Transparent SiOxCyHz Barrier Film Prepared by PECVD with Upper and Lower Pair Electrode Rolls Structure

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Abstract. Flexible and transparent barrier film is demanded in the fields of organic solar thin-film cells, flexible organic light-emitting diodes, electronic paper and vacuum insulation boards. To prepare films with high water resistance, flexible SiOxCyHz films were prepared on PET using HMDSO as monomer and Oxygen (O₂) as reaction gas. SiOxCyHz films were prepared by plasma enhanced chemical vapor deposition (PECVD) with upper and lower pair electrode rolls structure, with the width of electrode rolls up to 600 mm. The influences of oxygen content, film thickness, oxygen/monomer ratio, reaction vacuum degree on water vapor transmission rate (WVTR) were studied. This coating method of oxide high barrier film has great application potential in the development of barrier film industry.

1. Introduction

With the development of electronic technology, flexible devices have been more and more applied. Typical applications of flexible devices include organic solar film cells, quantum dot TV and organic light-emitting diode (OLED) display screens [1-2]. Because commonly used films (such as PE, PP, PET, etc.) can permeate small gas molecules, such as water vapor and oxygen, it is necessary to develop a barrier film to prevent these molecules permeating those devices. In addition, industry requires continuous coating as it enables efficient and inexpensive manufacturing techniques such as roll-to-roll (R2R) processing [3-5].

Transparent oxide (alumina oxide, silicon oxide) are excellent gas barrier material [6-8]. Different from crystalline film, oxide film deposited by PECVD grows at low temperature and has amorphous properties without grain boundary. Amorphous oxide film atoms provides characteristics such as blocking the ions, gas molecules and moisture migration. Inorganic film quality depends on the film growth equipment, the commonly used physical vapor deposition, chemical vapor deposition, high vacuum thermal deposition, magnetron sputtering method such as the growth of the oxide film or poor quality, or need higher temperature. The method of low temperature growth of inorganic oxide films are mostly pinhole defect, and pinhole defects is the main factor that causes water oxygen permeation, it is urgently needed to solve a problem. In this study, we used R2R-PECVD to prepare high-performance SiOxCyHz films on flexible PET substrates. This method has great application potential in the development of barrier film industry.
2. Experiment

2.1. Upper and lower pair electrode rolls structure PECVD system

The principle of discharge structure of PECVD coating machine is shown in Figure 1. The system uses two pairs of rollers to form a structure of opposed-electrode rollers with upper and lower structure. The base film is fixed on the surface and is a part of the roller to roll coating system. At the same time, these opposite rollers act as electrodes to produce plasma. One of the important features of this new PECVD coating machine is the application of bipolar MF power to the twin rolls, where a non-rotating magnet system is assembled to produce an elliptical deposition coating track on the surface of the opposing rolls. According to the vacuum design, the upper electrode is located in the middle of the air plate, and the lower electrode is located in the middle of the air pump group opening position. The \( \text{O}_2/\text{HMDSO} \) mixture was used as the process gas. According to the molecular dynamics theory, HMDSO monomer had a high molecular weight and a slower movement speed than \( \text{O}_2 \). From the air outlet to the air outlet, a gradient distribution of high monomer on the top and high oxygen on the bottom was formed.

![Figure 1. Schematic diagram of upper and lower opposite electrode structure.](image)

Inside the two electrode rollers is a completely symmetrical magnetic system in which the magnetic system is aligned with each other so that the AC magnetron discharge plasma is excited. Although the surface of the deposition roller is covered with an insulating polymer substrate, the discharge frequency (usually tens to hundreds of kHz) is sufficient to penetrate the polymer substrate and successfully produce plasma. At the same time, the process gas used for deposition is distributed to the area between the rolls. In this way, the source gas is decomposed by the plasma and the resulting film grows on the base film on the rolls.
2.2. Deposition
The high barrier film PECVD coating principle prototype is a system capable of roller to roller deposition through PECVD. The structure of upper and lower opposite electrode roller is adopted, and the plasma is restrained by magnetic field around the electrode roller.

A 50 micron thick PET film was used. The source gas, a mixture of O₂/HMDSO, is supplied by a blanket between the upper pair of electrode rollers at the top of the deposition area, and the waste gas is pumped away by a turbo molecular pump at the bottom. The pressure in the deposition area is kept within a range of several Pa by adjusting the gas flow and the opening of the plunger valve at the pump port. The working power of intermediate frequency power source used for plasma generation is 200-2000W, and the speed adjustment range of winding system is 0.5-5m/min.

Table 1. Experimental parameters of PECVD principle prototype coating.

| Parameter                  | Parameter Variation range |
|----------------------------|----------------------------|
| Oxygen-to-HMDSO flow ratio | 0.5–20                     |
| Reactor pressure           | 1-10Pa                     |
| MF power                   | 200–2000 W                 |
| Winding speed              | 0.5-5m/min                 |

3. Results and Discussion

3.1. Analysis of barrier film composition
XPS denudation was used to measure the oxygen content in the film with the change of thickness, and the oxygen content increased and then decreased. The film contains SiO$_2$ and SiOxCyHz, and the presence of organic functional groups increases the flexibility of the film and makes up for the cracks generated by PVD coating method.

$$\frac{dN}{N} = F(v) \, dv = 4\pi \left( \frac{m_o}{2\pi kT} \right)^{3/2} \cdot \exp \left( -\frac{m_o v^2}{2kT} \right) \cdot v^2 \, dv$$

(1)

The most feasible rate VM is the velocity with the highest probability among the various thermal motion velocities of gas molecules, that is, the $v$ value corresponding to the maximum value of $F(v)$, $v_m = \sqrt{\frac{2RT}{m_o}}$. Molecular weight, the greater the speed of the slower, because the cloth was the top plate added gas gas, gas structure beneath the molecular pump sucking gas model, two on the electrode, electrode on the plasma region monomer is more, the generated film oxygen content is low, the lower the oxygen electrode plasma area is more, the generated film closer to pure SiO$_2$, high barrier property of SiO$_2$ thin films are SiOxCyHz coated low oxygen content, good flexibility, SiO$_2$ provides good barrier property, the structure of PECVD discharge technique for the preparation of high-performance oxide thin films have greater benefits.

3.2. Barrier properties

Figure 3 shows the water vapor transmittance of SiOx films with different thickness. As can be seen from the figure, the water vapor transmittance decreased significantly with the increase of thickness, and the SiOxCyHz coating at 300nm exhibited high barrier performance, as low as below $1 \times 10^{-2}$g/m$^2$/day. Notably, the increase in SiOxCyHz thickness from 150nm to 300nm resulted in an order of magnitude improvement in barrier performance. This behavior cannot be explained by theories based on the diffusion of gas molecules. Therefore, we believe that with the increase of coating thickness, the sharp decrease of the leakage amount is due to the defect in the coating being gradually covered during the increase of coating thickness. The film thickness was up to 500nm, and the permeability value was less than $1 \times 10^{-3}$g/m$^2$/day, and the barrier property changed little with the increase of thickness thereafter.
Figure 4. Changes of water permeability with film thickness.

The ratio of reaction gas to monomer has a significant influence on the barrier property of the film layer. As the ratio of reaction gas to oxygen increases, the barrier property of water vapor improves significantly. When oxygen/monomer is greater than 3, the water vapor transmission rate is less than \(5 \times 10^{-3} \text{g/m}^2/\text{day}\). The subsequent increase of oxygen content shows no significant change in moisture barrier property. Analysis shows that when the inorganic property of the film increases, pinholes and microcracks caused by microscopic defects are adverse to the barrier property.

Figure 5. Changes of water permeability with oxygen/monomer ratio.
The vacuum degree in plasma discharge is crucial to the growth of the film layer. When the vacuum degree is low, organic debris such as -CH$_3$ and -CH$_2$ in the plasma glow is high in content and the film layer is not compact, which will affect the barrier property of water vapor.

![Figure 6. Changes of water permeability with vacuum degree.](image)

4. Conclusions
A novel plasma-enhanced chemical vapor deposition (PECVD) system with upper and lower counterrolls was developed for the deposition of SiOxCyHz transparent high barrier coatings on polymer substrates. The system has the advantages of stable process, high gas utilization rate, high deposition rate, low pollution and strong process expansibility. The transparent SiOxCyHz coating was prepared with O$_2$/HMDSO mixture as the process gas. The barrier property of the film is closely related to the thickness of the film, and the water permeability increases with the increase of the coating thickness. Under optimized conditions, the water permeability of SiOxCyHz films at 600nm was lower than 5x10$^{-3}$g/m²/day. The oxygen content of the SiOxCyHz film varies with its thickness, and it is found that the film has high water-resistance characteristics.

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