaxially stretched polyetheretherketone (PEEK) films. While surfaces of general films tend to be rough in roll-to-roll (R2R) mass-production of films, the surface of EXPEEK is flat because it has low aggregability and excellent surface slipperiness. It is noted that this feature gives rise to no issue that is induced by additional planarization layers for applying to OLEDs. Fig. 6 shows a SEM image of EXPEEK. It is obvious that the surface of EXPEEK is very smooth.

The EXPEEK films are cleaned by wet cleaning containing atomizing spray cleaning in the R2R line before depositing barrier layers.

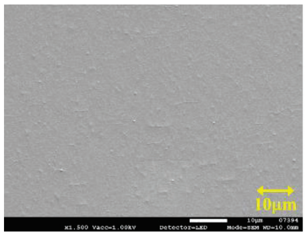


Fig. 6 SEM image of EXPEEK.

3.2 Single barrier layers by sputtering or ALD

Barrier abilities of single barrier layers on EXPEEK were investigated. Fig. 7 shows typical temporally changes of Ca devices of such single barrier layers as Si_3N_4 layers (100nm) by sputtering or Al_2O_3 layers (90nm) by ALD. Remarkable degradations of Ca were observed.

Fig. 8 shows WVTR values calculated from the temporal change of degradation of Ca. In each case, the results from four samples are plotted.

The WVTR values of single Si_3N_4 barrier layers with the thickness of 100nm deposited by sputtering are in order of 10^{-3}g/m^2/day, being still poor. This result suggests that such thin Si_3N_4 layer deposited by sputtering would possess many defects and pinholes as passes of gas penetration.

The WVTR values of single Al_2O_3 layers with the thickness of 90nm deposited by ALD are in order of 10^{-2}g/m^2/day, being worser than Si_3N_4 with the thickness of 100nm. This result implies that the barrier ability of Al_2O_3 with the thickness of 90nm deposited by ALD is not so excellent by itself.

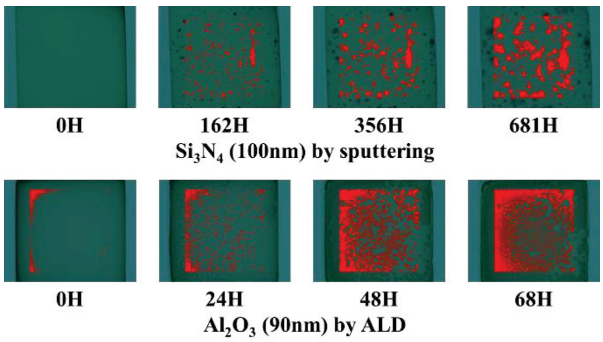


Fig. 7. Typical results of Ca corrosion tests of EXPEEK films with a single Si_3N_4 layer (100nm) by sputtering or a single Al_2O_3 layer (90nm) by ALD. The pictures are modified by binarization for calculating the ratio of damaged (red) and undamaged Ca areas. The results of only one sample are shown in each case.

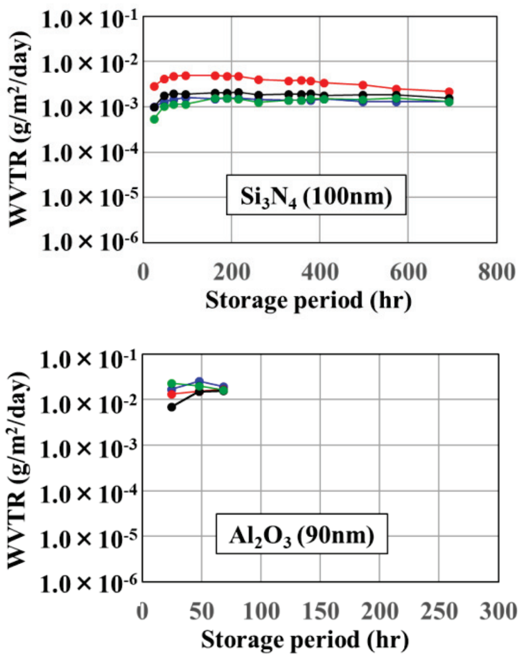


Fig. 8. WVTR values calculated by Ca corrosion tests of EXPEEK films with a single Si_3N_4 layer (100nm) by sputtering or a single Al_2O_3 layer (90nm) by ALD. The results from four samples are plotted in each case.

3.3 Stacking barrier layers of Si_3N_4 and Al_2O_3

In order to improve barrier properties, stacking barrier layers with the architectures of $Si_3N_4/Al_2O_3/Si_3N_4$ were investigated in two cases with different thickness.

Fig. 9 shows typical temporally changes of the Ca devices of stacking barrier layers of $Si_3N_4/Al_2O_3/Si_3N_4$. No serious degradation is visually observed.

The calculated WVTR values are shown in Fig. 10. Drastic improvement of barrier properties is obvious, comparing with the results of the single barrier layers. Both barrier layers of Si_3N_4(100nm)/Al_2O_3(90nm)/Si_3N_4(100nm) and Si_3N_4(50nm)/ Al_2O_3(45nm)/Si_3N_4(50nm) show WVTRs with the order of 10^{-5}g/m^2/day, which are applicable value for flexible OLEDs.

Further stacking barrier layers with five layers also shows good barrier ability as is shown in Fig. 11. However, it can be said that the effect of the increase in the number of layers is not so clear. Rather, two samples show WVTRs with the order of 10^{-4}g/m^2/day. From practical point of view, three alternative stacking layers would make compatibility of barrier property and productivity.

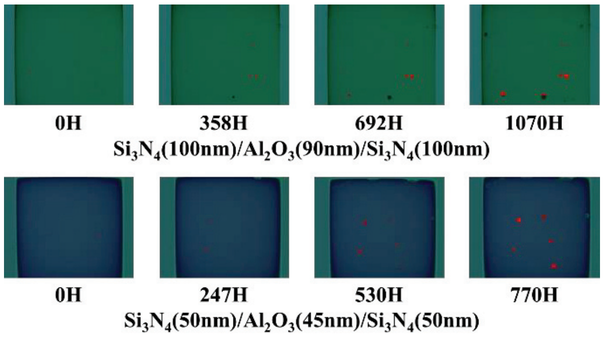


Fig. 9. Typical results of Ca corrosion tests of EXPEEK films with stacked $Si_3N_4/Al_2O_3/Si_3N_4$ layers. The pictures are modified by binarization for calculating the ratio of damaged (red) and undamaged Ca areas. The results of only one sample are shown in each case.

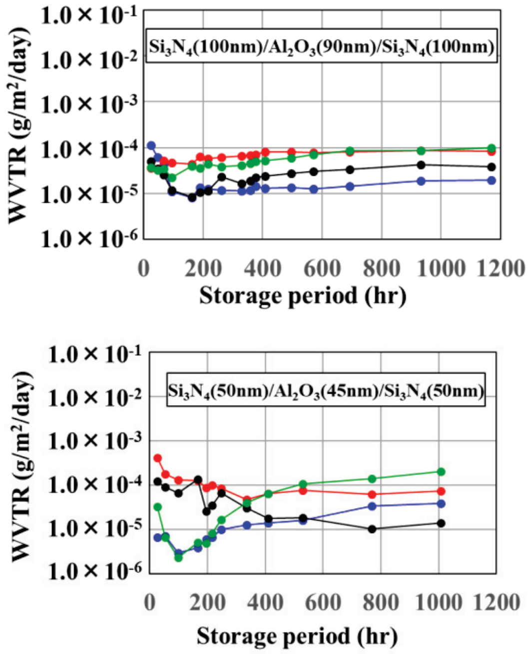


Fig. 10. WVTR values calculated by Ca corrosion tests of EXPEEK films with Si_3N_4(sputtering)/Al_2O_3(ALD)/ Si_3N_4(sputtering) architecture.

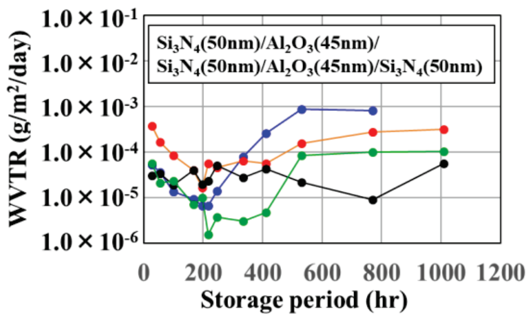


Fig. 11. WVTR values calculated by Ca corrosion tests of EXPEEK films with Si_3N_4(sputtering)/Al_2O_3(ALD)/ Si_3N_4(sputtering)/Al_2O_3(ALD)/ Si_3N_4(sputtering) architecture.

3.4 Flexible OLEDs on EXPEEK

The developed high gas barrier EXPEEK films with a Si_3N_4(100nm)/Al_2O_3(90nm)/Si_3N_4(100nm) stacking barrier layer were applied to flexible OLED devices. The device structure and the emitting picture are shown in Fig. 12. Flexible OLEDs were successfully fabricated with no serious problem.

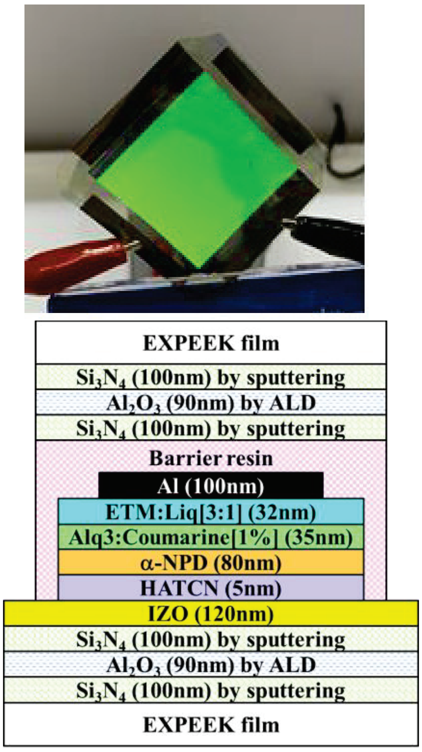


Fig. 12. Device structure and emission picture of flexible OLED fabricated on the developed high gas barrier EXPEEK film with high temperature tolerance. The substrate size is 50mm × 50mm. The emission area is 32mm × 32mm.

4 SUMMARY

High temperature tolerant barrier films were developed by depositing stacked barrier layers by sputtering and ALD on simultaneously biaxially stretched PEEK films. The barrier properties of investigated barrier layers are summarized in Fig. 13. The plural stacking layers with Si_3N_4 and Al_2O_3 layers achieved high gas barrier ability with WVTR values of the order of 10^{-5}g/m^2/day. Using the developed barrier films, flexible OLED devices were successfully fabricated.

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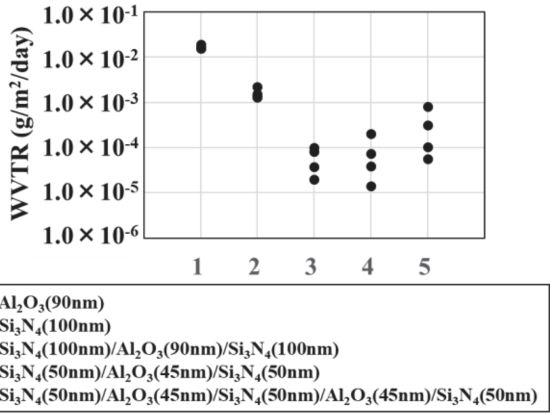

Fig. 13. Summary of the developed barrier layers on EXPEEK.

REFERENCES

[1] K. Taira, T. Furukawa, N. Kawamura, M. Koden, T. Takahashi, "High gas barrier film for OLED", Proc. IDW'17, FLXp1-8L (2017).

[2] K. Taira, T. Suzuki, W. Konno, H Chiba, H. Itoh, M. Koden, T. Takahashi, T. Furukawa, "Development of High Gas Barrier Film Using Novel Precursor by Roll to Roll PECVD", Proc. IDW'18, FLX2-4L (2018).

[3] T. Suzuki, W. Konno, K. Taira, H Chiba, H. Itoh, M. Koden, T. Takahashi, T. Furukawa, "High Gas Barrier Films with Heterogeneous Multilayer", Proc. IDW'18, FLXp1-10L (2018).

[4] T. Mori, Y. Gotou, C. Takemura, K. Hirabayashi, "Development of a Barrier Film for Flexible OLED Lighting", KONICA MINOLTA TECHNOLOGY REPORT, **11**, 83 (2014).

[5] Y. Suzuki, K. Nishijima, S. Naganawa, K. Nagamoto, T. Kondo, "Ultra-High Gas Barrier Films Based on a Few Barrier Layer Stack Fabricated by a Wet Coating and a Plasma Assisted Surface Modification", SID 2014 DIGEST, 6.4 (2014).

[6] M. Koden, T. Furukawa, T. Yuki, H. Kobayashi, H. Nakada, "Substrates and Non-ITO Electrodes for Flexible OLEDs", Proc. IDW/AD'16, FLX3-1 (2016).

[7] M. D. Groner, S. M. George, R. S. McLean, P. F. Carcia, "Gas diffusion barriers on polymers using Al_2O_3 atomic layer deposition", Appl. Phys. Lett., 88, 051907 (2006).

[8] JP-5847522B.

[9] G. Nisato, M. Kuilder, P. Bouten, L. Moro, O. Philips, N. Rutherford, "Thin Film Encapsulation for OLEDs: Evaluation of Multi-layer Barriers using the Ca Test", SID 2003 DIGEST, P-88 (2003).

[10] SEMI D78-1018 "Test Method of Water Vapor Barrier Property for Plastic Films with High Barrier for Electronic Devices".

[11] https://inoel.yz.yamagata-u.ac.jp/yu-flec/