

Hybrid multilayer thin-film fabrication by atmospheric deposition process for enhancing the barrier performance

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Abstract In this paper, a multilayer barrier thin film, based on polyvinylidene difluoride (PVDF)–silicon dioxide (SiO₂), has been fabricated on a PET substrate through a novel method of joint fabrication techniques. The inorganic SiO₂ thin film was deposited using a roll-to-roll atmospheric atomic layer deposition system (R2R-AALD), while the organic PVDF layer was deposited on the surface of SiO₂ through the electrohydrodynamic atomization (EHDA) technique. The multilayer barrier thin films exhibited very good surface morphology, chemical composition, and optical properties. The obtained values for arithmetic surface roughness and water contact angle of the as-developed multilayer barrier thin film were 3.88 nm and 125°, respectively. The total thickness of the multilayer barrier thin film was 520 nm with a high optical transmittance value (85–90%). The water vapor transmission rate (WVTR) of the barrier thin film was $\sim 0.9 \times 10^{-2} \text{ g m}^{-2} \text{ day}^{-1}$. This combination of dual fabrication techniques (R2R-AALD and EHDA) for the development of multilayer barrier thin films is promising for gas barrier applications.

Keywords Atmospheric deposition, Hybrid multilayer barrier thin film, Roll-to-roll atmospheric atomic layer deposition (R2R-AALD), Organic–inorganic, Electrohydrodynamic atomization (EHDA)

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Introduction

In recent years, flexible electronic devices have begun to be regularly used in our daily lives for communications, renewable energy resources, and information technology.^{1–3} Conventional glass substrates can provide excellent protection from permeation species, but since the glass substrate is rigid it cannot be used for flexible electronics. On the other hand, electronic devices made on flexible plastic substrates such as solar cells, organic thin-film transistors (OTFTs), organic light-emitting transistors, and organic light-emitting diodes (OLEDs) enable low cost, flexibility, mass production, and weight reduction in these devices.^{4,5} However, flexible polymer substrates can be easily damaged by the atmospheric gas molecules oxygen (O₂) and water (H₂O),^{6,7} and therefore these substrates must be protected with some additional encapsulating nanolayer. Atmospheric species can be easily oxidized and damage electrodes, resulting in a decrease in the overall device lifetime.^{8,9}

There are several inorganic materials that play a vital role in polymer substrate encapsulation, such as Al₂O₃, SiO₂, Al₂O₃/ZrO₂, and Al₂O₃/TiO₂, due to their permeability to environmental species and high optical transparency.^{10–12} SiO₂ is a well-known dielectric material, and it can be applied in many research areas, such as the semiconductor industry, flexible electronics, optoelectronics, and passivation layer coating of electronic devices.¹³ Several deposition techniques have been reported for the successful development of encapsulating thin films in order to protect electronic devices. These fabrication techniques include sputtering,¹⁴ chemical vapor deposition,¹⁵ and thermal evaporation¹⁶ with good values of WVTR. However, these methods are only suitable for thick layer coating and rigid device encapsulation and therefore cannot meet the requirements of flexible electronics.¹⁷ ALD is a good choice for defect-free,

conformal coatings and high-quality barrier thin films.¹⁸ ALD-grown SiO₂ thin films achieved excellent coverage and a highly controllable thickness range.¹⁹ The low-temperature ALD-grown SiO₂ thin film plays a major role in gas barrier applications.²⁰ SiO₂ thin-film coating on polymer substrate has received great attention in the food packaging, beverage packaging, and pharmaceutical industries.²¹ Inorganic thin films displayed effective protection against water and oxygen; however, a low-temperature fabrication process introduced pinholes into the barrier film that can allow atmospheric species through them, thereby damaging the device.²² To solve this permeation issue, organic thin films are recommended for the barrier encapsulation. Organic/inorganic hybrid barrier thin-film layers offer supreme protection from atmospheric molecules.^{23,24} Furthermore, the organic materials filled the pin holes of the inorganic thin film, leading to the delayed penetration of H₂O and O₂, as well as increasing the diffusion period of atmospheric species.^{22,25}

The current trend for using thin-film barriers is to use a single inorganic layer²⁶ or organic–inorganic barrier bilayer.²⁷ Multilayer²⁸ barriers can improve the quality of the thin-film barriers. Jo et al. had prepared SiO₂-PTPT (Poly(trimethylolpropane triacrylate)) composite barrier for encapsulation purposes with decreasing WVTR results.²⁹ Kim et al. reported on combined thin-film techniques for multilayer Al₂O₃/ppTTMSS/Al₂O₃ barrier thin films.³⁰ Yun et al. reported on organic–inorganic barrier thin films from hexamethyldisiloxane (HMDSO) and achieved a WVTR range of 3.6×10^{-6} g m⁻² day.³¹ Chen et al. made ZrO₂/zirconia hybrid thin films and reported 3.078×10^{-5} g m² day⁻¹.³² Fan et al. reported on Teflon/SiO₂ bilayer films, and the WVTR value for SiO₂ deposited on polycarbonate was shown to be 0.59 ± 0.16 g/m²/day.¹³ Han et al. fabricated an S–H nanocomposite with Al₂O₃ using two different combined thin-film techniques and displayed 1.14×10^{-5} g/m² day.²⁴ Kim et al. reported on Al₂O₃/TiO₂ thin films by the plasma-enhanced atomic layer deposition method with a WVTR value of 9.16×10^{-5} g m² day⁻¹.⁸ However, these reported results showed low permeation but required higher temperature for deposition as well as vacuum conditions for the fabrication. Only a few of studies, which reported atmospheric and roll-to-roll-based techniques, are being utilized for barrier encapsulation applications. These can also be part of the mass production and cost reduction technology.

PVDF is a well-known fluoropolymer, and it has piezoelectric property, excellent mechanical stability, and high chemical resistance.^{33,34} Also, the main advantage of PVDF is that it has significant permeability against small molecules such as nitrogen, carbon dioxide, nitrous oxide, oxygen, and water.³⁵ Many methods such as vapor deposition, spin coating, and wire bare coating have been reported in the literature to fabricate PVDF thin film, but these techniques are

limited to surface nonuniformity and high temperature requirements.^{36–38} Very recently, the EHDA technique has drawn great attention on the deposition of high-quality organic and inorganic thin-film fabrication at atmospheric and room temperature. Organic thin films like PVA, P3HT:PCBM, and PEDOT:PSS and PVDF based on EHDA deposition technique were reported.^{39–41} On the other hand, the inorganic materials formed by blending with PVDF including zirconium oxide (ZrO₂), titanium oxide (TiO₂), alumina (Al₂O₃), and silica (SiO₂) using sol–gel technique for the application of antifouling.^{42–45} To the best of our knowledge, there have been no reports so far on the coupling of the PVDF layer with SiO₂ layer as a multilayer barrier for the purpose of encapsulating flexible substrates through the dual fabrication technologies EHDA and R2R-AALD, respectively.

In this paper, the development of PVDF/SiO₂ hybrid barrier thin films, through a innovative technology of low-temperature R2R-AALD along with the EHDA technique, is illustrated in Fig. 1. The objective of this study is to combine hydrophobic nature PVDF with SiO₂ thin films for surface passivation of flexible substrates. The combination of deposit barrier thin films was investigated for its thickness, surface morphology, chemical composition, and optical properties, respectively. These fabricated barrier films exhibited better WVTR results. Mechanical robustness of these fabricated multilayer barrier thin films was evaluated; even after 500 bending cycles, no significant changes in the barrier film were observed. The main advantage of using this joint fabrication technique is the mass production of encapsulating thin films in less time.

Experimental details

Materials and method

Polyvinylidene difluoride (PVDF) pellets, dimethylformamide (DMF), and ammonia were purchased from Sigma-Aldrich. Tris(tert-pentoxysilanol) (TPS) was purchased from Sigma-Aldrich for the SiO₂ source, and the trimethylaluminum (TMA) catalyst precursor was purchased from UP Chemical. The 5 wt% concentration of PVDF was dissolved in dimethylformamide (DMF) under the magnetic stirrer at 50°C for 6 h. Furthermore, 2.20 mM ammonia was added into the solution and continuously stirred for 3 h.

Roll-to-roll atmospheric atomic layer deposition of SiO₂

The SiO₂ thin-film deposition was done through the R2R-AALD system. The ALD head was placed above the PET substrate, and the distance between the substrate and the head was ~ 400 μm. The precursor channel outlets and exhaust channels were connected

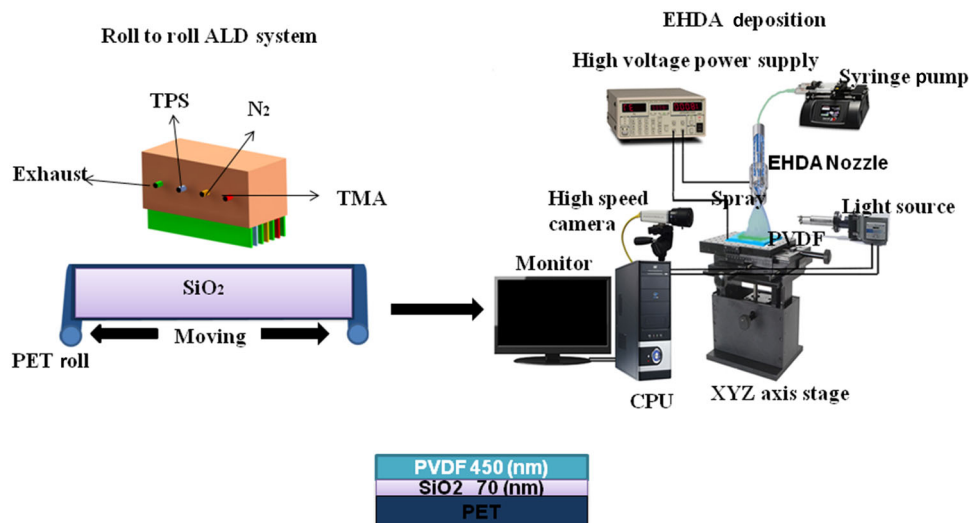


Fig. 1: Schematic illustration of the multilayer barrier film preparation as well as thickness of each film

to the head. The role of the nitrogen gas was to act as a carrier gas and inert separation gas. The major precursor was tris(tert-pentoxo) silanol (TPS) as the SiO_2 source, and trimethylaluminum (TMA) acted as a catalyst.⁴⁶ The canister of TPS was maintained at 110°C , and the TMA was maintained at 10°C . The precursor channels were maintained at 100°C for preventing the recondensation of the precursor. The delivered flow rate of the precursor TPS and catalyst TMA was fixed at 100 and 50 SCCM, respectively. To prevent the intermixing of the precursors, the nitrogen gas flow rate was fixed at 1000 SCCM. The flow rates were adjusted by the mass flow controllers (MFC). The unreacted gas was purged out through the rotary pump, and the reaction pressure was maintained at 740 Torr. This reaction pressure was closely related to the atmospheric pressure. The web velocity of the PET substrate was fixed at 7 mm s^{-1} , and the tension was fixed at 10 KgF. This SiO_2 thin film was fabricated at 90°C on a flexible PET substrate.

PVDF deposition through EHDA technique

EHDA technique can be used to deposit a variety of materials with supreme, uniform thin films.^{47–51} The required flow rate was maintained by the syringe pump (Harvard Apparatus, PHD 2000 Infusion). The PVDF ink-filled syringe was connected to the metallic capillary with a diameter of $210 \mu\text{m}$. A high electric field between the metallic capillary and the ground was applied. The EHDA operation had several modes of deposition such as dripping, microdripping, stable, unstable, and multijet process whose snap shots were captured through the high-speed CCD camera. The substrate stage was able to move in the X–Z direction, and the metallic holder could move in the Y direction. After careful adjustment between the nozzle and substrate, the uniform spray result was achieved. The

PVDF organic thin film was achieved at room temperature on the substrate at a speed of 0.35 mm/s . The uniform deposition was achieved at the flow rate of $400 \mu\text{l/h}$. The prepared sample was sintered at 90°C for 3 h. The EHDA deposition was performed under various flow rates at a fixed distance of 20 mm. The electrical current was increased for every flow rate by the applied voltage between the stage and nozzle.

Characterization

The thickness of the barrier thin film was measured using focused ion beam spectroscopy (FIB) (Helios NanoLab 600i). The surface morphology and roughness of the films were observed using Field Emission Scanning Electron Microscopy (FESEM, JSM -6700F) and Surface Profiler (NanoView high accuracy 3D nano noncontact), respectively. The contact angle measurement of each film was carried out using the SEOPhoenix 3000 Touch system. The chemical composition of the films was obtained by X-ray photoelectron spectroscopy (XPS, VG Microtech). The optical transmission range of each film was measured with UV-3150 UV/VIS/NIR spectrophotometer (Shimadzu UV-3150). The permeation value of the barrier thin film was measured by MOCON (AQUATRAN Model 1) under the conditions of 37.8°C 100% relative humidity. Mechanical stability of the barrier thin film was observed by the bending machine.

Results and discussion

Surface morphology

The surface morphology of the R2R-AALD-deposited SiO_2 and EHDA-deposited hybrid thin films was performed through field-emission scanning electron

microscopy (FESEM) and 2D surface profiler. The hydrophobicity levels of the films were analyzed through the contact angle measurement system. Figure 2a illustrates SiO₂ thin film deposited by R2R-AALD which shows uniform and pinhole-free surface morphology. Figure 2b shows the EHDA-deposited PVDF thin film's surface is quite nonuniform, as seen in the figure. The surface roughness of the SiO₂ thin film deposited by R2R-AALD and the PVDF thin film deposited by EHDA is shown in Figs. 2c and 2d, respectively. Although the surface roughness of the PVDF thin film deposited through EHDA is inferior to the surface roughness of the SiO₂ deposited through R2R-AALD, it is still superior to other deposited organic thin films through EHDA.^{39,52} The 2D surface profiler arithmetic roughness values of the SiO₂ and PVDF were 1.84 and 3.88 nm, respectively. Contact angle results revealed the hydrophobicity difference between the SiO₂ and PVDF/SiO₂ thin films shown in Figs. 2e and 2f. The hydrophobic nature of barrier thin films can be induced by increasing the surface roughness and reducing the surface energy. The addition of

ammonia to the PVDF mixture has significant result on the membrane's surface energy. This hydrophobic nature thin film was achieved by adding a 2.20 mM concentration of ammonia to the PVDF mixture which resulted in a higher value for the contact angle.⁵³ The PVDF/SiO₂ thin-film (CA = 125°) hydrophobicity level is greater than a single-layer SiO₂ (CA = 90°) thin film. Higher hydrophobicity films are preferable for barrier coating applications. Based on the contact angle results, we can verify that multilayer PVDF/SiO₂ thin films can enhance the barrier properties for protecting plastic substrates.

The thickness of each layer was analyzed through focused ion beam (FIB) images as shown in Fig. 3. The thickness of the EHDA-deposited organic PVDF layer was 450 nm, and that of R2R-AALD-deposited inorganic SiO₂ layer was 70 nm. The higher thickness of the organic layer provides the delayed penetration of molecules to the inorganic layer. The results of the FIB image clearly showed the existence of each layer separately.

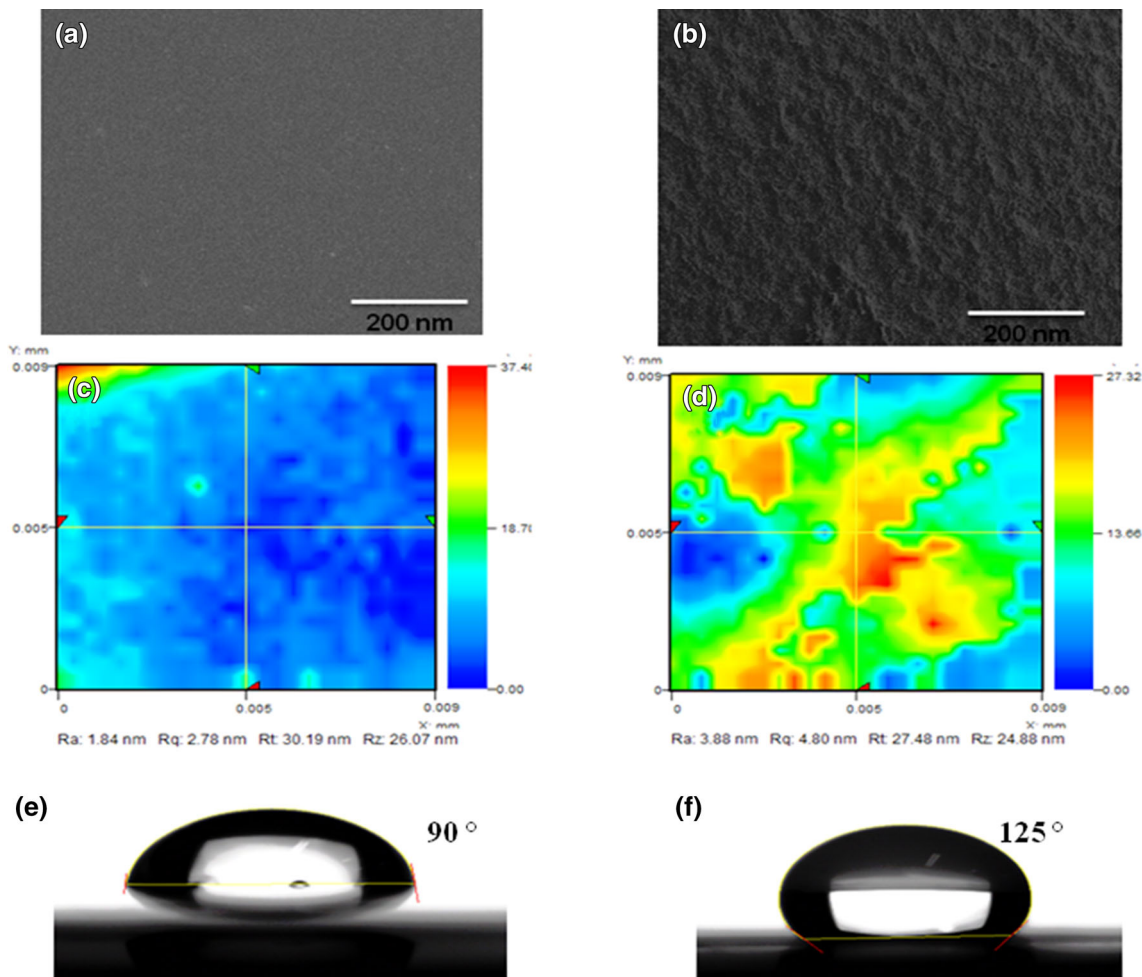


Fig. 2: FESEM images of (a) R2R-AALD SiO₂ thin film, (b) EHDA-deposited PVDF on SiO₂ thin film, (c) 2D surface profile of the R2R-AALD SiO₂ thin film, (d) EHDA-deposited PVDF on SiO₂ thin film, and (e) contact angle of the R2R-AALD SiO₂ thin film (f) PVDF/SiO₂

Compositional analysis

The chemical composition of each thin film was determined through X-ray photoelectron spectroscopy

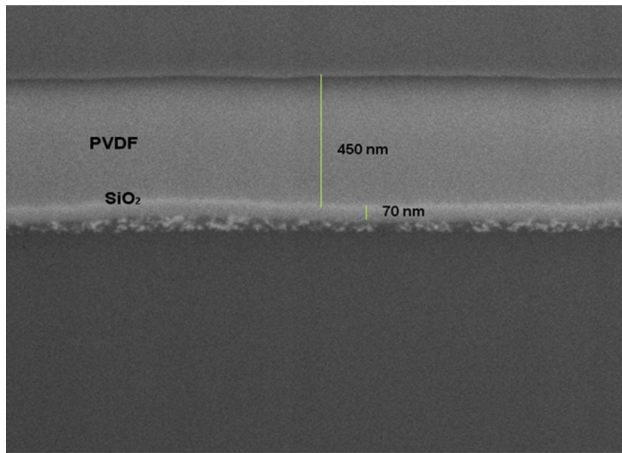


Fig. 3: FIB cross-sectional image illustrating the thickness of each layer

(XPS). The XPS analysis for SiO_2 , PVDF, and hybrid PVDF/ SiO_2 thin films is shown in Fig. 4. The R2R-AALD-deposited SiO_2 thin-film XPS results exhibited excellent quality chemical composition. XPS results of the EHDA-deposited PVDF and hybrid PVDF/ SiO_2 thin films also revealed a good quality chemical composition. Based on these chemical composition results, it can easily be deduced that the R2R-AALD with EHDA combined technique can fabricate high-quality multilayer barrier thin films. Figure 4a presents the XPS results of the R2R-AALD-deposited SiO_2 thin film, which contains Si 2s, Si 2p, oxygen (O), and carbon (C) peaks. The binding energy values attributed at 103.2, 284.6, and 532.6 eV were a representation of silicon, carbon, and oxygen, respectively. Figure 4(b) shows the pure PVDF, which contains only two major peaks, carbon (C) and fluoride (F1 s), denoted by the values of 285.4 eV (C) and 688.1 eV (F1 s). The PVDF thin-film XPS spectrum does not reveal any irrelevant particle in the film. Finally, the hybrid PVDF/ SiO_2 thin-film XPS spectrum, shown in Fig. 4c, clearly indicates the required peaks of fluoride (F1s), carbon (C), and oxygen (O). These hybrid PVDF/ SiO_2 XPS results clearly exhibit that the PVDF layer is perfectly

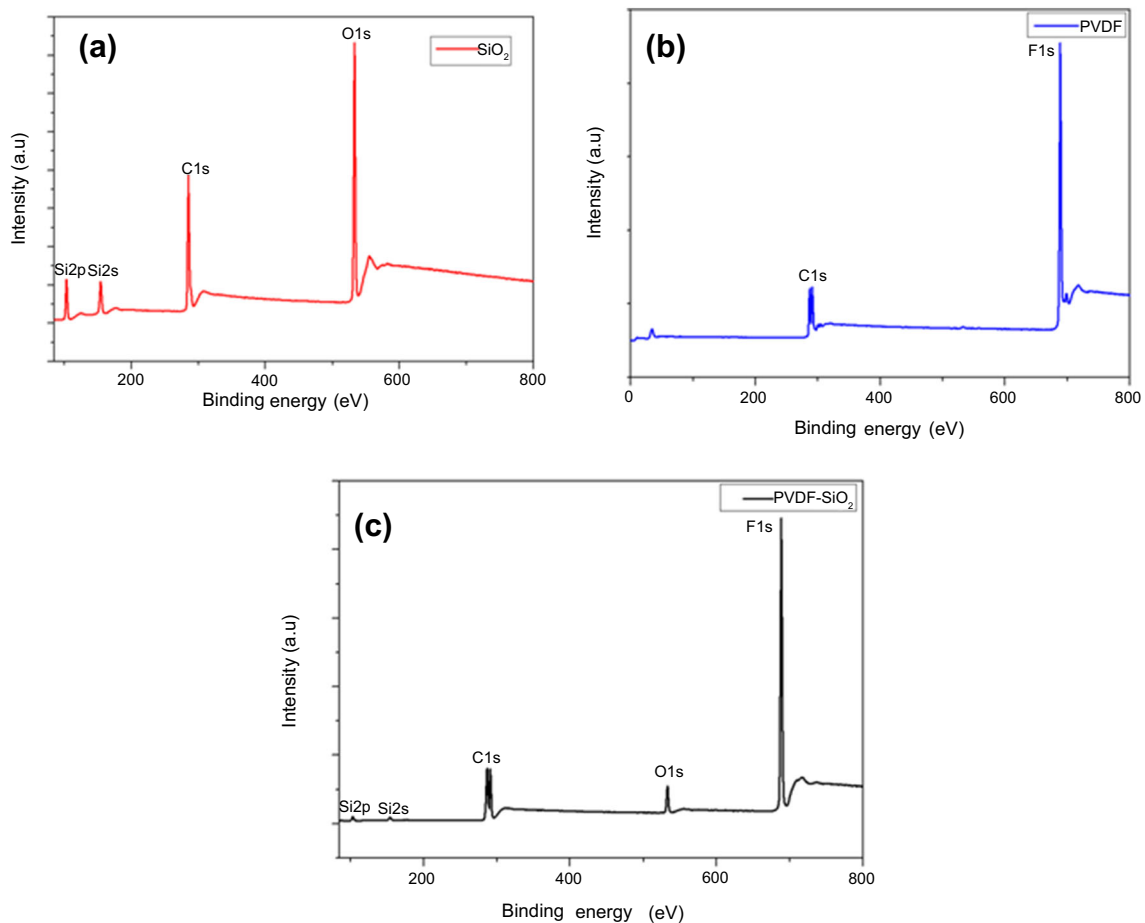


Fig. 4: XPS spectrum of the multilayer barrier thin film: (a) R2R-AALD SiO_2 thin film, (b) EHDA-deposited PVDF thin film, (c) hybrid PVDF/ SiO_2 barrier thin film

coupled with SiO₂ thin films. These hybrid chemical composition results were well matched in the previously reported literature.⁵⁴ The XPS results affirm the high quality of the fabricated barrier thin films.

Optical properties

The optical properties of the barrier thin films are presented in Fig. 5. The device to be protected by the barrier layer encapsulation requires higher transparency for optical applications. This is because while most of the materials have hindering properties against atmospheric molecules, it has a poor optical transparency range. Obviously, such materials are not suitable for optical applications such as OLEDs, solar cells, and other organic electronics barrier layer production. The transparency range of the barrier PVDF/SiO₂ and SiO₂ thin films was measured by UV–visible spectroscopy. Figure 5 displays the optical transmittance range of the SiO₂ thin film to be 92% in the visible region. The hybrid PVDF/SiO₂ barrier thin film also exhibited very good optical transmittance and can conclude that the organic PVDF membrane does not damage the optical transmittance of barrier thin films. These results clearly signify that the fabricated multilayer barrier hybrid thin films are suitable for barrier application in flexible organic electronic devices.

Barrier properties

The barrier properties such as the WVTR permeation range was performed through the MOCON (AQUATRAN Model 1). The WVTR permeation measurement was carried out under conditions of 37.8°C and relative humidity. The SiO₂ single-layer WVTR results show $1.1 \times 10^{-1} \text{ g m}^{-2} \text{ day}^{-1}$. It can be deduced, on the basis of WVTR value, that the SiO₂ layer fabricated at low temperature has shown better results compared to the other reported SiO₂ layers deposited

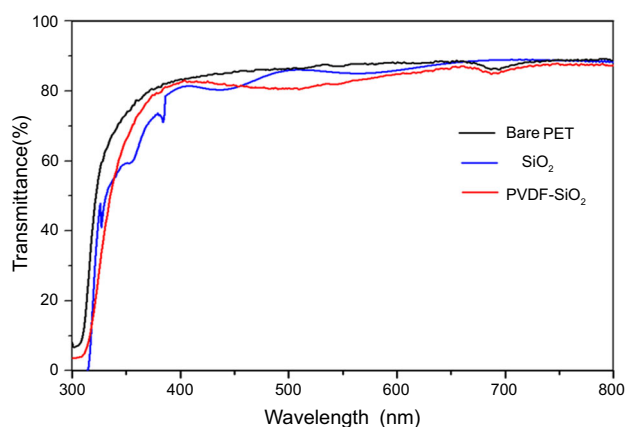


Fig. 5: UV–vis optical transmittance value of the multilayer barrier thin films with the comparison of bare PET substrate

at a higher temperature through the ALD system.⁵⁵ However, the inorganic–organic multilayer barrier thin film displayed a superior performance than the single-layer inorganic thin film. Organic thin film creates tortuous paths which can elongate the H₂O and oxygen molecules' permeation to the inorganic layer. This multilayer PVDF/SiO₂ approach has shown promising WVTR results as compared to the single-layer SiO₂ thin film.

When the PVDF organic layer was introduced on top of the SiO₂ layer, the range of the WVTR value improved to $0.9 \times 10^{-2} \text{ g m}^{-2} \text{ day}^{-1}$ as shown in Fig. 6. The presence of pinholes in the bottom layer of SiO₂ inevitably allows water vapor and oxygen to penetrate through it; however, by depositing the second layer of PVDF, these pinholes are blocked and hence the permeability of water vapor and oxygen is reduced as indicated by the WVTR values. The thickness of SiO₂ is only 70 nm; therefore, the higher thickness value of PVDF (450 nm) also plays a vital role in elongating the delay time of water vapor to diffuse through the hybrid barrier thin film. The mechanism of water vapor and oxygen permeability through the hybrid barrier thin film is illustrated in Fig. 7. The combination of R2R-AALD and EHDA offers a good quality barrier thin film, and it can be utilized as a gas barrier in the organic electronics industry.

Mechanical property

Determination of the permeation of barrier thin films before and after the bending test is shown in Fig. 8. The bending test is required to ascertain the flexible barrier thin film's resistance against strain induced by the bending machine. The addition of an organic PVDF layer on the surface of SiO₂ layer enhances the flexibility of the barrier thin film as organic polymers

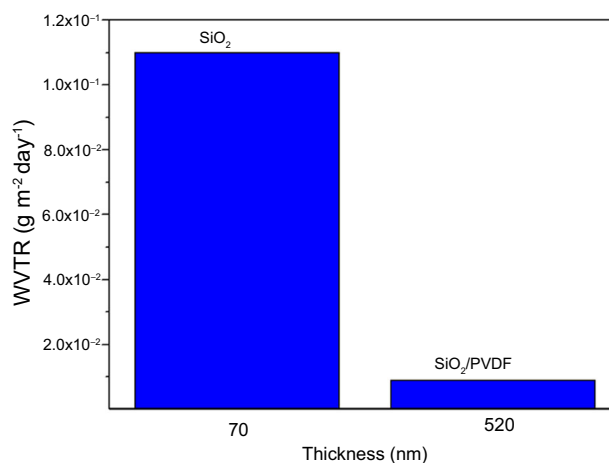


Fig. 6: WVTR values of the single- and multilayer barrier thin film depending on the film thickness. Here, the decrease in WVTR value increases the film thickness

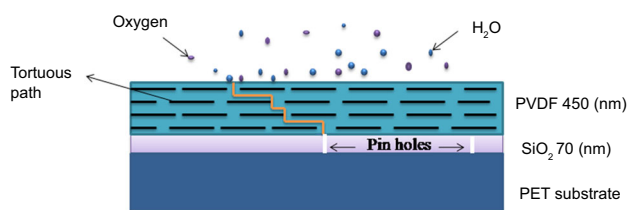


Fig. 7: H₂O and oxygen molecules travel through the PVDF tortuous path, so the H₂O and oxygen molecule permeation delayed to the SiO₂ inorganic layer

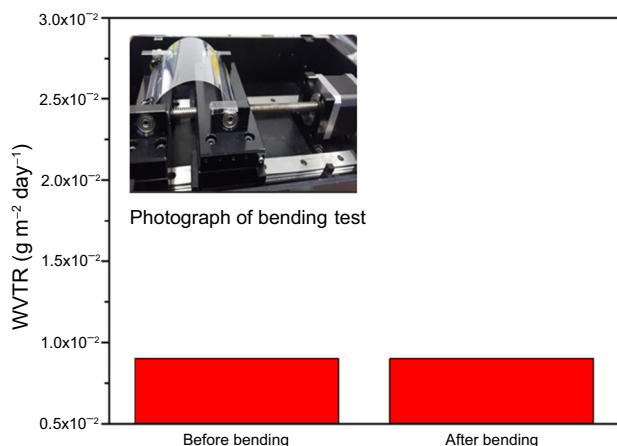


Fig. 8: Water vapor transmission rate (WVTR) of the multilayer barrier film before and after bending test

have a high value of elastic modulus that protects them under large, applied stress and does not allow cracks to appear on their surface. The barrier thin film was checked after 500 bending cycles, but there were no significant changes in the WVTR results. The bending test results clearly showed that the organic PVDF layer was mechanically stable and it also decoupled perfectly with the SiO₂ thin film. Based on the mechanical bending test, this PVDF/SiO₂ multilayer barrier thin film can sustain the higher mechanical stress.

Conclusion

In this study, we established a multilayer barrier PVDF/SiO₂ hybrid barrier thin film by combining R2R-AALD and EHDA fabrication techniques. The barrier thin film expressed significant physical and chemical properties. The arithmetic roughness of the barrier thin film was 3.88 nm with a very good contact angle (125°). The chemical composition results clearly illustrate that the fabricated barrier thin film is of good quality with no impurities. The optical transmittance range of the barrier and SiO₂ thin films was observed to be between 85–90%. The WVTR of the hybrid PVDF/SiO₂ barrier films showed $\sim 0.9 \times 10^{-2} \text{ g m}^{-2} \text{ day}^{-1}$. Even after more than 500 cycles of the bending

test, no noticeable changes in the barrier films were observed. The combination of R2R-AALD and EHDA developed barrier thin films which showed good quality and promising results for gas barrier applications in the electronics industry.

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