



## Materials science communication

## Dependence of electrochemical migration of sintered nanosilver on chloride

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## H I G H L I G H T S

- Silver oxide and silver chloride play important roles in the migration of sintered nanosilver.
- Slight chloride can shorten the time to short electrodes.
- High chloride concentration hinders the electrochemical migration of sintered nanosilver.

## A R T I C L E I N F O

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## A B S T R A C T

We studied the influence of chloride on electrochemical migration (ECM) of sintered nanosilver (SNS) by in-situ electrochemical and optical techniques, as well as ex-situ characterization. The results show that time to bridge electrodes appears an increasing tendency with increasing the chloride because of produced precipitates that may retard silver dissolution and migration. Mechanisms have been proposed to explain the electrochemical migration of SNS in chloride electrolytes.

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## 1. Introduction

The European power electronics industry is leading the way of introducing a superior lead-free die-attach technology, low temperature joining technology, to the market place. Recently, Lu et al. [1–3], had demonstrated a strategy of replacing the high mechanical pressure with a chemical driving force by using silver nanoparticles to lower the sintering temperature. Although sintered silver has several potential benefits over other die-attach materials, e.g., higher melting temperature than solders and lowest resistivity at room temperature of any metal [4], silver is susceptible to migration because silver is anodically soluble [5,6].

Electrochemical migration (ECM) occurs between two oppositely biased and closely spaced electrodes by an aqueous electrolyte [7]. Silver ECM is a serious concern for the reliability of silver because growth of conducting filament is likely to cause the failure

of electronic components in high humidity and impurities [8–11]. Closer spacing due to demand for miniaturization and contamination issues is contributing to dramatic increases in the risk of failures due to the ECM [12,13]. Some studies have shown that impurities and moisture plays crucial roles in ECM of silver [6,14–17]. Chloride is one of the most common chemistry elements in electrochemical processes [18–23]. It was investigated that chloride also plays important roles in ECM processes. For example, Zhong et al. [24], and Noh et al. [25], studied the chloride influence on the ECM of tin and copper, respectively. However, there are few reports on the effect of chloride on ECM of sintered nanosilver (SNS).

In our study, the ECM behavior of SNS in thin electrolyte layer (TEL) with various chloride concentrations was studied by in-situ and ex-situ techniques. TEL test can improve the reproducibility relatively compared to the thermal humidity bias (THB) test and droplet test [17,24].

In order to provide possible ways to mitigate ECM of SNS, we studied the ECM in NaCl electrolyte by TEL tests and proposed a

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mechanism of the ECM.

## 2. Experimental

The particles in the nanosilver paste have an average size of around 30 nm [2]. Fig. 1 shows the electrode pattern and a sample for TEL tests. The paste was stencil-printed onto a typical 96.5% alumina substrate (30 mm × 22 mm) [22]. The heating profile was suggested by the manufacturers [26,27]. The area for TEL tests was fixed as 8 mm × 8 mm × 78 μm. The thickness of SNS is 50 μm. The closest spacing between the electrodes is 1 mm. Approximately 50 μL NaCl electrolyte containing pH indicator was dropped on the sintered electrodes. The pH indicator added to the electrolytes is a kind of universal reagent to visualize pH distribution on the electrodes and the gap between the electrodes during the ECM process. A constant DC bias, i.e., 3 V, was applied between the electrodes. A video microscope was used to in-situ record the ECM of SNS. Optical microscopy and X-ray Diffraction (XRD) were used to characterize the ECM at ambient temperature. The leakage current between the electrodes was in situ recorded by a galvanometer (±0.1 μA). The chloride concentration in the electrolytes ranges from 0 to 400 ppm by weight (0 mM–6.8 mM).

## 3. Results and discussion

In electrolytes containing chloride with different concentrations, the dominant reactions before forming silver dendrites could be expressed as follows:

Anode:

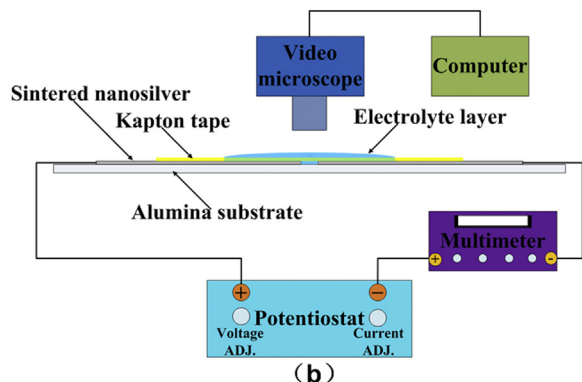
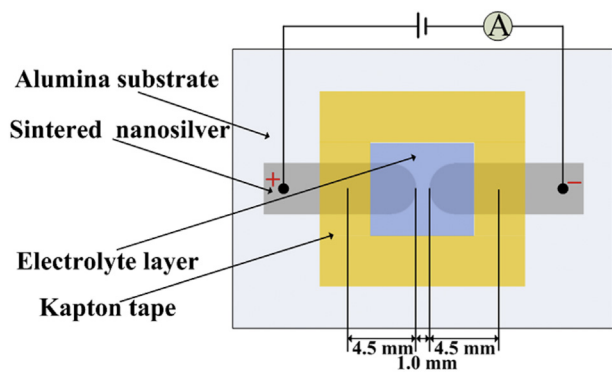
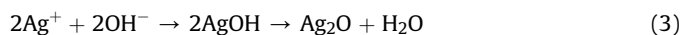
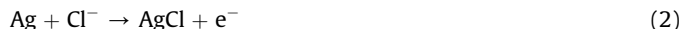


Fig. 1. Schematic diagram of (a) pattern of SNS for TEL tests, and (b) setup layout of TEL tests.



Cathode:

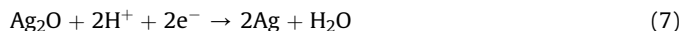


Fig. 2 shows the optical images of the ECM of sintered nanosilver electrodes after 30 s. Bubbles are not observed at the cathode (right) in the de-ionized water (Fig. 2a), but appear in chloride electrolytes. The amount of the bubbles increases with increasing the chloride. Meanwhile, precipitates at the anode (left) increase with increasing the chloride. Both the electrical conductivity and the current were increased with increasing the chloride concentration. Both the cathodic reaction and anodic corrosion speed in the chloride (reaction (2)) should be faster than that in de-ionized water (reaction (1)) [28,29]. Dendrites can be observed in de-ionized water, 10 ppm and 100 ppm chloride electrolytes (Fig. 2b and c). The dendrites were usually formed at the middle position of the cathode because voltage drop is largely located between the electrodes with the closest gap [30]. However, dendrites are not

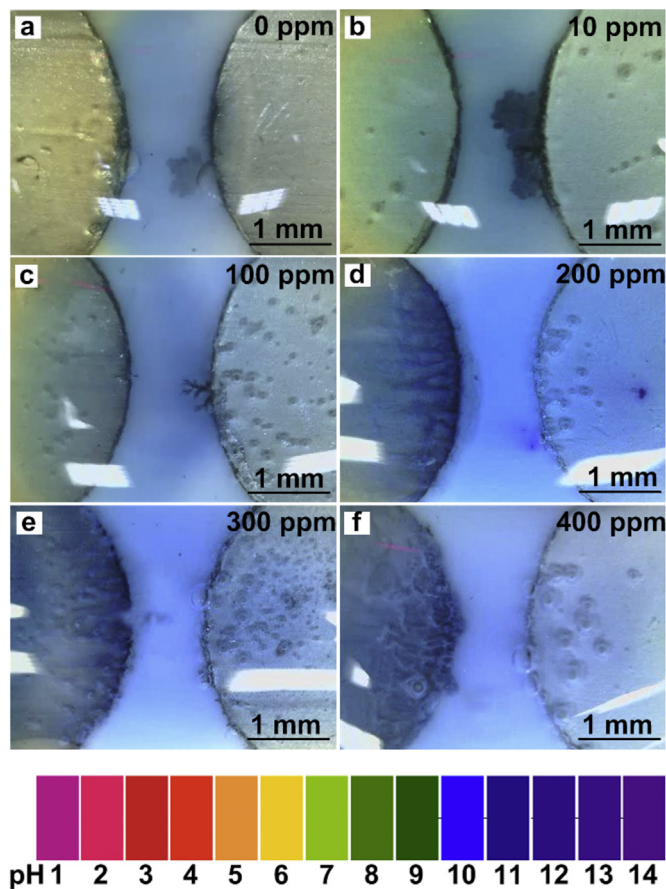


Fig. 2. Optical micrographs of pH distribution during ECM on the both electrodes using pH indicator in electrolyte layer with various chloride concentrations under 3-V of bias at 30 s.

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