Preparation and Characterization of ATO/PS Bilayer Films with Superior Hydrophobicity

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Abstract. The hydrophilic films are widely used in industrial and domestic fields. Here, we report a Tin oxide film doped with antimony and Potassium silicate (ATO/PS) hydrophilic bilayer films deposited on aluminum substrates. The ATO film was prepared first on the substrates by spray pyrolysis and then PS film was deposited on ATO film by a simple dip-coating method. The structure, morphologies, wettability, stability of hydrophobicity and thermal conductivity of four kinds of samples have been analyzed in detail, including Al substrates (Al), Al substrate with ATO film (ATO), Al substrate with PS film (PS) and Al substrate with ATO/PS bilayer films (ATO/PS). The results show that the hydrophobicity of ATO/PS bilayer films is superior with contact angle of 12.5°. And the angle of ATO/PS sample is approach to 20° after being immersed in water for 48h, while 44.5° is obtained for the PS sample. The thermal conductivity value of ATO/PS sample is almost the same as the Al substrate, and also better than PS film. These results indicate that ATO/PS bilayer films have potential application in heat exchanger and other heat dispersing fields.

1. Introduction

Hydrophilic coatings have received considerable attention in recent years. Hydrophilic coatings are widely used in the application fields of self-cleaning [1] and anti-fogging [2] and especially in the aluminum fin of heat exchanger [3]. At present, the role of hydrophilic coating role is to improve the hydrophobicity of basal surface and prevent the corrosion of the substrates surface. Thompson et al. [4] prepared hydrophilic nano-SiO₂ coating on the glass substrates, the water contact Angle is less than 10°, and further validate the hydrophilic coating possess good self-cleaning performance. However, the preparation process of hydrophilic coatings is complicated and the thermal performance of hydrophilic films usually is worse [5-7]; these are problems that need to resolve in actual application.

On the other hand, ATO film possesses excellently chemical stability and dramatically thermal conductivity properties. The preparation methods mainly include spray pyrolysis method [8], chemical vapor deposition [9] and sol gel method [10]. Spray pyrolysis is one of the most commonly preparation methods due to its low cost, uniform film formation and suitable for large-scale industrial production. Due to ATO thin film has good thermal conductivity. So we prepared a bilayer film, which ATO film was prepared by spray pyrolysis method on the surface of substrates and hydrophilic film was fabricated on the ATO film by a simple dip-coating method.

In this paper, an ATO/PS bilayer film was deposited on the Al substrate by spray pyrolysis and dip-coating successively. The structures and morphologies of the ATO/PS bilayer films were investigated by X-Ray Diffraction, SEM and X-ray photoelectron spectroscopy. The hydrophobicity,
stability of hydrophilic properties and thermal conductivity were investigated, respectively.

2. Experimental

The schematic illustration of prepared ATO/PS bilayer films was shown in Figure 1. Al Substrates were cleaned by 5wt% sodium hydroxide solution and absolute ethyl alcohol for 10min by ultrasonic bath, respectively. Then, the substrates dried by blower. ATO film was prepared by spray pyrolysis method. The hydrophilic film was prepared by dip-coating on the surface of ATO film.

Tin (IV) chloride pent hydrate (SnCl$_4$·5H$_2$O) was dissolved in an aqueous solution of 10wt% hydrochloric acid (HCl). Then, antimony (III) chlorides (SbCl$_3$) were added to the above-mentioned solution, and adjust the molar ratio of Sn: Sb=9:1. Stirring until the yellowish solution was formed. Following, the prepared solution was transform into Medical atomizer. The ATO film was prepared on Al and glass substrates by spray pyrolysis method when the temperature of Al substrate was heated to 500°C. The time of atomization was maintained 15 minutes. After the substrates with ATO film were cooled to room temperature. The prefabricated ATO film was dipping into 10wt% potassium silicate solution. The potassium silicate solution was deposited onto ATO film by dip-coating with 2mm/s withdrawal rate and dried. This process was repeated 3times, respectively. And then the ATO/PS hydrophilic films were formed by heat treatment in an oven at 250°C for 1h. For comparison, Al substrate with ATO film (ATO) using same process of spray pyrolysis as described above, and Al substrate with PS film (PS) using same process of dip-coating as ATO/PS sample.

![Figure 1. The schematic illustration of prepared ATO/PS bilayer films](image)

The X-ray diffraction patterns were collected using a small angle X-ray diffract meter with CuK$_\alpha$ radiation (XRD, DMAX-UltimaIV, Japan). The scanning electron microscope (SEM, SU8010, Hitachi, Japan) was used to assess the surface morphologies of the films. The surface chemical compositions were obtained by X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD, Kratos, Japan). The contact angle system (OCA20, Data physics, Germany) was used to measure the wettability of the films. The heat conductivity coefficient of the films was detected by thermal conductivity measuring apparatus (LFA–447, NETZSCH, Germany).

3. Result and discussion

The XRD pattern of the ATO/PS bilayer films, ATO film and Al substrate are shown in Figure 2. For the sample of ATO film, the peak positions were agreed well with the reflections of tetragonal rutile structure of SnO$_2$. And the thickness of ATO film is enough to cover the peaks of Al substrate. As no other phases were detected, indicating that all antimony ions were embedded into the crystal lattice of rutile SnO$_2$ [11]. No obvious sharp diffraction peaks were found for the sample of ATO/PS bilayer films. This result suggested that the hydrophilic film formed on the surface of ATO film has an amorphous structure.
Figure 2. XRD pattern of ATO/PS hydrophilic films, ATO film and Al substrate

The morphologies of ATO film and ATO/PS bilayer films were shown in Figure 3. Figure 3(a) exhibited the surface morphology of ATO film prepared by spray pyrolysis at 500°C. It is obviously that ATO film consists of tiny, dense grains and no obvious holes are observed. The size of grains is approximately 400nm, and there are also a few large grains were formed. The cross-sectional SEM micrograph of ATO film (inset of Figure 3a) shows that the ATO film had a thickness of about 1.05μm. After dip-coating in potassium silicate solution, the ATO surface formed a smooth and uniform PS hydrophilic film layer with a thickness of about 0.82μm (as shown in inset of Figure 3b). The cross-section images of ATO/PS bilayer films also shows that this bilayer structure was considerable dense after dip-coating and have good protective effect for substrates.

Figure 3. SEM images of simples: (a) the morphology of ATO film and the cross-section. (b) The morphology of ATO/PS bilayer films and the cross-section.

In order to determine the chemical composition of the films prepared by spray pyrolysis (ATO film) and dip-coating (PS film), the films were further studied by XPS analysis. The Figure 4(a) showed the spectrum for the ATO film. The binding energies of 530.51eV and 539.71eV correspond to the Sb 3d$_{5/2}$ and Sb 3d$_{3/2}$, respectively. The peak of O1s at 530.38eV near overlap with Sb 3d$_{5/2}$. The Sn3d is observed at binding energy of 498.27eV, corresponding to SnO$_2$[12]. This result implies that the ATO film is successful prepared by spray pyrolysis. The Figure 4(b) exhibited the wide scanning of XPS spectra of ATO/PS hydrophilic films. The peaks near 531.93eV is attributed to O1s, and the peak near 101.8eV in attributed to Si2p [13]. This fact implies that the hydrophilic film contained silica with amorphous structure.
Figure 4. XPS spectrum of films: (a) the ATO film and (b) the ATO/PS hydrophilic bilayer films

Figure 5 shows the changes in the contact angle of water droplets on the four samples and the stability of hydrophobicity of Al/PS hydrophilic film and ATO/PS bilayer films. Figure 5(a) shows that the water contact angles are high on the Al substrate and ATO film. This mainly attributed to the rough morphology structure and without corresponding groups form hydrogen bonds with water molecules [14]. However, the water contact angle was significant reduced to 13.9° and 12.5° respectively after PS film was deposited on Al and ATO film. Such excellent hydrophobicity can be understood from the smooth surface morphology and the form of hydrogen bonds by amorphous SiO₂. These results indicated that the structure of ATO/PS bilayer films exhibited ideal wetting behavior. At the same time, it is obviously that the stability of hydrophobicity of PS sample gradually becomes worse along with the immersing time as shown in Figure 5(b). The water contact angle was increased to 44.5° after the film was immersed in water for 48h. Meanwhile, the water contact angle of ATO/PS sample maintain less than 20°, showing superior stability of hydrophobicity. These results shown that the ATO/PS bilayer film possess superior hydrophobicity and stability of hydrophobicity.

Figure 5. (a) The water contact angle of Al substrate, ATO film, PS film and ATO/PS bilayer films. (b) The water contact angle of PS film and ATO/PS films in different soak time

Figure 6 shows the variation of heat conductivity coefficient for Al substrate, ATO film, Al/PS film and ATO/PS bilayer films. The thermal conductivity of the ATO sample is higher than Al sample and other samples. The reason maybe is because that the Al substrate surface formed a layer of aluminum oxide reduced the heat conductivity property. The tightly ATO film deposited on Al substrate could prevent the oxidation of Al surface, and the thermal performance of ATO film is excellent. It is clear the thermal conductivity property of PS film is worse due to the amorphous structure.
4. Conclusions
The ATO/PS bilayer films have been deposited on the Al substrate by spray pyrolysis and dip-coating method successively. The morphologies and phase structure of the films have been characterized by SEM, XRD and XPS. The results show that amorphous PS film was deposited on ATO film. The results show obviously that the ATO/PS film possess superior hydrophilic properties than PS film. The water contact angle of ATO/PS bilayer films is only 12.5°, and maintained less than 20° after being dipped in water for two days. The thermal conductivity of the ATO/PS bilayer film deposited on aluminum substrate is similar to that of aluminum, while the value of PS film sample coated on Al plate is significantly decreased. It can be concluded that ATO/PS bilayer films have superior hydrophilic properties and good thermal conductivity.

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