Effect of Discharge Properties of the Oxide High Barrier Film Deposited by Roll-to-Roll MF-PECVD

Maojin Dong(✉), Yudong Feng, Jizhou Wang, Lili Qin, Yi Wang, Xianhu Han,
Yuhong Cai, Erpeng Feng, Guan Wang, and Fengying Ma

Key Laboratory of Vacuum Technology and Physics, Lanzhou Institute of Physics,
Lanzhou 730000, China
klmdmj@126.com

Abstract. In accordance with the application of magnetically enhanced plasma discharge in high barrier film, the discharge parameters of roll-to-roll medium-frequency magnetic enhanced chemical vapor deposition (MF-PECVD) were studied. We discuss the discharge parameters, such as voltage, current, with the different vacuum pressure, and barrier property change rule by the parameters change. The results show that with the increase of discharge current, the voltage increases, and the deposition rate increases. The optimize vacuum pressure is 3 Pa, the water permeability decreases significantly with the increase of thickness, and the 300 nm films show high barrier properties, as low as 1×10^{-2} g/(m^2·day). The film thickness reached 500 nm, and the water permeability value was less than 5×10^{-3} g/(m^2·day), and the water permeability changed little with the increase of the thickness. And the average transmittance is 88.6%@380 nm–760 nm, film has good optical properties for display devices.

Keywords: Discharge Parameters · High Barrier Film · MF-PECVD · Vacuum Pressure

1 Introduction

Flexible electronic devices have the characteristics of miniaturization and deformability, and are widely applied. Typical applications include organic light-emitting devices (OLEDs), organic photovoltaic devices, thin-film transistors (TFT) array, and quantum dot TVs. The barrier property of flexible polymer materials is relatively weaker than the glass or metal encapsulating materials. The shelf-life and working lifetime of encapsulated flexible organic electronic devices are closely related to the barrier property against small molecules such as oxygen (O_2) or water vapor. We need coating barrier film to prevent the penetration of these molecules into the working device, which is called high barrier film [1–5].

Magnetic-enhanced chemical vapor deposition (PECVD) technology has been widely used due to its high vacuum environment, high quality, few impurities, and good performance of the deposited films. Meanwhile, it is generated by the dielectric barrier

D. Dai et al. (Eds.): ISPEC 2022, SPPHY 391, pp. 64–72, 2023.
https://doi.org/10.1007/978-981-99-1576-7_7

discharges (DBD) structure with medium-frequency power [6–11]. In this paper, an MF-PECVD system with a pair of rollers was used to deposit transparent siloxane films with a high barrier property on the polymer substrate. In the MF-PECVD process, the chemical reaction species generated in the plasma may help to obtain higher deposition rate at relatively low process temperature, while in the conventional thermal CVD process, thermally stable precursors are needed. The coating depositions have been intensively investigated due to the high growth rate and the good uniformity. This method can be continuously winding, and has the characteristics of the transparent visible spectrum and high barrier. It has great application potential in the development of the barrier film industry [12–14].

To obtain accurate information about the problems encountered in the glow discharge coating process, one of the main purposes of this study is to measure the electrical parameters of the PECVD process and further understand the influence of parameters on the depositing process. Understanding the basic principles of these reactive plasmas is important for optimizing the coating function, as well as process and quality control [15–19].

2 Experimental Procedure

2.1 Structure of System

A schematic diagram of discharge PECVD apparatus is shown in Fig. 1. The system uses the opposite electrode dual rollers to tighten the substrate film on the roller surface for continuous winding and coating. One of the important features of this coating device is the application of a medium-frequency power supply to the dual rollers, where a non-rotating magnet system is assembled to produce an oval magnetic enhanced discharge area on the surface of the pair rollers. The inside of the electrode roller is a completely symmetrical magnetic system, the magnetic system of the two rollers is relative, the plasma is confined between the rollers by the magnetic field, and the AC magnetically controlled discharge helps to excite the plasma. The surface of the deposition roll is covered with an insulating organic substrate film, but the medium-frequency discharge is sufficient to penetrate the polymer substrate film and achieve glow discharge. At the same time, the process gas used for deposition is distributed to the area between the rollers, and the source gas is decomposed, dissociated, and excited by plasma, adsorbed on the organic substrate film on the surface of the electrode roller to grow the high barrier oxide film.

The source gas is O_2/HMDSO mixture supplied by a gas distribution system located at the top of the deposit to keep the pressure within 0.5–10 Pa range.

2.2 Experimental Parameters

The vacuum system is composed of mechanical pump, roots pump group and a molecular pump. The power type is TruPlasma Bipolar 4010, using full-waveform mode control. The vacuum is measured by Inficon thin film vacuum gauge, and the gas flow is adjusted by gas mass flowmeter. The gas flow and experimental parameters in this experiment are shown in Table 1.

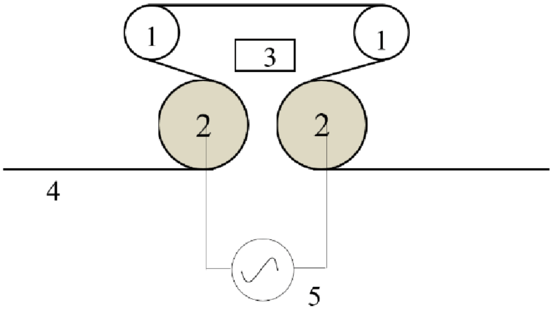

Fig. 1. Diagram of magnetic field distribution of electrode ① guide roller, ② magnet, ③ air distribution plate, ④ substrate film, ⑤medium-frequency power supply

Table 1. Experimental parameters

content	range
vacuum/Pa	0.5–10
HMDSO/sccm	80 (99.99%)
O_2/sccm	600 (99.999%)
power/w	0–2000
voltage/V	0–800
background vacuum/Pa	5×10^{-3}
winding speed	600 mm/min

The KEITHLEY DAQ6510 multimeter was used to test the electrical parameters during the discharge, which were collected and recorded by the computer. Film Thickness Mapping with an Astigmatic Optical Profilometer, the water permeability was tested by MOCON AQUATRAN MODEL 2. The spectrum of thin film was tested by Perkin Elmer LAMBDA 900 UV-Vis Spectrophotometer.

3 Results and Discussion

3.1 Medium Frequency Discharge

Plasma discharge is an important step in the study of MF-PECVD. According to the characteristics of plasma power, voltage, and power density, the deposition rate, compactness, and thickness uniformity of the coating can be analyzed. We get the change rules of the plasma discharge parameters to deposition rate [20, 21].

In the synthetic insulation film process, in order to effectively neutralize the charge accumulation on the edge target surface, a negative pulse bias of about 400–600 V is usually applied to the target surface. In order to characterize the variation of voltage with time during discharge, a rectangular wave medium frequency discharge is used with a duty cycle of 50%. The discharge characteristic was test by The KEITHLEY DAQ6510 multimeter (Fig. 2).

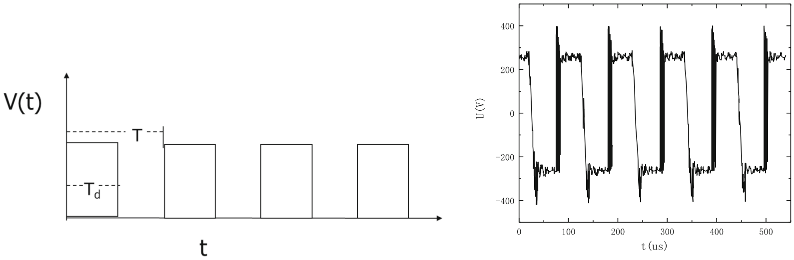

Fig. 2. Comparison of model voltage (left) and measured voltage (right)

The discharge of medium-frequency PECVD state is a periodic breakdown, discharge and extinction process. Firstly, with the increase of the power supply voltage, the voltage between the two rollers increases, and then the breakdown and discharge cause the voltage at both ends of the roller to decrease and the first spike appears. As the supply voltage continues to rise, the voltage between the roller's rebounds and a second downward spike appears. Then discharge tends to be stable appear relatively straight line. As the power supply voltage of the cycle decreases, the voltage at the roller end also decreases. However, where the discharge is extinguished cannot be determined from the diagram. So, it can be seen as a periodic DC discharge.

After averaging the discharge voltage by filtering, the relationship between power and voltage is discussed. As the discharge power increases, the voltage increases, but it is not completely linear. It increases sharply first and then slowly. At the same time, the sputtering effect of plasma has a certain influence on the base film. The higher the discharge voltage is, the more easily the thin substrate will wrinkle.

Power supply drive and test voltage characteristics. To meet the stable glow, discharge characteristics appear a voltage peak each cycle. Can see composite pulse power waveform takes on the form of high and low pulse superposition, is a high peak voltage pulse beginning but shorter pulse width of the pulse, with the rising of an ignition pulse voltage, the corresponding time is proportional to the test current is also rising, ignition pulse voltage of vacuum indoor gas discharge has an important influence.

3.2 Electrical Characteristics

Figure 3 shows the normal coating discharge state. The curve results are the same as the DC magnetron sputtering V-I curve. The discharge current can be freely adjusted in this section. This is also the curve segment interval we usually use for anti-IF pecvd. The film prepared in this state is a transparent insulator. Although the values measured under different pressures are slightly different, they can be basically regarded as a linear relationship. The voltage increases with the increase of the current to the positive resistance region, that is, the resistance R = dv/dI; is a positive value. Compared with the

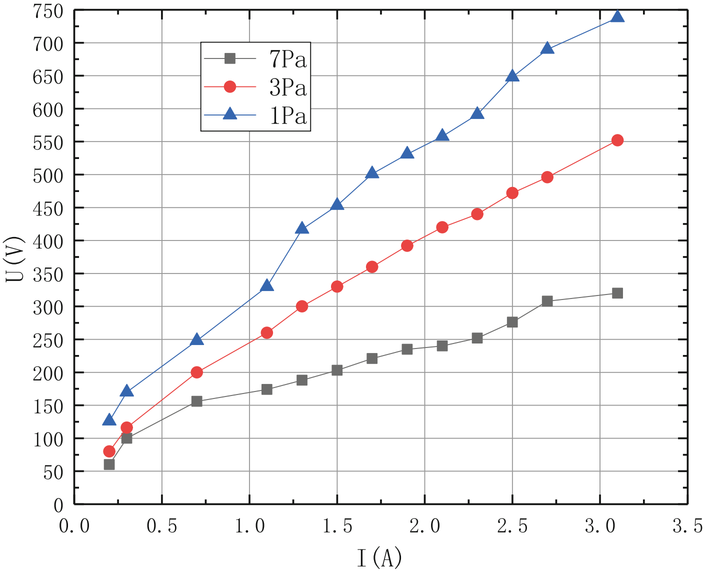

Fig. 3. Volt-ampere characteristics at different vacuum pressures

standard gas discharge voltammetry, this section conforms to the characteristics of the abnormal glow discharge section. The average current density varies from 24 mA/cm^2 to 250 mA/cm^2 with the average voltage, which is similar to the relationship between the current density of magnetron sputtering and the target voltage (Fig. 4).

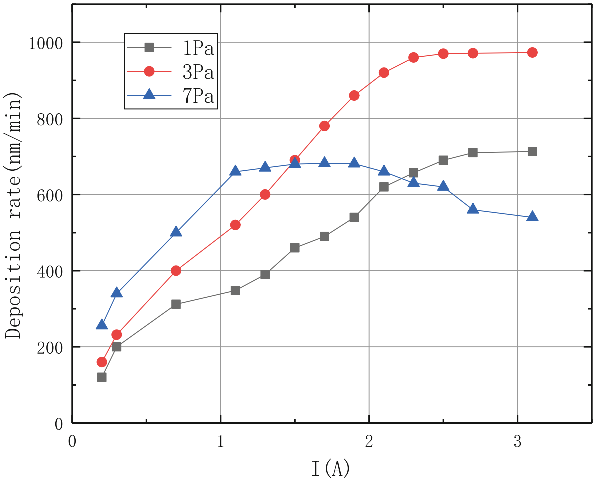

Fig. 4. Deposition rate and current characteristics under different vacuum pressures

The film deposition rate increases with the increase of plasma discharge current at 1 Pa vacuum pressure, the deposition rate increases faster than that at 3 Pa vacuum pressure. For 7 Pa vacuum pressure, in the initial stage, the deposition rate increases rapidly with the increase of current, but it quickly becomes gentle, and the deposition rate does not increase but decreases. Combined with Fig. 3, it can be seen that the discharge voltage also increases sharply with the increase of current. After 600 V, the sputtering effect of voltage increase exceeds the influence of current increase on the deposition rate. A higher deposition rate is achieved at 3 Pa vacuum pressure.

3.3 WVTR and Spectrum with Plasma Discharge Characteristics

The winding speed is constant 600 mm/min. The relationship between water permeability and discharge current under different vacuum pressure is discussed. For 1 Pa vacuum pressure, with the increase of plasma discharge current, the permeability has been reduced. When the vacuum pressure is 3 Pa, compared with 1 Pa condition, the permeability decreases faster with the increase of current, and better water vapor barrier is obtained. When the vacuum pressure is 7 Pa, in the initial stage, the permeability decreases faster with the increase of current, but it soon becomes gentle, and the permeability no longer decreases. The water permeability of oxide barrier film is closely related to the film thickness. Generally speaking, the thicker the film prepared under the same vacuum pressure, the better the barrier property (Fig. 5).

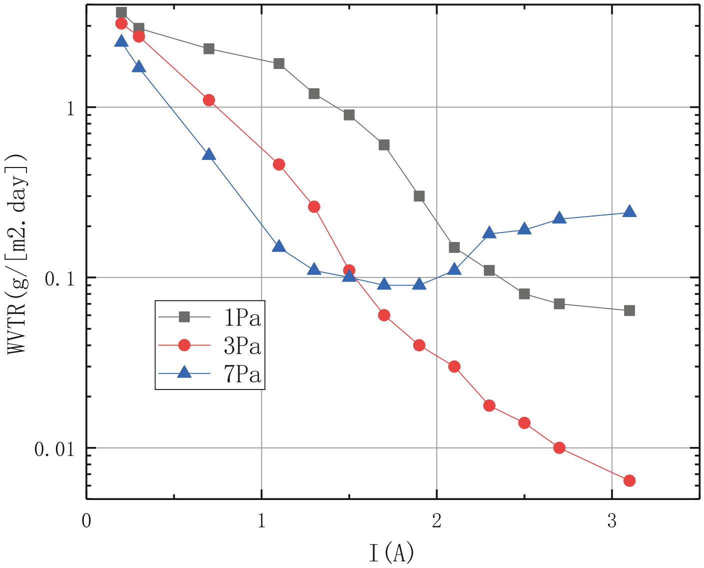

Fig. 5. Permeability and current characteristics under different vacuum pressures

Figure 6 shows the water permeability (WVTR) of different thickness. As can be seen from the figure, the water permeability decreases significantly with the increase of thickness, and the 300 nm films show high barrier properties, as low as 1×10^{-2} g/(m^2·day).

The film thickness reached 500 nm, and the water permeability value was less than 5×10^{-3} g/(m^2·day), and the water permeability changed little with the increase of the thickness.

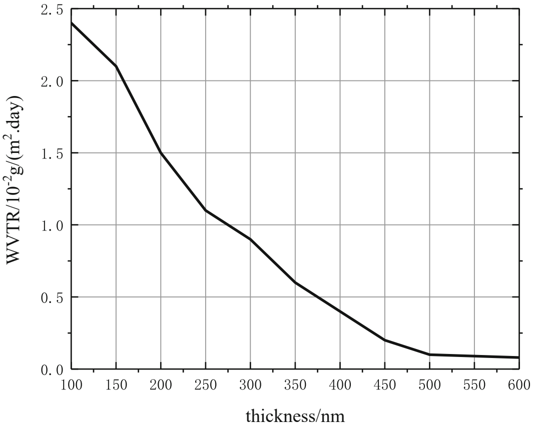

Fig. 6. The water permeability varies with the thickness of the film

We believe that there are two reasons for this result: one is that the film plated contains organic components, has good flexibility, and fewer cracks appear with the increase of film thickness, as shown in the figure; Second, there are a small number of large-size particles on the surface of the base film. With the increase of film thickness, these particles are gradually completely covered and the water permeability decreases.

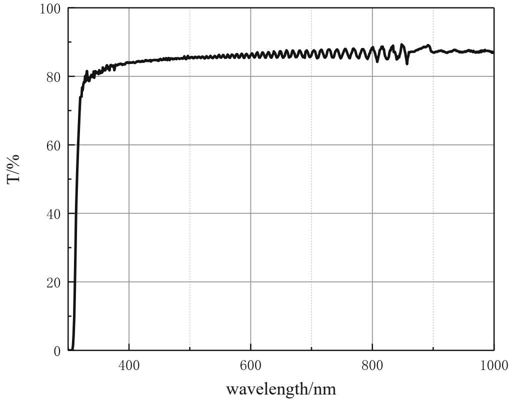

Fig. 7. Light transmittance spectrum of siloxane film

The optical transmission of 500 nm thin film is shown in Fig. 7. The average transmittance of 300–600 nm band is more than 86%, and above 600 nm band is more than 90%, and the change is gentle. It is proved that the siloxane film prepared by MF-PECVD has good optical properties for display devices. When the transmittance @380 nm–760 nm is 88.6%, it can have good barrier performance at the same time. The ripples in the spectrum are due to interference by thin film and base film, but does not affect the overall transmittance.

4 Conclusions

A roll-to-roll PECVD system was developed for the deposition of transparent and high barrier films on organic substrates. Transparent oxide barrier film was prepared by using O_2/ HMDSO mixture as process gas. we discuss the discharge and deposition parameters with different vacuum pressure The main parameters, such as magnetic field distribution, discharge characteristics, were obtained by testing different discharge parameters and characteristics. The results show that the deposition rate increase with the increase of discharge current. The optimize vacuum pressure is 3 Pa, the water permeability decreases significantly with the increase of thickness, and the 300 nm films show high barrier properties, as low as 1×10^{-2} g/(m^2·day). The film thickness reached 500 nm, and the water permeability value was less than 5×10^{-3} g/(m^2·day), and the water permeability changed little with the increase of the thickness. And the average transmittance is 88.6%@380 nm–760 nm, film has good optical properties for display devices.

References

1. Lee, S., Han, J.-H., Lee, S.-H., Baek, G.-H., Park, J.-S.: Review of organic/inorganic thin film encapsulation by atomic layer deposition for a flexible OLED display. JOM **71**(1), 197–211 (2018)
2. Park, K.W., et al.: High-performance thin H:SiON OLED encapsulation layer deposited by PECVD at low temperature. RSC Adv. **9**(1), 58–64 (2018)
3. Shin, S., Yoon, H.W., Jang, Y., Hong, M.: Stoichiometric silicon nitride thin films for gas barrier, with applications to flexible and stretchable OLED encapsulation. Appl. Phys. Lett. **118**(18), 181901 (2021)
4. Wu, J., et al.: Efficient multi-barrier thin film encapsulation of OLED using alternating Al2O3 and polymer layers. RSC Adv. **8**(11), 5721–5727 (2018)
5. Bari, G.A.K.M.R., Kim, H.: High-barrier polymeric multilayer film with organic and interactive materials. Prog. Org. Coat. **147**, 105814 (2020)
6. Banerjee, D., Mukherjee, S., Chattopadhyay, K.K.: Synthesis of amorphous carbon nanowalls by DC-PECVD on different substrates and study of its field emission properties. Appl. Surf. Sci. **257**(8), 3717–3722 (2011)
7. Gosar, Ž, et al.: PECVD of Hexamethyldisiloxane coatings using extremely asymmetric capacitive RF discharge. Materials **13**(9), 2147 (2020)
8. Gosar, Ž, Kovač, J., Mozetič, M., Primc, G., Vesel, A., Zaplotnik, R.: Deposition of SiOxCyHz protective coatings on polymer substrates in an industrial-scale PECVD reactor. Coatings **9**(4), 234 (2019)
9. Hegemann, D., Bülbül, E., Hanselmann, B., Schütz, U., Amberg, M., Gaiser, S.: Plasma polymerization of hexamethyldisiloxane: Revisited. Plasma Processes Polym. **18**(2), 2000176 (2020)
10. Liehr, M., Dieguez-Campo, M.: Microwave PECVD for large area coating. Surf. Coat. Technol. **200**(1–4), 21–25 (2005)

11. Top, M., et al.: Hollow-cathode activated PECVD for the high-rate deposition of permeation barrier films. Surf. Coat. Technol. **314**, 155–159 (2017)
12. Kwon, S., et al.: Effect of plasma power on properties of hydrogenated amorphous silicon carbide hardmask films deposited by PECVD. Vacuum **174**, 109187 (2020)
13. Lukianov, A.N., et al.: Effect of discharge power and silicon content on optical and mechanical properties of carbon-rich amorphous silicon carbide films obtained by PECVD. J. Alloy. Compd. **801**, 285–294 (2019)
14. Zajíčková, L., et al.: Comparative Study of Films Deposited from HMDSO/O2 in Continuous Wave and Pulsed rf Discharges. Plasma Processes Polym. **4**(S1), S287–S293 (2007)
15. Grüniger, A., Bieder, A., Sonnenfeld, A., von Rohr, P.R., Müller, U., Hauert, R.: Influence of film structure and composition on diffusion barrier performance of SiOx thin films deposited by PECVD. Surf. Coat. Technol. **200**(14–15), 4564–4571 (2006)
16. Israel, D., Riemann, K.U., Tsendin, L.: Relaxation of a collisionless ion matrix sheath. J. Appl. Phys. **95**(9), 4565–4574 (2004)
17. Lee, S.H., Lee, D.C.: Preparation and characterization of thin films by plasma polymerization of hexamethyldisiloxane. Thin Solid Films **325**(1), 83–86 (1998)
18. Lin, H., et al.: Moisture-resistant properties of SiNx films prepared by PECVD. Thin Solid Films **333**(1), 71–76 (1998)
19. Sansonnens, L., Bondkowski, J., Mousel, S., Schmitt, J.P.M., Cassagne, V.: Development of a numerical simulation tool to study uniformity of large area PECVD film processing. Thin Solid Films **427**(1–2), 21–26 (2003)
20. Xiao, W., et al.: A flexible transparent gas barrier film employing the method of mixing ALD/MLD-grown Al2O3 and alucone layers. Nanoscale Res Lett **10**, 130 (2015)
21. Zhang, H., Sang, L., Wang, Z., Liu, Z., Yang, L., Chen, Q.: Recent progress on non-thermal plasma technology for high barrier layer fabrication. Plasma Sci. Technol. **20**(6), 063001 (2018)