Short Communication

Effect of direct current electric field on atmospheric corrosion behavior of copper under thin electrolyte layer

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A B S T R A C T

A thin layer electrochemical cell was successfully developed to study the atmospheric corrosion behavior of copper film in printed circuit board (PCB-Cu) under thin electrolyte layer (TEL) and direct current electric field (DCEF) by electrochemical impedance and electrochemical noise analysis. The electrochemical measurements and SEM morphologies after corrosion test indicate that DCEF decreases the corrosion of PCB-Cu under TEL. The corrosion rate and probability of pitting corrosion of PCB-Cu under DCEF decrease due to the electric migration of aggressive Cl⁻ ion out of working electrode surface.

1. Introduction

Electronic components in integrated circuit (IC) are the core parts of electronics and communication technology, and prone to atmospheric corrosion failure due to the humidity and contaminants (Cl⁻, SO₄²⁻, SO₂, etc.)[1]. With the continual microminiaturization of IC, the corrosion of electronic components could damage the electrical properties of the adjacent regions due to the formation of the conductive corrosion products. Even slight corrosion of electronic components would result in the complete failure of IC.

The atmospheric corrosion of electronic components in IC generally occurs under thin electrolyte layer (TEL). When the relative humidity (RH) is lower than 100%, the thickness of TEL is less than 1 μm[2]. It is expected that corrosion behavior of electronic components under TEL is different from that in bulk solution since there would be different corrosion-related processes under TEL, such as the mass transport of dissolved oxygen, the accumulation of corrosion products and the hydration of dissolved metal ions. Many studies on atmospheric corrosion of metals or alloys have been reported under thin electrolyte layers (TEL, thickness >10 μm) during the past decades [3–9]. However, due to the difficulty in the study on atmospheric corrosion by electrochemical methods, most studies were carried out via exposure test in outdoor [10–14] and indoor [15,16].

Copper is a critical material for printed circuit board (PCB) in electronics industries and prone to atmospheric corrosion [17–20]. In communication and electronic industries, copper is used to connect to various electronic chips in IC. Upon running the IC, a strong electric field will form between these copper wires. The different corrosion behavior of copper film in printed circuit board (PCB-Cu) is expected under electric field. However, the effect of electric field on atmospheric corrosion behavior of PCB-Cu under TEL has not been reported so far.

In the present work, a thin layer electrochemical cell was developed to study the corrosion behavior of PCB-Cu under TEL by electrochemical method, the detail of the cell are shown in previous reported literature[21]. Schematic diagram of PCB-Cu with electric field shown in Fig. 1. It is seen that four identical PCB-Cu electrodes were connected in series with a battery for applying DCEF. The advantage of this cell is to minimize the ohmic drop between the reference and working electrodes and the uneven current distribution over the working electrode. With this cell, the corrosion behavior of PCB-Cu under TEL and DCEF were investigated by electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN). The surface morphologies of PCB-Cu after corrosion were observed by scanning electron microscopy (SEM).

2. Experimental

To study the corrosion mechanism of PCB-Cu under TEL and DCEF by electrochemical method, a thin layer electrolytic cell was developed, the detail of the cell are shown in previous reported literature [21]. Schematic diagram of PCB-Cu with electric field shown in Fig. 1. It is seen that four identical PCB-Cu electrodes with the size of 20 × 1.5 × 0.035 mm. The distance between any two adjacent PCB-Cu electrodes was 0.5 mm. The two outermost PCB-Cu electrodes, as the positive and negative poles, were connected with a battery for applying DCEF. The two PCB-Cu electrodes in the middle were used as working electrode (WE) and counter electrode (CE). These two electrodes were welded to
copper wires respectively to assure the electric connection for electrochemical measurements. Prior to test, the PCB-Cu electrodes were ground to 1000 grit silicon carbide paper and then polished with 14–20 μm diamond paste, degreased with acetone, rinsed with distilled water.

The test temperature and RH was 65 °C and 95%. 1.5 mL of 0.1 M NaCl solution was naturally dripped on the surface of PCB-Cu electrodes, and then was spread on the surface of plexiglass cylinder, the surface area of the electrolyte spreading was about 12.5 cm², so the thickness of the initial TEL in this experiment was 1.2 mm. When temperature and humidity reached and maintained the set value, TEL would be formed on the whole electrode surface, but the thickness of TEL (thickness <1 μm) was too thin to measure, so the thickness of TEL was not given in this paper. Usually, when the RH and temperature maintain a constant, the thickness of TEL is also a constant on the surface of the same metal.

The EIS measurements were performed at open circuit potential with a 10 mV AC perturbation at the frequency from 100 kHz to 50 mHz with five points per decade after the system stabilized for 2 h by using CS350 electrochemical workstation. After stabilized for 75 min, the ATEL was formed, and then the different dc bias was applied for 45 min before EIS measurement. The current values between positive and negative poles were less than 50 μA and did not almost change the DC bias.

EN measurements were performed using a CS500 Zero Resistant Ammeter (ZRA). Two PCB-Cu electrodes were used as WEs, SCE was used as the reference electrode. The coupling potential and current between the two identical WEs was measured simultaneously [21]. The electrochemical measurements were repeated more than three times.

The electrodes were rinsed with deionised water after exposed for 24 h, the surface morphologies of PCB-Cu were observed by SEM. The composition of corrosion product was also determined by EDXA.

3. Results

Fig. 2 shows the Nyquist diagrams and Bode plots of PCB-Cu under TEL containing 0.1 M NaCl for 2 h at 95% RH and 65 °C with and without DCEF: (a) Nyquist diagrams, (b) Bode plots.

Fig. 3 shows the EN plots of PCB-Cu under TEL with and without DCEF. It is seen that the significant potential and current fluctuations, which is the indicator of initiation of metastable pits, are observed on the PCB-Cu electrode without DCEF. However, the amplitude of potential and current reduces with DCEF, which suggests that the DCEF to some extent can inhibit the initiation of metastable pits. The maximum amplitude of noise potential and current is 0.133 V and 0.506 μA cm⁻² without DCEF, the maximum amplitude of noise potential is 0.005 V, 0.007 V, 0.004 V for 44.4 V m⁻¹, 111.1 V m⁻¹ and 222.2 V m⁻¹ respectively, and the maximum amplitude of noise current is 0.298 μA cm⁻², 0.190 μA cm⁻², 0.101 μA cm⁻² for 44.4 V m⁻¹, 111.1 V m⁻¹ and 222.2 V m⁻¹ respectively, which indicates that the maximum amplitude of noise potential and current with DCEF is also lower than that without DCEF. So all these results confirm that the DCEF reduces the initiation rate of metastable pits.

Fig. 4 shows the SEM morphologies of PCB-Cu under TEL with different DCEF. Relative severe corrosion, including general corrosion and localized corrosion, is observed on the PCB-Cu electrode.
Fig. 3. EN plots of PCB-Cu under TEL containing 0.1 M NaCl at 95% RH and 65 °C for 12 h with and without DCEF: (a) 0 V m\(^{-1}\), (b) 44.4 V m\(^{-1}\), (c) 111.1 V m\(^{-1}\), (d) 222.2 V m\(^{-1}\).

Fig. 4. SEM surface morphologies of PCB-Cu under TEL containing 0.1 M NaCl after 24 h at 95% RH and 65 °C with and without DCEF: (a) 0 V m\(^{-1}\), (b) 44.4 V m\(^{-1}\), (c) 111.1 V m\(^{-1}\), (d) 222.2 V m\(^{-1}\).
surface without DCEF. With increasing DCEF, the degree of PCB-Cu corrosion reduced. Only slight corrosion is observed on the PCB-Cu electrode surface with applying 222.2 V m$^{-1}$ DCEF.

4. Discussion

EIS measurements and the SEM surface morphologies after corrosion test indicate that the corrosion of PCB-Cu without DCEF is more severe than those with DCEF. Moreover, the corrosion rate decreases with increasing DCEF. EN measurements also show that initiation rate of metastable pits on the PCB-Cu electrode decreases under DCEF. All these results indicate that DCEF decreases the corrosion of PCB-Cu under TEL. The effect of DCEF on the corrosion of PCB-Cu under TEL can be ascribed to the effect of DCEF on the transfer process of ions in TEL and the formation of the copper chlorides. Moreover, anodic dissolution of copper positive pole electrode under DCEF binds the chloride that decreases it concentration in thin electrolyte layer. The anions (mainly Cl$^-$/C$_0$ ions) on the PCB-Cu surface would transfer to positive pole under the effect of DCEF while the cations would transfer to negative pole. This effect becomes more significant with increasing DCEF. When Cl$^-$ ions transfer out of PCB-Cu electrode surface without complement, the aggression of TEL decreases and a low corrosion rate of PCB-Cu would be expected. Moreover, the decrease of aggressive Cl$^-$ ion concentration reduces the localized corrosion of PCB-Cu electrode. To verify the effect of DCEF on the ions transfer process, the EDXA of the corrosion products was performed after corrosion test. The results show that the content of Cl in the corrosion product without DCEF ($5.37$ wt.%) is higher than those with DCEF ($3.23$ wt.$\%$, $2.03$ wt.$\%$ and $1.35$ wt.$\%$ for $44.4$ V m$^{-1}$, $111.1$ V m$^{-1}$ and $222.2$ V m$^{-1}$ DCEF, respectively). Furthermore, an enrichment of Cl is found at the positive pole ($11.8$ wt.$\%$) after corrosion test, which further confirms the immigration of ions under DCEF. It is clear that the immigration of ions out of PCB-Cu surface should account for the reduction of the corrosion rate of PCB-Cu under TEL and DCEF.

5. Conclusions

The thin layer electrochemical cell is effective to study the corrosion behavior of PCB-Cu under TEL (thickness <1 μm) and DCEF by electrochemical measurements. DCEF decreases the corrosion of PCB-Cu under TEL. The reduction of corrosion rate and probability of occurring pitting corrosion of PCB-Cu under TEL and DCEF is attributed to migration of Cl$^-$ ion out of PCB-Cu electrode surface and formation of sparingly soluble copper chlorides.

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References