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Inhibitory effect of cetyltrimethylammonium bromide on the electrochemical migration of tin in thin electrolyte layers containing chloride ions

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ABSTRACT

This paper presents a new strategy involving the introduction of the common cationic surfactant cetyltrimethylammonium bromide (cetrimonium bromide, CTAB) to inhibit the electrochemical migration (ECM) of tin in thin electrolyte layers containing chloride ions. The inhibitory effect of different CTAB concentrations on tin ECM under different bias voltages was evaluated using in situ electrochemical and optical techniques, as well as ex situ characterizations. Results showed that CTAB can effectively inhibit tin ECM, and CTAB affected the electrodeposition during tin ECM by selective adsorption. Mechanisms were proposed to explain the beneficial role of CTAB.

1. Introduction

Electrochemical migration (ECM), which is a form of corrosion influenced by the bias voltage, compromises the reliability of electronic devices significantly [1]. This phenomenon can occur when two closely spaced electrodes are connected by moisture or condensed water drops with applied potential difference. During ECM, metal ions are dissolved at the anode and migrate toward the negatively charged cathode, where they can be deposited to their metallic state and form dendrites. Under conducive conditions, dendrites outward from the cathode extend toward the anode, causing a short circuit between the two electrodes and catastrophic failure of electronic devices [2]. ECM has become a severe potential problem, considering the miniaturization and high density of electronics over the year [3].

Due to the inherent toxicity of lead and lead-containing compounds, many countries have introduced legislation to ban lead from electronic products in the past decade; for instance, Japan has required all new electronic products to be lead-free since January 2005 [4]. Extensive efforts have focused on searching for alternatives to lead-containing solder, such as lead-free alloys and electrical adhesives [5–7]. To date, the most promising lead-free alloys contain tin as the primary element because of its low melting temperature (232 °C) and good wettability properties on substrates such as Cu, Ag, and Au [8,9]. Considering the key roles of tin and tin based solder alloy in the modern electronics industry, many investigation focused on the mechanism of tin ECM [1,10,11], ECM test methods [12,13], and the effects of alloy elements [14,15], bias voltage [16,17], and pollutants [18,19] on tin ECM. However, a strategy to inhibit tin ECM remains lacking to date. Therefore, developing an effective method to inhibit tin ECM is of great significance.

Additives are commonly used to produce a desirable deposit in electroplating applications [20]. Additives can be classified as surface-active agents, oxidation inhibitors, grain refiners and brighteners, etc. [21]. Quaternary ammonium surfactants have been used extensively as leveling compounds in the industry [22]. Cetyltrimethylammonium bromide (CTAB) is an important common quaternary ammonium surfactant that has been used extensively as a structure-directing agent to control the nucleation, growth, and alignment of crystals [23,24]. Nayana et al. [25] reported that the presence of CTAB inhibited the growth {002} and

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{004} planes of zinc deposit while it caused the growth of {110} preferred orientation. CTAB was also used to modify the surface of CuO spheres to needle-like hierarchical structure as an anode for lithium-ion batteries [26]. One step in ECM is the electrodeposition of metal ions at the cathode. In this case, CTAB may be used as a structure director to retard tin ions from depositing to form tin dendrites and thus inhibit tin ECM. To the best of our knowledge, few studies have applied such an organic additive as CTAB to inhibit tin ECM.

The present study investigated the inhibitory effect of CTAB on tin ECM in thin electrolyte layers (TELs) containing chloride ions by using in situ electrochemical and optical techniques. The morphology and composition of products were analyzed using scanning electron microscopy (SEM) coupled with an energy dispersive spectrometry (EDS), X-ray diffraction (XRD), attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR), and X-ray photoelectron spectroscopy (XPS). Moreover, the effects of different CTAB concentrations on tin ECM under various applied bias voltages were investigated. Relevant mechanisms have been discussed in detail.

2. Experimental

2.1. Materials and apparatus

Pure tin (>99.999 wt.%) was used in this experiment. Two identical specimens with dimensions of 2 mm × 5 mm × 10 mm were sealed using epoxy resin with 0.1 cm^2 exposed areas and applied in ECM tests as the working and counter electrodes. A gap size of 0.5 mm was in parallel direction and a copper wire was welded to the backside of each electrode to ensure the electric connection. All test surfaces were ground to 1200 grit with silicon carbide paper. The surfaces were then rinsed with deionized water, degreased with acetone, and dried in cool air. The experimental setup was based on our previous work with slight modifications, as shown in Fig. 1. [13,27]. During the experiment, a Zahner IM6e electrochemical workstation was used for the ECM tests. The current flowing through the two electrodes was recorded as a function of time after required direct current bias voltage (2–8 V) was applied between the two tin electrodes. Here, the potential bias means the potential drop across the electrodes. The ECM cell was covered with a glass lid to minimize the evaporation of the TEL.

All solutions were prepared using deionized water (18.2 MΩ cm in resistivity) and analytical-grade reagents. The surfactant concentrations (0.1–0.8 g/L) were selected taking into account the critical concentration (ca. 0.31 g/L) [28]. During the ECM tests, typical morphologies of the electrode surface were recorded under a VHX-1000E digital 3D microscope (Keyence, Japan). All ECM measurements were repeated at least three times to ensure reproducibility.

2.2. Preparation of tin deposits

Tin deposits were plated from a solution containing 0.01 mol/L SnCl_2 using the galvanostatic method for 90 min with a current density of 3 mA/cm^2 at room temperature under a slight N_2 flux [29]. The electroplating cell consisted of three electrodes. A 316 stainless steel plate (1 cm^2) was used as the working electrode, the counter and reference electrodes were a large Pt foil (2 cm^2) and a saturated calomel electrode (SCE), respectively. Prior to each electrodeposition, the surface of working electrode was ground with 1200 grit silicon carbide paper and then polished with 1.5 μm diamond paste and 0.3 μm Al_2O_3. The electrodeposited films were then rinsed thoroughly in deionized water, dried in nitrogen stream, and used for surface analysis.

2.3. Ex situ characterizations of dendrites and precipitates

After the ECM tests, the samples were dried in nitrogen gas at room temperature. Then, morphologies of the dendrites and the surface of cathode were ex situ examined using a Phillips Quanta 200 SEM system. XPS analysis of the specimen surfaces was carried out using a commercial VG Multilab 2000 system (America). The base pressure in the experimental chamber was in the low 10^{-9} mbar range. The XPS spectra were obtained using Al Ka (1486.6 eV) radiation, and the overall energy resolution was about 0.45 eV. The surface charging effect during measurements was calibrated through referencing the binding energy (BE) to the C1 s line of the residual carbon peak (around 284.6 eV). Spectral decomposition was performed after background subtraction with a least square fitting program. The products of tin ECM were analyzed using a Vertex 70 ATR-FTIR spectrophotometer in reflectance mode to verify the adsorption of CTAB on the electrode surface. The ATR-FTIR spectra were collected with a resolution of 4 cm^{-1}, and 64 scans were averaged for each sample. XRD analysis was carried out using a PANalytical B.V. X-ray diffractometer (model X'Pert PRO) with Cu Kα radiation ($\lambda = 0.15604$ nm). The diffractograms were obtained in the 2θ range of 10°–90° with a 0.02° step and an acquisition time of 2 s/step.

3. Results

3.1. Current density vs. time curves with varied CTAB concentrations and bias voltages during ECM

The current density transients measured between the two electrodes when a bias voltage was applied between them, showed

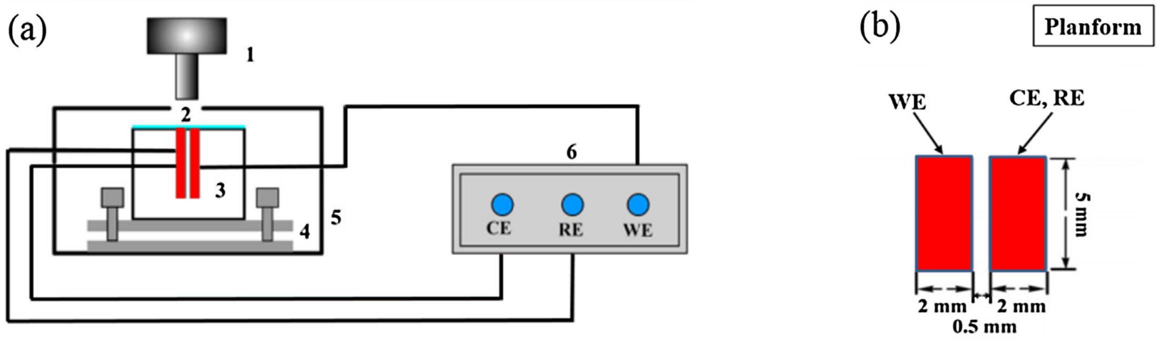

Fig. 1. (a) Schematic of setup for electrochemical migration under TEL: 1 3D microscope, 2 thin electrolyte layer, 3 electrode, 4 horizontal stage, 5 thermal humidity chamber and 6 electrochemical workstation; (b) Planform of the electrode.

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