Plasma-polymerized n-hexane and its utilization as multilayer moisture-barrier film with aluminum oxide

Kyu-Hyun Hwang, Seung-Woo Seo, Eun Jung, Heeyeop Chae, and Sung Min Cho†

School of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Korea
(*Received 16 August 2013 • accepted 13 December 2013*)

Abstract−Organic-inorganic multilayer structures were prepared for a moisture barrier. As the organic polymer and inorganic layers, plasma-polymerized n-hexane and aluminum-oxide layers were utilized, respectively. The plasma polymerization of n-hexane was confirmed by the appearance of carbon double bonds in the produced polymer layer. The organic and inorganic layers were prepared sequentially in vacuum, and the repeated growth sequence produced the multilayer structures. The organic-inorganic multilayer structures show about 35% better moisture-barrier property than those obtained from individual organic and inorganic layers.

Keywords: Moisture Barrier, Plasma Polymer, Hexane, Multilayer, Atomic Layer Deposition

INTRODUCTION

Since organic devices such as organic light-emitting diodes (OLEDs) and organic photovoltaic (OPV) cells degrade easily by the attack of oxidative species such as moisture and oxygen, they require moisture barriers to protect themselves from the species for stable operation. For the moisture barrier, aluminum oxide (Al_2O_3) grown by atomic layer deposition (ALD) has been the most widely utilized material for the purpose [1-3]. The ALD is known to produce highly dense Al_2O_3 thin films at low temperatures, so that they are suitable for applications in organic electronics. The Al_2O_3 films are often multilayered with organic layers to enhance the moisture-barrier and mechanical properties [4-6]. Defects in the Al_2O_3 layer are inevitable, through which moisture can permeate. To reduce the moisture permeation through defects, organic-inorganic multilayer structures are effective since the structures make the moisture permeation path more tortuous and in turn taking much longer time [6,7].

It is desirable to deposit organic layers in vacuum such as the ALD for Al_2O_3 layers, in order for the two deposition processes to be carried out in a chamber. Otherwise, substrates should travel between separate deposition chambers many times, taking a long time to produce the multilayer structures on. There are a few methods to obtain polymer layers in vacuum: Parylene-polymer deposition by pyrolysis of xylene [8], initiated chemical vapor deposition (i-CVD) utilizing an initiator [9], and plasma polymerization [10-16]. Among them, the simplest method for depositing organic polymer layers in vacuum is plasma polymerization in that it does not require an initiator or a high process temperature. Plasma polymerization is nothing but a gas-phase radical polymerization process utilizing radicals generated in plasma. For the plasma polymerization, there have been a number of previous studies utilizing different organic monomer sources, which include n-hexane [10,11], hexamethyldisiloxane [12, 13], furan [14], and fluorocarbon compounds [15,16].

In this study, we report the utilization of a plasma polymer derived from n-hexane for organic-inorganic multilayer structures with inorganic ALD-grown Al_2O_3 layers. The plasma polymerization of n-hexane was confirmed by measuring Fourier-transform infrared (FTIR) spectroscopy for both n-hexane monomer and plasma-polymerized n-hexane. To monitor the sequential growth of the organic-inorganic multilayer structures, the changes in the contact angle of water were measured on the surfaces produced after each deposition process. The measured cyclic change in the water contact angle confirmed the growth of multilayer structures. To show the effect of the plasma polymer in the multilayer structures, the moisture-barrier property was directly measured by an electrical calcium (Ca) test for an organic layer, inorganic layers, and an organic-inorganic multilayer structure.

EXPERIMENTAL

Polyethylene naphthalate (PEN) films were used as substrates. Plasma polymerization was carried out in an inductively-coupled plasma reactor which was a coiled tube chamber 60 cm long and 8 cm in diameter. The reactor was evacuated down to 1.0×10^{-3} torr prior to the supply of organic monomers. As the monomer, n-hexane was used with argon carrier gas. The flow rates of monomer and argon gas were set to 10 and 30 sccm, respectively, and the radio-frequency input powers were 50, 100 and 150 W for the generation of plasma. The polymerization of n-hexane was confirmed by measuring FTIR transmittance spectra before and after the plasma polymerization of the monomer.

To deposit Al_2O_3 by ALD process, an in-house designed and built deposition equipment was utilized, with two precursors of trimethyl aluminum (TMA) and water, which were vaporized at 5 °C and room temperature, respectively. The base pressure of the deposition chamber was 6.0×10^{-3} torr and all the depositions were at 80 °C. A growth cycle of Al_2O_3 was TMA injection for 2 s, purging with argon for 10 s, water injection for 2 s, and purging for 10 s. One cycle growth produces 1.1 Å-thick Al_2O_3 on average, at the temperature.

To prepare organic-inorganic multilayer structures, the n-hexane

†To whom correspondence should be addressed.
E-mail: sungmcho@skku.edu

plasma polymer and Al_2O_3 were sequentially grown in a connected deposition system. After the deposition of the plasma polymer, the hydrophobic surface was treated with oxygen plasma to leave hydroxyl groups for the subsequent growth of Al_2O_3 on the surface. By measuring the contact angle of water on each surface after the sequential deposition steps, we confirmed the growth of the multilayer structures.

The moisture barrier property was measured by an electrical Ca test. For the test, a Ca layer was deposited on a glass substrate such that the Ca was connected to two aluminum electrical leads. The Ca layer was then covered with a coated barrier layer on a PEN film, the edges of which were sealed with a UV-curable epoxy resin (UV resin ZNR 5570 from Nagase & Co., LTD). During the Ca test measurement, the electrical conductance through the Ca layer decreased as the Ca was oxidized with water vapor transmitted through the barrier film. All the measurements were carried out in an accelerated condition of 85 °C and 85% relative humidity. Detailed description of the electrical Ca test can be found in the literature [17].

RESULTS AND DISCUSSION

Due to the simple molecular structure of n-hexane, the FTIR transmittance spectrum exhibits a few well-defined characteristic peaks as shown in Fig. 1. Detailed assignments of all the peaks associated with the n-hexane polymerization to the corresponding func-
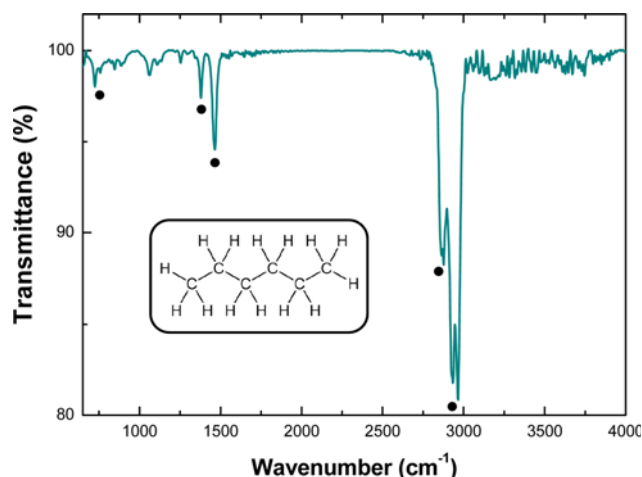
tional groups are listed in Table 1. Among many functional groups in the table, only a few peaks of C-H stretching in methyl and methylene groups, C-H bending and -CH₂- rocking in methylene were found in n-hexane monomer. After the plasma polymerization of n-hexane in argon plasma at 150 W, the FTIR spectrum of the resulting polymer showed new peaks representing the polymerization as shown in Fig. 2. With the generation of the new peaks around 1,600-1,680 cm^{-1}, the relative intensity of C-H stretching peaks around 2,865-2,970 cm^{-1} was reduced significantly. The new peaks were assigned to C=C bond stretching vibrations, which were produced as the result of the plasma polymerization. The plasma polymerization occurs at lower plasma powers. As shown in Fig. 3, the C=C characteristic peaks were present after the plasma polymerization at 50 and 100 W. The intensity ratio of the C-H bending peaks around 1,450 cm^{-1} and C=C stretching around 1,650 cm^{-1} was found close to 1.15 for both 50 and 100 W plasma polymerizations. For the plasma polymer obtained at 150 W, however, the ratio increased to 1.47, which showed higher degree of polymerization of n-hexane. The plasma

Fig. 1. FTIR spectra of n-hexane monomer.

Table 1. Peak positions and assignments for n-hexane monomers and the plasma-polymerized films

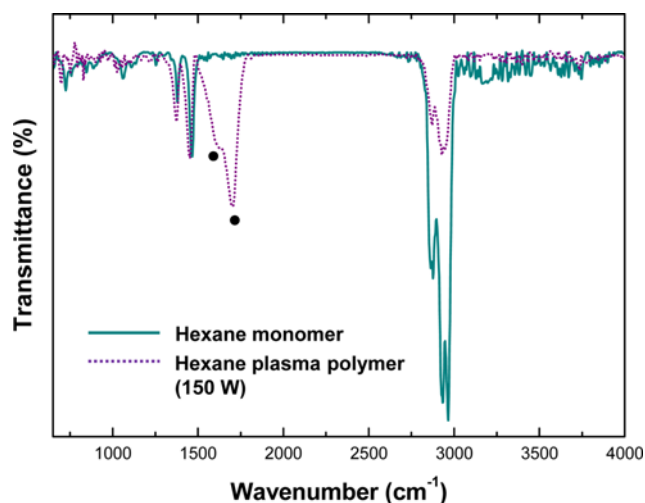| Group frequency (cm^{-1})	Functional groups assigned
2970, 2880	C-H asym./sym. stretch in methyl (-CH₃)
2935, 2865	C-H asym./sym. stretch in methylene (-CH₂-)
1620-1680	C=C stretch in alkenyl
1600	Conjugated C=C
1450-1470, 1370-1380	C-H asym./sym. bend in methyl
1445-1485	C-H bend in methylene
1410-1420	C-H in-plane bend in vinyl
1300-1320	C-H in-plane bend in vinylidene
720-750	-(CH₂)ₙ- rock in methylene

Fig. 2. FTIR spectra of n-hexane monomer and the plasma polymer layer formed at the plasma power of 150 W.
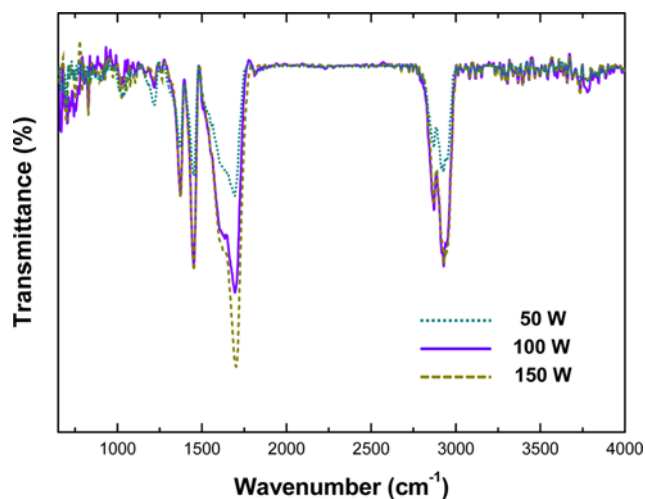

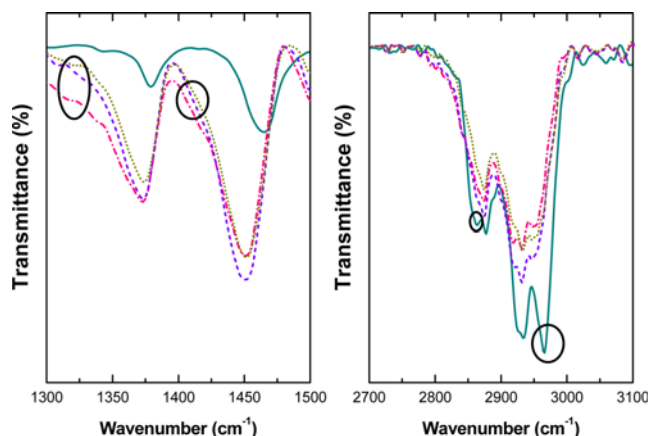Fig. 3. FTIR spectra of plasma-polymerized n-hexane layers grown at different RF power.

Fig. 4. FTIR spectra of n-hexane monomer (solid line) and the plasma polymer layers (dotted and dashed lines).
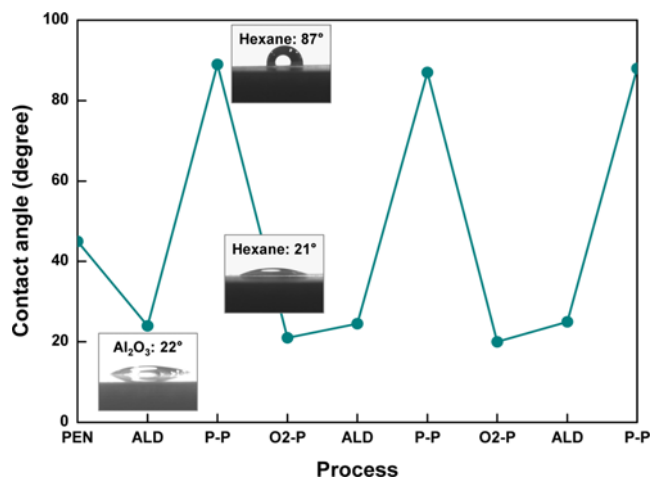

Fig. 5. A cyclic change of water contact angle for the preparation of organic-inorganic multilayer structures. The ALD, P-P, and O2-P denote atomic layer deposition, plasma polymerization, and oxygen plasma treatment, respectively.

polymerization can also be evidenced by investigating the changes of characteristic peaks for C-H bending in vinyl group (1,410-1,420 cm^{-1}) and vinylidene group (1,300-1,320 cm^{-1}). As shown in Fig. 4(a), the shoulders in the above wavelength ranges seem to show the generation of C=C bonds in the dotted and dashed spectra which represent the plasma-polymerized layers produced at different plasma powers. In Fig. 4(b), the intensity reduction of a peak at 2,970 cm^{-1} in the plasma-polymerized layers is due to the C=C bond formation at the methyl groups of n-hexane molecules during the plasma polymerization.

The growth rate of plasma polymer derived from n-hexane was found 21 nm/min at the plasma power of 50 W. The thickness increased linearly with the growth time. The optical transmittance of 1 μm-thick plasma polymer was above 80% in the wavelength range of 450-800 nm. The root-mean-square surface roughness of the plasma polymer was 2.1 nm.

To form an organic-inorganic multilayer structure with the plasma polymer and ALD-grown Al$_2$O$_3$, a thin Al$_2$O$_3$ layer was first grown by ALD process on a bare PEN substrate at 80 °C. The contact angle of water on the PEN surface was 44° and it dropped to 22° on the surface produced by the ALD of Al$_2$O$_3$. After the plasma polymerization of n-hexane, the produced surface on the Al$_2$O$_3$ exhibited a high contact angle of 87°. For the continued ALD growth of Al$_2$O$_3$ on the hydrophobic plasma-polymer surface, an oxygen plasma surface treatment was performed on the surface to form hydroxyl groups. After the treatment the contact angle was significantly reduced to 21°. On the highly hydrophilic surface, Al$_2$O$_3$ layer was grown successfully by ALD process and confirmed with the restored contact angle of 22°. From then on, repeated growth cycles were carried out to form organic-inorganic multilayer structure of the plasma polymer and ALD Al$_2$O$_3$ layers. The periodic change of water contact angle is shown in Fig. 5, along with the contact angle measurements.

When a pattern of Ca was covered with a bare PEN film in an electrical Ca test, the electrical conductance of Ca was reduced by half in 40 min at the measurement condition of 85 °C and 85% RH. With the PEN film deposited with 1 μm-thick plasma polymer, however, the reduction time increased to 120 min, which means that the plasma polymer itself is a good moisture-barrier material. On the other hand, PEN films deposited with 5 and 10 nm-thick Al$_2$O$_3$

layers grown by ALD lasted 5 and 10 h, respectively. The ALD-grown Al$_2$O$_3$ layer is known to have superior moisture-barrier property. The moisture-barrier property of 1 μm-thick plasma polymer is similar to that of only 2 nm-thick Al$_2$O$_3$ grown by ALD. When the plasma polymer and Al$_2$O$_3$ layers are multi-layered, the Al$_2$O$_3$ layer plays a major role in protecting moisture in the multilayer film. It is well known that an organic-inorganic multilayer structure shows better moisture-barrier property than a single layer of the same summed thickness of inorganic layers, which are the major moisture barrier. It is because the multilayer structure demands longer tortuous paths of moisture to permeate through the structure, providing a fixed density of defects exists in Al$_2$O$_3$ barrier sub-layers.

A multilayer barrier structure of 10 dyad of Al$_2$O$_3$ (1 nm)/plasma polymer (20 nm) lasted 13.5 h for the half reduction of the conduc-
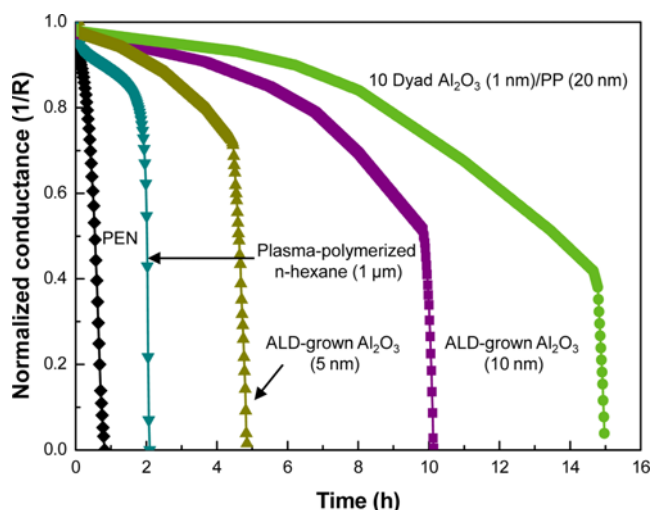

Fig. 6. Electrical calcium test results of bare PEN film, plasma polymer layer, ALD-grown Al$_2$O$_3$ layers, and organic-inorganic multilayer on PEN film. All the measurement was done at 85 °C and 85% relative humidity.

tance, which was improved by about 35% compared with the 10 nm-thick Al_2O_3 layer. Even if we take the extra 200 nm-thick plasma-polymer into account, the improvement in the barrier property seems remarkable. This improvement is considered as the result of the formation of organic-inorganic multilayer structure.

CONCLUSIONS

Plasma polymerized n-hexane layers were utilized with ALD-grown Al_2O_3 layers to construct organic-inorganic multilayer structures for a moisture barrier. Since both the plasma polymer and Al_2O_3 layers were grown in vacuum, the organic and inorganic layers could be grown sequentially in a vacuum chamber to reduce long process time for the multilayer preparation. The preparation of organic-inorganic multilayer structure was confirmed by measuring a cyclic change of water contact angle during the repeated growth of the organic and inorganic layers. The organic-inorganic multilayer structures show better moisture-barrier properties than those obtained from individual organic and inorganic layers.

ACKNOWLEDGEMENT

REFERENCES

1. M. D. Groner, S. M. George, R. S. McLean and P. F. Carcia, *Appl. Phys. Lett.*, **88**, 051907 (2006).
2. P. F. Carcia, R. S. McLean, M. H. Reilly, M. D. Groner and S. M. George, *Appl. Phys. Lett.*, **89**, 031915 (2006).
3. P. F. Carcia, R. S. McLean and M. H. Reilly, *Appl. Phys. Lett.*, **97**, 221901 (2010).
4. B. D. Vogt, H.-J. Lee, V. M. Prabhu, D. M. DeLongchamp, E. K. Lin, W. Wu and S. K. Satija, *J. Appl. Phys.*, **97**, 114509 (2005).
5. S.-W. Seo, E. Jung, C. Lim, H. Chae and S. M. Cho, *Thin Solid Films*, **520**, 6690 (2012).
6. S.-W. Seo, H. Chae, S. J. Seo, H. K. Chung and S. M. Cho, *Appl. Phys. Lett.*, **102**, 161908 (2013).
7. J.-S. Park, H. Chae, H. K. Chung and S. I. Lee, *Semicond. Sci. Technol.*, **26**, 034001 (2011).
8. P. Kramer, A. K. Sharma, E. E. Hennecke and H. Yasuda, *J. Polym. Sci.*, **22**, 475 (1984).
9. G. Ozaydin-Ince, A. M. Coclite and K. K. Gleason, *Rep. Prog. Phys.*, **75**, 016501 (2012).
10. T. R. Gengenbach, Z. R. Vasic, R. C. Chatelier and H. J. Griesser, *J. Polym. Sci. A: Polym. Chem.*, **32**, 1399 (1994).
11. I.-S. Bae, C.-K. Jung, S.-J. Cho, Y.-H. Song and J.-H. Boo, *J. Alloys. Comp.*, **449**, 393 (2008).
12. J. Fang, H. Chen and X. Yu, *J. Appl. Polym. Sci.*, **80**, 1434 (2001).
13. L. Körner, A. Sonnenfeld, R. Heuberger, J. H. Waller, Y. Leterrier, J. A. E. Manson and P. R. von Rohr, *J. Phys. D: Appl. Phys.*, **43**, 115301 (2010).
14. A. Gok and L. Oksuz, *J. Macromol. Sci. A: Pure. Appl. Chem.*, **44**, 1095 (2007).
15. K. Kim, B.-J. Jeon and I. Jung, *Korean J. Chem. Eng.*, **17**, 33 (2000).
16. W.-I. Sohn, J.-K. Koo and S.-J. Oh, *Korean J. Chem. Eng.*, **17**, 678 (2000).
17. S.-W. Seo, E. Jung, H. Chae and S. M. Cho, *Org. Electron.*, **13**, 2436 (2012).