Barrier Mechanism Analysis of Silicon Oxide Film by SEM

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Abstract Since barrier packaging materials go through low barriers of polyethylene (PE) to middle barriers of polyester (PET) and even to high barriers of Polyvinyl Dichloride (PVDC), Ethylene vinyl alcohol copolymer (EVOH) and Aluminum foil, the rise of silicon oxide film represents the novel trend in the barrier packaging area due to super-barrier, transparent, micro-wave able, printing adaptability and high addition values, however, how to effectively test the barrier properties of silicon oxide film will become key point to realize the industrial application of its lamination packaging materials. Given that barrier characteristics of barrier materials is relate with all kinds of factors, based on the previous study, we compare different samples manufactured by different preparation methods and found that Scanning Electron Microscopy (SEM) is an effective and direct measurement tool to characterize the barrier properties. The interface variations of coating samples induced by electron beam evaporation, magnetron sputtering, ion assisted electron beam evaporation and plasma enhanced chemical vapor deposition were compared in this study, and it could be concluded that surface roughness and internal stress mainly contribute to coating quality and barrier properties, which could be used to determine the level of barrier performance.

Keywords Silicon oxide film · Barrier properties · SEM

1 Introduction

In the food packaging industry, more and more packaging materials appear with advanced requirements from the customers and manufacturers to further reduce the barrier coefficient against oxygen gas, special flavor and water vapor. Especially,

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some ready-to-eat food in short shelf life will decay or deteriorate when exposed to gas, moisture and flavor if no barrier packaging process is performed. Otherwise, some food juice, beer or liquid beverage is also easy to be oxidized due to long transportation and storage period. Thus, barrier packaging technology has been strongly demanded to be widely used in food packaging application. Based on the barrier coefficients and related performance, barrier packaging material can be divided into three stages, take OTR for example, those include low barrier in more than 200 cc/m^2 day atm, middle barrier from 10 to 200 cc/m^2 day atm and high barrier levels in less than 10 cc/m^2 day atm. Correspondingly, all the packaging polymer materials can be obviously classified into three groups from the viewpoint of packaging materials: First, normal organic polymers with no barrier functions are usually used as packing or to laminate with other films, such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), cast polypropylene film (CPP), Polyamide (6); Second, normal barrier packaging polymers with middle barrier dominate the barrier market, such as PET, PVDC and EVOH; Third, high barrier packaging materials in development are gradually showing its faces in public, such as laminated aluminum foil, metal container and ceramic oxide compounds [1].

As one of representative ceramic oxides, silicon oxide film shows its outstanding characteristics, such as super-barrier, transparent, micro-waveable, excellent printing adaptability and high addition values. Theoretically, silicon oxide film has absolutely zero permeation against gas, moisture or flavor since barrier property can mainly be determined by diffused and transmitted coefficients, both of which can be reduced to zero for silicon oxide films. As for the optimized barrier depth for different preparation method is in the nanoscale of 50–300 nm [2], barrier performance of silicon oxide film is sincerely affected by surface topology and roughness. In fact, defect, pinhole and micro crack always exits inside [3] during various preparation processes, such as sol-gel methods [4], electron beam vapor deposition [5], magnetron sputtering [6] and plasma enhanced chemical vapor deposition [7]. Although more attention and efforts has been paid on the relationship between barrier properties and film components, discharge source, film structure for different preparation methods [8], barrier mechanism and dominant influence factors are seldom elucidated in detailed to distinguish and filter the most possible preparation methods for the future potential applications.

In this study, a novel and effective comparison method has been brought out to obviously elucidate barrier principle of silicon oxide film though different preparation methods.

2 Experiments

Testing samples, which are manufactured by four typical manufacturing methods including plasma enhanced chemical vapor deposition (PECVD), electron beam evaporation (EB), ion source assisted electron beam deposition (IAEB) and magnetron sputtering deposition (MS), are analyzed by Scanning Electron Microscopy (Sirion, S-4800IIFE-SEM, Holland and Shimadzu, SEM-5500, Japan) to reveal the surface topology and thus indicate the barrier principle. In order to guarantee the consistency of experimental results, all the films are deposited on PET substrate with the depth of 12.5 μm.

For PECVD, Hexamethyldisiloxane (HMDSO) is used as the precursor with addition of oxygen gas, which was deposited based on the magnetic field enhanced plasma technology [9]. The voltage for EB method is set as 6 kV with SiO_2 as original evaporated source and Argon is chosen to be sputtering gas with oxygen as reactive gas to oxide sputtered grains from silicon target for MS.

3 Results and Discussions

Silicon oxide film can be deposited on various polymers to improve the barrier properties of matrix, and PET is one of most alternative substrates due to relative higher glass temperature and strong mechanical strength. Before deposition process, organic polymer substrate are usually pretreated by surface corona treatment, which indicate in our previous results that pretreated samples have a higher barrier performance and better interfacial adhesion due to surface cleaning and bond activation [9]. As for no pretreated samples, debris, micro grains and impurity usually exist on the surface and subsequently change subsequently coating surface, as shown in Fig. 1a. This micro impurity always leads to micro cracks or pinhole, which have a detrimental effect on the barrier properties since Grüniger et al. [7] found that the existence of persistent pores in the substrate is in direct relation with the success of a silicon oxide coating in terms of the reduction of the oxygen permeability. Meanwhile, cross section indicate that substrate is a lay-by-lay stacked in the three dimensional direction, and could not guarantee absolute barrier functions [5]. Therefore, the surface coatings of silicon oxide film will compensate this drawback by forming ceramic and dense barrier walls as will be elucidated later.

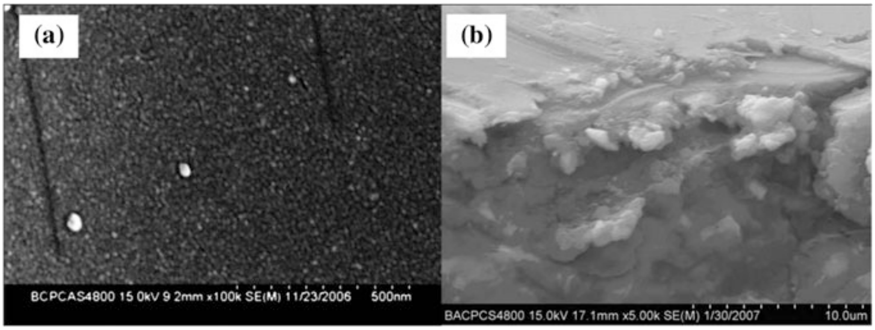

Fig. 1 Surface (**a**) and Cross (**b**) section of blank PET for next deposition process

Generally, silicon oxide layer coated on PET substrate is less than several hundred nanometers to completely cover the whole surface while keep flexible properties in a certain degree for post laminated process. However, some preparation methods can not produce this kind of ideal barrier samples in a nanoscale depth. For example, coating topology through MS can be clearly seen in Fig. 2a, the whole coated film is not complete and continuous, which have a little positive effect on the barrier properties. Although electron beam evaporation method has a high deposition rate by direct solid grain evaporation [5], the deposited coating consists of various islands, leaving cracks and pinholes as shown in Fig. 2b. It can be deduced that barrier properties of samples manufactured by above two methods can not fit for modern enhanced barrier requirements, such as food and organic light emitting diode packing.

In comparison to EB and MS, PECVD has a low deposition rate but good adhesion to substrate by covalent binding to surface groups of substrate as shown in Fig. 3a. Interface line is not clearly figured out, indicating the coating is strongly combined to the substrate. Literatures indicate that PECVD coated film has a certain degree of carbon content originating from the organic silicon precursor, which

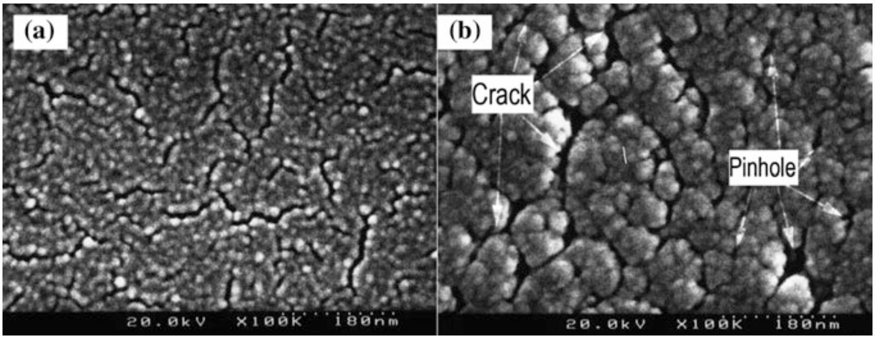

Fig. 2 Surface topology of silicon oxide films by MS (**a**) and EB (**b**)

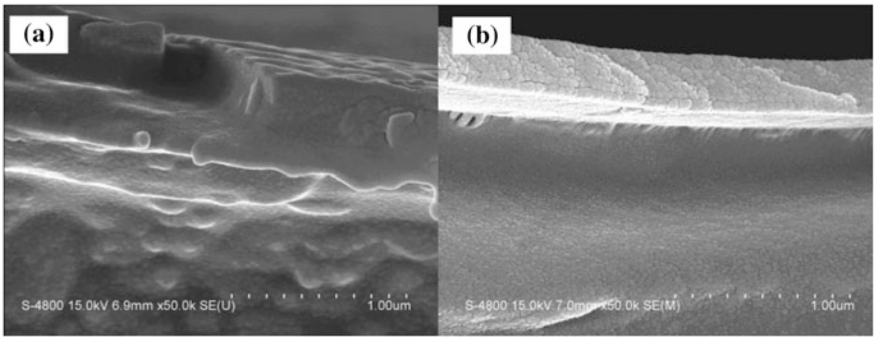

Fig. 3 Cross topology of silicon oxide films by PECVD (**a**) and IAEB (**b**)

Table 1 OTR and WVTR scope of silicon oxide films as indicated by OTR and WVTR [2, 6, 11]

Items	MS	EB	IAEB	PECVD
OTR (cc/m^2 day atm)	>20	1–20	1–5	0.1–1
WVTR (g/m^2 day, RH 90%, 38 °C)	>20	–	1–5	0.1–1

breaks crystalline order of silicon oxide and form amorphous state [6, 9]. Therefore, the amorphous silicon oxide film shows a good barrier property against to gas or moisture. In contrast, EB coated film is assisted by ion source to gain a dense and homogenous silicon oxide layer as shown in Fig. 3b, but high crystalline degree will reduce the adhesion to substrate and increase the brittleness, leading to the gas permeation through grain boundary.

Barrier properties for silicon oxide coatings can be expressed as follows:

$$Q = \frac{K \times A \times t(p_1 - p_2)}{L} \quad (1)$$

where, Q is transmission rate, L is coating depth, K is the permeation coefficient, A is the effective surface area, P is the gas pressure.

It can be easily deduced that the key point for barrier function is the permeation coefficient, which can be indicated as K = D · S, D is diffusion degree and S is solubility degree. For organic polymer films, it is difficult to avoid gaps between polymer chains due to high free volume of each atom, resulting in higher D and S since polymer films have low density and more flexibility [5]. However, the value of S for ceramic coating is nearing to zero and that of D is strong dependent on the surface topology since micro cracks and pinholes will give gas or moisture the channel to pass through [3], as can be diagnosed by surface topology. Therefore, it can be concluded that SEM is a directive and effective tool to assess the barrier properties of silicon oxide films. Meanwhile, OTR and WVTR results indicate that samples deposited by magnetron sputtering and electron beam evaporation are more than 20.0 cc/m^2 day atm while those by PECVD and IAEB are less than 5.0 cc/m^2 day atm as shown in Table 1, which is consistent with our SEM measurements from the viewpoint of defect barrier mechanisms [10], and the close relationship between the surface topology and barrier properties will need to be further studied in the future research, such as grain size, inert stress, adhesion force and coating density and so on.

4 Conclusions

Silicon oxide films are prepared on PET substrate to enhance the barrier properties of composite films in food packaging application by four typical deposition methods such as magnetron sputtering, electron beam evaporation, ion assisted electron beam evaporation and plasma enhanced chemical vapor deposition.

The surface topology indicate that micro crack and pinhole exist for samples from electron beam evaporation and magnetron sputtering while continuous and good adhesive to substrate is observed for plasma enhanced chemical vapor deposition and ion assisted electron vapor deposition. Finally, from the view point of barrier mechanism, our results indicate that SEM is directive and effective tool to assess the barrier properties of silicon oxide films, which is consistent with OTR and WVTR results.

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