



# Influence of reactive surface groups on the deposition of oxides thin film by atomic layer deposition



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## ABSTRACT

In this study, polyethylene terephthalate (PET) substrate was successfully coated Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> films by atomic layer deposition (ALD). The experiment results demonstrate that the Al<sub>2</sub>O<sub>3</sub> can be deposited more efficiently than TiO<sub>2</sub> on PET substrates. Further characterization on the coated substrates reveals that the density of hydroxyl –OH groups play a significant role on the growth of the oxides ALD film. Chemical composition of the coated substrates is characterized by X-ray photoelectron spectroscopy, which shows that the C=O elements are replaced by the Al - related elements in the Al<sub>2</sub>O<sub>3</sub> - coated PET and the Ti - related elements in the TiO<sub>2</sub> - coated PET. The results demonstrate that the C=O has a strongly contribution to facilitate the initial ALD growth of the oxides thin films.

## 1. Introduction

Atomic layer deposition (ALD) is an interesting technique for producing conformal inorganic thin films at relatively low temperatures [1,2]. Oxides thin films such as titanium oxide (TiO<sub>2</sub>) attracts increasing interests due to its advantageous properties such as photocatalytic activity, photo-induced hydrophilicity, electron transport properties in solar cell applications, gas sensing, biocompatibility and optical properties [2–6]. ALD on polymers with lack of hydroxyl –OH groups is considered to be complicated in order to produce uniform layer and conformal film coverage without substantial subsurface growth [7,8]. For nucleation, the substrate must have reactive surface groups with which the precursor molecules can react to initiate ALD growth [9–11]. Hydroxyl groups on oxide surfaces are typical examples of such reactive groups [9,12,13]. In that case, the deposited thin film is chemically bonded to the substrate, and will therefore usually have a good adhesion [9]. In addition, the aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) growth on the molecular porous polymeric substrates with lack of reactive groups was demonstrated to occur through the adsorption of the trimethylaluminum (TMA) precursor as initial nucleation period of 10–20 ALD cycles onto the surface or into the porous material leading to the formation of Al<sub>2</sub>O<sub>3</sub> clusters [9,14,15]. In our previous study, it has shown that the deposited Al<sub>2</sub>O<sub>3</sub> was amorphous with numerous reactive

hydroxyl –OH groups [16]. The remarkable properties of Al<sub>2</sub>O<sub>3</sub> that it was able to be deposited on a variety substrate at low temperature may have great potential applications [7,17,18]. In this study, it was shown that the reactive surface groups like hydroxyl –OH groups and –(C=O)–O– groups are necessary for ALD. Furthermore, it obviously indicates that Al<sub>2</sub>O<sub>3</sub> ALD layer can be used as pre-treatment-like on polyethylene terephthalate (PET) surfaces to generate reactive surface hydroxyl –OH groups which can be used as the initial nucleation growth for the subsequent ALD.

## 2. Experimental details

In this study, polyethylene terephthalate (PET) and silicon were used as the substrates. The substrates were cleaned by an ultrasonic cleaner machine for 20 min with ultrasonic power and temperature of 80 W and 30 °C, respectively, which then were dried in the vacuum oven for 1 h at 50 °C. After that, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> were deposited on the substrates by ALD with 100 cycles. For comparison, it was also prepared Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> bilayer structure on the substrate with both materials of 100 ALD cycles. In ALD of TiO<sub>2</sub>, Tetrakis (dimethylamido) titanium (TDMAT) and water vapor (H<sub>2</sub>O) were sequentially exposed for 20 and 30 ms with purge times of 15 and 18 s, respectively. For ALD of Al<sub>2</sub>O<sub>3</sub>, TMA and H<sub>2</sub>O were sequentially exposed with the same pulse and purge

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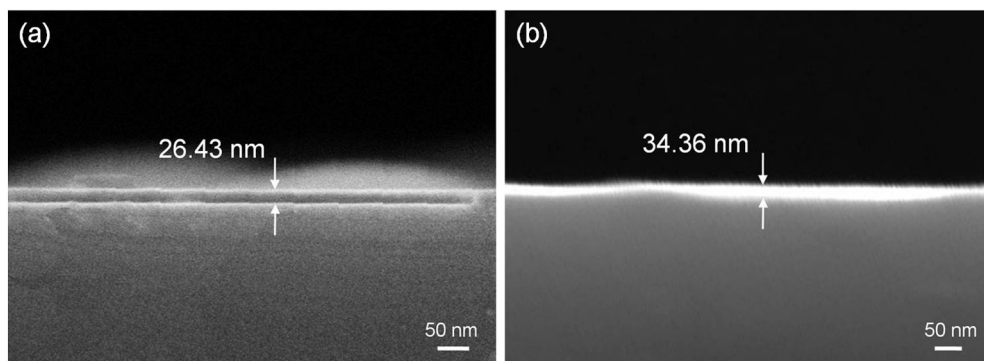


Fig. 1. Cross-sectional SEM images of silicon coated (a)  $\text{Al}_2\text{O}_3$  and (b)  $\text{TiO}_2$  films by ALD with 100 cycles.

times as used in the case of  $\text{TiO}_2$ . The deposition temperatures of  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  were 90 and 120 °C, respectively.

Cross section of the coated silicon and the surface view of the coated PET were imaged by a high resolution scanning electron microscopy (Magellan 400, FEI Company, USA). Atomic force microscopy (AFM; Nanoscope IV SPM, Model 920-006-101, Veeco Metrology, Santa Barbara, USA) was used to examine the surface morphology by using tapping mode. Wetting property of the surface was measured by a static contact angle analysis system (JC2000A, Powereach, Shanghai, China) and 0.4- $\mu\text{L}$  droplet was used on each test. Chemical composition of the uncoated PET and the PET coated  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  films were evaluated by X-ray photoelectron spectroscopy (XPS).

### 3. Results & discussion

Fig. 1 show cross-sectional images of silicon substrates coated  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  films by ALD with 100 cycles (Fig. 1(a)–(b)). The SEM images demonstrate smooth surfaces with thicknesses of approximately 26.43 and 34.36 nm for  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ , respectively. It implies that the parameters used in the ALD process are able to deposit the oxides thin films onto both silicon and PET, as the substrates are deposited in the same ALD reactor.

Fig. 2 show the SEM images of uncoated PET (Fig. 2(a)) and PET surface coated  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3/\text{TiO}_2$  bilayer films by ALD (Fig. 2(b)–(d)). The surface of PET without ALD film shows particle-like

with wavy feature morphologies (Fig. 2(a)). The surface roughness reduces by presence the ALD film and it decreases significantly on the PET surface deposited by ALD with better film coverage (Fig. 2(c)–(d)). It was shown that PET surface coated  $\text{Al}_2\text{O}_3$  film is smoother than that of  $\text{TiO}_2$  film, which clearly indicates that the surface with  $\text{Al}_2\text{O}_3$  has better film coverage than that of  $\text{TiO}_2$  ALD. The smoothness of the PET surface can further increase by presence of  $\text{Al}_2\text{O}_3/\text{TiO}_2$  bilayer film as shown in Fig. 2(d), which shows that the  $\text{TiO}_2$  can be well grown onto the  $\text{Al}_2\text{O}_3$  film acted as a buffer layer and the perfect coverage with regular ALD growth has been obtained as indicated by disappearing the wavy surface morphology.

Structurally, PET is a semi-crystalline polymer at room temperature which has functional groups of  $\text{C}=\text{O}$  as carbonyl site [16,19]. The presence of functional groups with Lewis base characteristics in polymer backbone makes the polymer reactive during exposure of precursor which is a strong Lewis acid [20,21]. Upon exposure of precursor, carbonyl site of the PET polymer coordinates with precursor (i.e. TMA, Lewis acid to form an aluminum-oxygen-alkyl unit) [21]. In  $\text{Al}_2\text{O}_3$  ALD onto the PET substrate, a reaction forming a covalent aluminum-oxygen bond can proceed via methyl migration from TMA to the electrophilic carbon site of PET [19]. The possible reaction mechanism for TMA and  $\text{H}_2\text{O}$  reaction that the carbonyl stretch of  $\text{C}=\text{O}$  is eliminated by the TMA reaction with the carbonyl forming acetal group and a methyl transferred to the carbon of polymer backbone [19]. The subsequent water dose is likely to react with methyl in the acetal unit

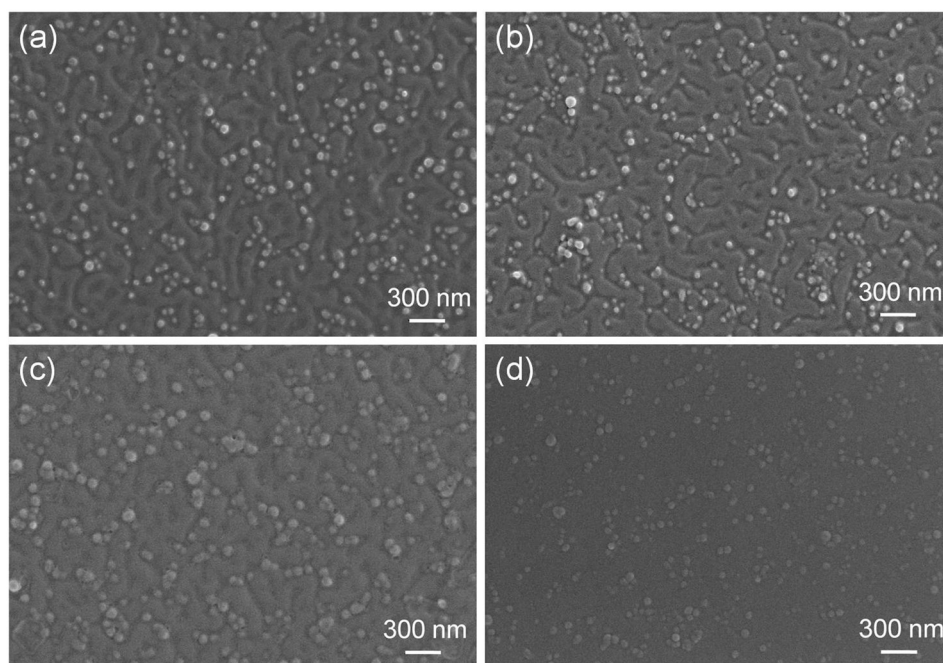


Fig. 2. SEM images of (a) uncoated PET and the PET surface coated (b)  $\text{TiO}_2$ , (c)  $\text{Al}_2\text{O}_3$  by ALD with 100 cycles., (d)  $\text{Al}_2\text{O}_3/\text{TiO}_2$  bilayer with both materials of 100 ALD cycles.

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