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The corrosion of tin under thin electrolyte layers containing chloride

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ABSTRACT

The corrosion of tin under thin electrolyte layers containing chloride was investigated by electrochemical measurements and surface characterization. The results show that the corrosion rate increases as the electrolyte layer thickness deceases in the initial stage. Moreover, the corrosion rate under the same electrolyte layer thickness increases firstly and then decreases with the exposure time. In the later stage, the anodic processes under thin electrolyte layers of 50 and 100 μm are inhibited due to the difficult diffusion of dissolved metal ions. The corrosion products formed on tin surface are composed of stannous and stannic oxides and hydroxides.

1. Introduction

Tin and tin alloys are widely used in the electronics industry for various purposes such as tin alloys as soldering materials and as coating connectors on structural materials. Tin and tin alloys used for these purposes are required to provide low degree of contact resistances and high degree of corrosion protection [1]. In the past few decades, the size of components and the space of conductors have rapidly reduced in connection with the production of high compact and lightweight electronic products [2]. It is believed that even minor surface changes with thin electrolyte layers or corrosion products can result in the failure of electronics components. Therefore, the corrosion of tin and tin alloys in humid environment has attracted more concern today in the aspect of the reliability of electronics materials.

It is acknowledged that the corrosion behavior of tin and tin alloys in bulk solution has been well investigated in recent years concerning three aspects. Firstly, some researchers focused on the effect of alloying elements [3–7] (e.g., Ag and Cu) and corrosion media (e.g., NaCl and Na_2SO_4 solution) [8] on the electrochemical corrosion behaviors of tin and its alloys. Secondly, some studies focused on the formation and characterization of the passive films or corrosion products films on tin and its alloys surfaces in different solutions including NaOH [9,10], NaCl [11], and carbonate [12] and fruits acids solutions [13]. Lastly, electrochemical migration derived from the corrosion of tin and tin alloys has also attracted more and more microelectronics or corrosion experts' attentions in recent years. Electrochemical migration is usually investigated using water drop experiment in distilled water [14], deionized water [15,16], NaCl or Na_2SO_4 solution [8,17–19].

However, considering the environments of the transportation, storage and usage of electronic devices, the corrosion of tin and its alloys is more similar to the atmospheric corrosion. The corrosion behavior in atmospheric environments is significantly different from that in bulk solution. Atmospheric corrosion of metals proceeds under thin electrolyte layers. A change in the thickness of the electrolyte layers affects some processes, e.g., the mass transport of dissolved oxygen, the accumulation of corrosion products, and the hydration of dissolved metal ions [20]. Over the last decades, several laboratory investigations on metals or alloys under thin electrolyte layers have been conducted to determine the significant factors initiating metal corrosion in atmospheric environments [21–27]. For tin, Sasaki and co-workers [1] employed IR spectra to study the corrosion products of tin in humid air containing sulfur dioxide and nitrogen dioxide at room temperature. Medgyes et al. [28] used thermal humidity bias test to investigate the electrochemical migration of the dissolved tin ions under atmospheric environments with 40 °C and 95 RH%. However, until now no attempt has been made to study the electrochemical corrosion behavior of tin under thin electrolyte layers. Therefore, as one of the most important electronic and micro-electronic materials, it is of great significance to study the corrosion of tin under thin electrolyte layers.

In the present work, electrochemistry impedance spectroscopy (EIS) and cathodic polarization measurements were conducted to investigate the cathodic reduction of oxygen, the formation of corrosion products films of tin under thin electrolyte layer containing chloride. Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy

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(XPS) were also employed to detect the composition and morphology of corrosion products films.

2. Experimental

2.1. Setup for in situ electrochemical measurements under thin electrolyte layers

The specimens used in this study were pure tin (>99.999 wt.%) with the dimensions of 2 × 5 × 10 mm. Two identical tin electrodes, i.e. a working electrode (WE) and a counter electrode (CE), were embedded in an epoxy resin cylinder with 0.5 mm distance in parallel direction, as shown in Fig. 1. A lead wire was welded to the backside of each electrode to ensure electrical contact for electrochemical measurements. On the upper surface of the epoxy resin cylinder, a hole with a diameter of 1 mm was drilled through at the position of 1 mm apart from the WE and CE. This hole was filled with saturated KCl agar as salt bridge. The bottom of the epoxy resin cylinder was connected to a U-shape tube which filled with saturated KCl solution, as shown in Fig. 2. A saturated calomel electrode (SCE) was placed in the U-shape tube as reference electrode (RE). This configuration, which is similar to that reported in our previous paper [29,30], makes it possible to perform electrochemical measurements of an electrode under thin electrolyte layers and minimized the ohmic drop between RE and WE. Before each experiment, the working electrode surface was ground up to 3000 grit silicon carbide paper. Subsequently, the surface was rinsed with distilled water, degreased with acetone, and dried in cool air.

After the pre-treatment for electrochemical measurements, the whole setup was put on a horizontal stage, which could be adjusted by using a spirit level. After being adjusted the horizontal position, the setup was put into a constant temperature and humidity chamber which controlled the test temperature and relative humidity (RH). All measurements were performed at 20 °C, 65% RH in this study.

After the electrochemical cell was set up, electrolyte was added to the electrochemical cell to form a thin electrolyte layer on electrode surface. The electrolyte was 0.5 M NaCl, which was prepared from deionized water and analytical grade reagent. The pH of the electrolyte was 6.7. The thickness of thin electrolyte layer on the electrode surface was determined by using a home-made setup (shown in Fig. 2), which consisted of a z-stage, a Pt needle (Φ = 0.1 mm), a micrometer and an ohmmeter. The Pt needle was welded on the edge of the z-stage and the micrometer was fixed at z-stage to measure the movements of z-stage and Pt needle. The Pt needle can be moved in z-axis direction by rotating the micrometer. The ohmmeter was used to measure the current between the electrode and Pt needle. During the measured process of the thickness of the thin electrolyte layer, the Pt needle was adjusted slowly toward electrolyte surface and electrode surface. Before the Pt needle touched electrolyte, the circuit between the electrode and Pt needle was break. Then, no current was observed in the ohmmeter. Once the Pt needle touched the electrolyte, there was a current observed in the ohmmeter. Then the position of Pt needle was recorded by micrometer. When the Pt needle further moved to touch the electrode surface, there was a sudden increase of the current in the ohmmeter. The position of Pt needle was also recorded by micrometer. Then, the difference in the position between the Pt needle touching the electrolyte and touching the electrode was the thickness of thin electrolyte layer. This technique enabled us to measure the thickness of the electrolyte layer with an accuracy of 10 μm. The setup for measuring the thin electrolyte layer thickness used in this work was similar to that reported by Nishikata et al. [25]. When the thickness of the electrolyte layer exceeds 1000 μm, the corrosion rate is almost the same as that in bulk solutions [20,29]. Therefore, the thickness of the thin electrolyte layer varied between 50 and 1000 μm in this study.

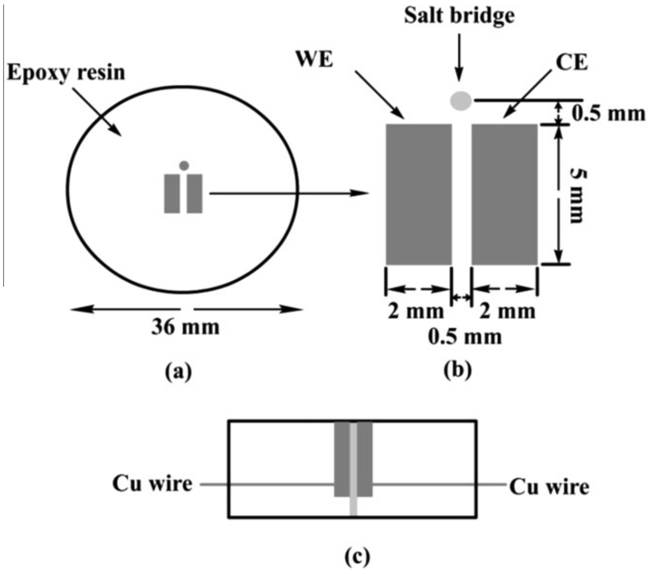

Fig. 1. Schematic diagram of the electrodes (a) and (b) top view, (c) transverse cross-sectional view.

2.2. Electrochemical measurements

The electrochemical measurements, including electrochemical impedance spectroscopy (EIS) and cathodic polarization curve measurements, were carried out with a CS350 electrochemical workstation. All the potentials were with respect to SCE. Cathodic polarization curve measurements were performed by shifting the potential from open circuit potential (OCP) to the cathodic direction with a scanning rate of 0.5 mV/s. EIS measurements were performed at OCP with a 10 mV sinusoidal perturbation at the frequency from 10 kHz to 10 mHz, with 12 points per decade. Zview software was used to analyze the EIS data with transmission line model. In order to check the reproducibility, all the electrochemical measurements were repeated at least three times.

2.3. Characterization of the corrosion products films

The surface morphologies of specimens were observed by SEM (Phillips Quanta 200, America). Meanwhile, the corrosion products films formed on electrodes surface under chloride-containing thin electrolyte layers were analyzed by FT-IR using a Vertex 70 FT-IR spectrophotometer under ATR reflectance mode. The XPS spectra were measured using a commercial VG Multilab 2000 system (America). The base pressure in the experimental chamber was in the range of 10^{-9} mbar. The spectra were measured using Al Ka (1486.6 eV) radiation and the overall energy resolution were about 0.45 eV. The surface charging effect during measurements was compensated by referencing the binding energy (BE) to C1s line of residual carbon at 284.6 eV. Spectral decomposition was performed by using background subtraction and a least square fitting program.

3. Results and discussion

3.1. Cathodic polarization curve measurements

Fig. 3 shows the cathodic polarization curves of tin under 0.5 M NaCl thin electrolyte layers with various thicknesses. Each cathodic