Observed Correlation of Sn Oxide Film to Sn Whisker Growth in Sn-Cu Electrodeposit for Pb-Free Solders

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Localized cracking of surface oxide has been proposed as a necessary step in the nucleation of Sn whiskers in Sn electrodeposited films. To evaluate the effects of the oxide film on Sn whisker growth, a bright Sn-Cu electrodeposited film was inserted into an ultrahigh vacuum Auger system, cleaned using an Ar^+ ion beam to remove the oxide film, and aged in the 2×10^{-9} Pa Auger system chamber. Whiskers and other features present during Ar^+ ion cleaning left visible "shadows" on the surface. During aging in the ultrahigh vacuum system, new whiskers, identified by the absence of the telltale shadows, nucleated and grew. Based on these observations, the presence or absence of an oxide film has a minimal effect on Sn whisker nucleation and growth.

Key words: Electrodeposition, Sn whisker, surface oxide film, Auger, Pb-free solder

INTRODUCTION

In general, Sn electrodeposits for surface finishes form whiskers spontaneously at room temperature in order to release the compressive film stress employed intrinsically or extrinsically. Thus, Sn-Pb alloys have been used extensively in part because Pb was found to be effective in retarding Sn whisker growth in electrodeposits. As Pb-free solder alloys replace the widely used Sn-Pb eutectic, electronic manufacturers are seeking a reliable Pb-free surface finish technology that can be guaranteed to produce no Sn whiskers. There is ample evidence that Pb should be avoided in surface finishes used with Pb-free alloys, particularly for high reliability applications, due to the possible formation of a low melting eutectic that could lead to fillet lifting and degradation during thermomechanical fatigue.[1,2]

As shown in Table I, Sn is a strong oxide former. Several authors[4–6] have postulated that the Sn oxide film plays a dominant role in inhibiting homogeneous stress relaxation. Fracture of the oxide film is then necessary for the localization of stress relief, whisker nucleation, and subsequent whisker growth. However, Moon et al.[7] showed that whiskers were observed only on bright Sn-Cu electrodeposits not on pure bright Sn electrodeposits if high-purity water (18 M Ω-cm) was used to prepare the commercial methanesulfonate electrolyte on pyrophosphate Cu substrates. Since Sn and Sn-Cu electrodeposits have the Sn oxide surface film, this result leads us to question whether the Sn oxide film plays the dominant role in inhibiting homogeneous stress relaxation.

The experiments presented here are aimed at evaluating the role of the oxide film in whisker formation by examining Sn whisker nucleation and growth before and after oxide film removal by an Ar^+ ion beam in an ultrahigh vacuum Auger system. In this research, a bright Sn-Cu electrodeposited film was cleaned using an Ar^+ ion beam to remove the oxide film, and aged in the 2×10^{-9} Pa Auger system chamber. Bright Sn-Cu films formed with the electrolyte and substrate system used in these experiments readily form whiskers during room temperature storage. Our results indicate that the oxide film plays little or no role in whisker nucleation and growth.

EXPERIMENTAL PROCEDURE

A Sn-1.5% Cu mass fraction electrodeposited film, 15.1-μm thick, was prepared from a commercial

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**Table I. Some Examples of Gibbs Energy of
Formation of Metal Oxide at 298 K in kJ/mol[3]
(Note That the Gibbs Energy of Sn Oxide
Formation is Based on the Liquid Phase)**

Reaction	Gibbs Energy
$2Al(s) + 3/2O_2 (\rightarrow Al_2O_3$	$-1,582.1$
$Sn(l) + O_2 \rightarrow SnO_2$	-519.6
$2Bi(s) + 3/2O_2 \rightarrow Bi_2O_3$	-493.2
$Zn(s) + 1/2O_2 \rightarrow ZnO$	-320.5
$2Cu(s) + 1/2O_2 \rightarrow Cu_2O$	-147.7

bright methanesulfonate electrolyte on a pyrophosphate Cu substrate. For details of the electrodeposition, refer to Reference 7. Fifteen minutes after plating, the electroplated sample was placed in an ultrahigh vacuum chamber for 20 h to degas the sample. The sample was then encapsulated in a 230-mm-long quartz tube at 2.7×10^{-7} Pa and stored at room temperature for 6 days while awaiting insertion into the Auger chamber.

After removal from the quartz tube and insertion into the Auger chamber, free oxygen and carbon were removed from the sample surface using an Ar^+ ion beam with energy of 3.0 keV. The sample surface was sputtered for 2 min, analyzed, cleaned an additional 5 min, and reanalyzed. With this ion beam energy, the measured sputtering rate of SiO_2 was 15 nm/min. Auger analysis was performed to quantify the oxygen level of the surface, using the following conditions (beam energy of 25 keV and 0.95×10^{-9} A, a tilt angle of 30°, and an analysis area of 100 μm^2).

After Auger analysis, the sample was aged in the Auger chamber for 9 days. Following aging, the sample was transferred promptly to a scanning electron microscope (SEM) in order to examine whisker nucleation and growth on the film surface. The sample was exposed to the ambient atmosphere for less than a half hour in the transfer from the Auger system to the SEM. The SEM operating conditions were 5.0 keV and 30 μA at 1×10^{-8} Pa.

RESULTS

The Auger analysis in Fig. 1 shows that 7 min of Ar^+ ion beam sputtering removed all the free oxygen and the oxide film from the sample surface. When the sample was analyzed by an SEM after 9 days of storage in the Auger chamber, the cleaned area and unclean area by the Ar^+ ion beam could be discriminated. Figure 2 shows a typical example of the cleaned and unclean area. A quartz chip, presumably from the breaking process of the encapsulation tube, blocked the ion beam and created the shadow. Consequently, the area in the shadow still has a surface oxide film. Thus, any object present on the sample surface prior to the Ar^+ ion beam sputtering will block the Ar^+ ion beam, resulting in a shadow of the object on the surface, as seen in Fig. 2. However, if the object was created on the sample
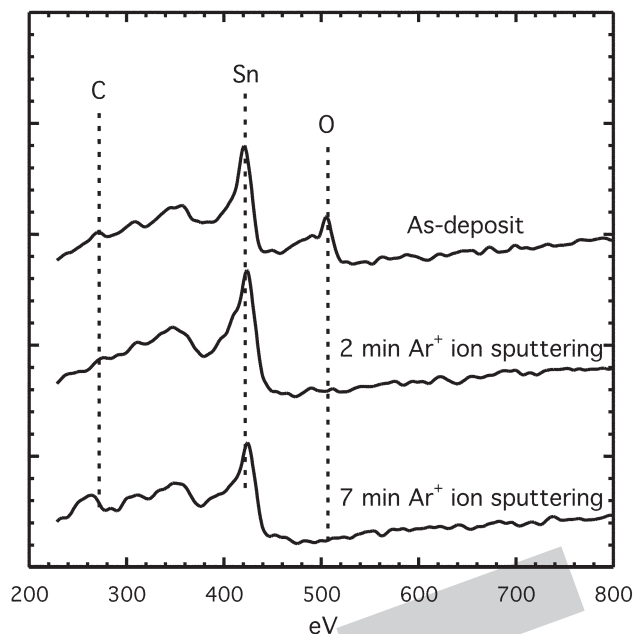

Fig. 1. Auger spectra of 100-μm^2 analyzed area from as-deposit sample after 7 min of Ar^+ ion sputtering.
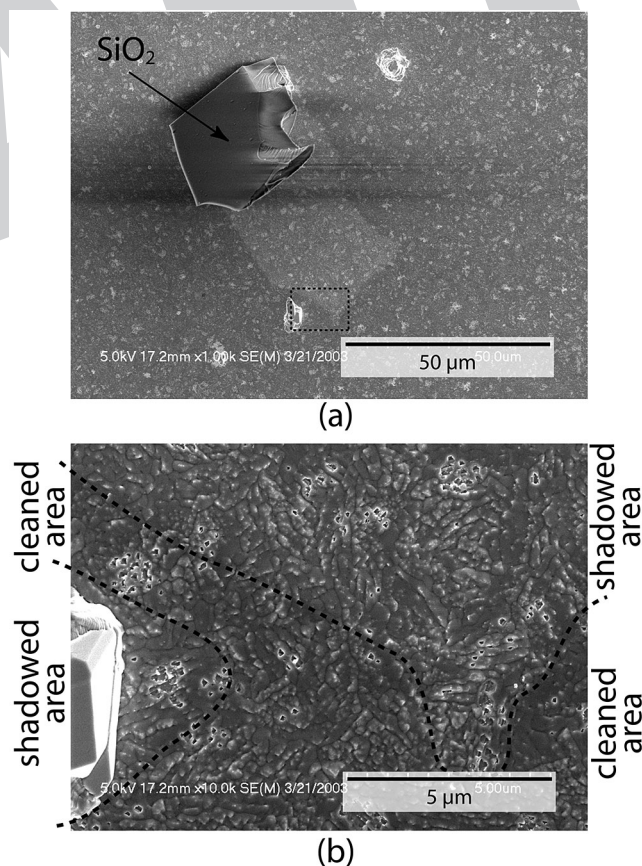

(a)

(b)

Fig. 2. (a) Shadow (unclean oxide film) formed because a SiO_2 particle blocked Ar-ion bombardment for surface cleaning prior to Auger analysis. (b) Zoomed area of the box in (a) details the surface structure.
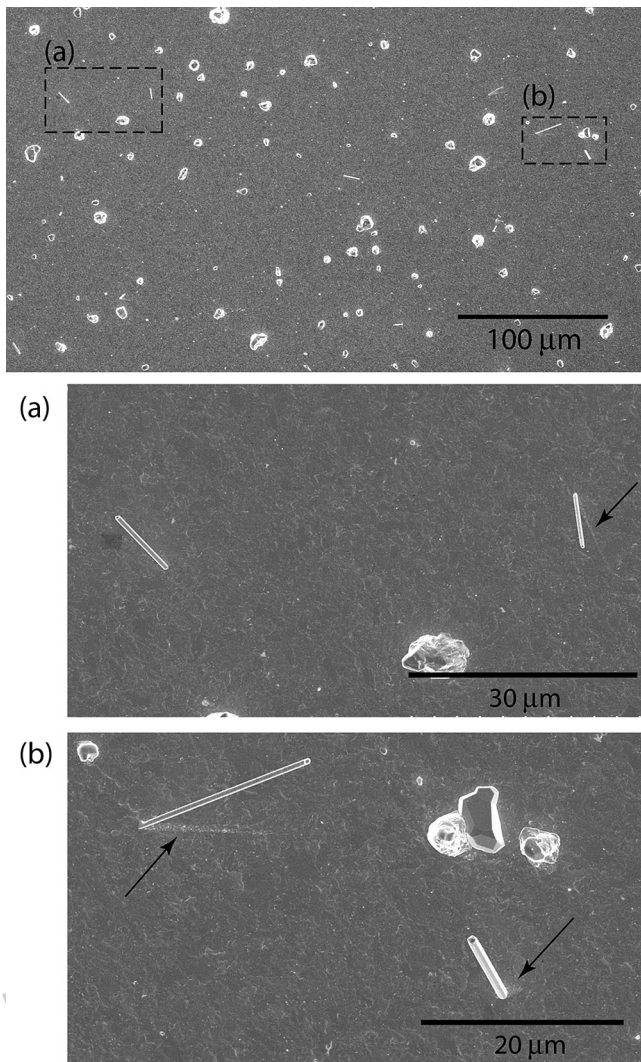
(a)

(b)

Fig. 3. Whiskers with and without shadows. The whisker without shadow implies that it was formed after the surface oxide film was removed by Ar$^+$ ion beam sputtering.

surface after sputtering, there will not be any residual surface oxide film as a shadow.

For the sample examined, whiskers with and without shadows are observed. Figure 3 shows an example where both type whiskers are present simultaneously. In the higher magnification micrographs (a) and (b), three whiskers have shadows (arrow marks), which indicates that they were present prior to sputtering with the Sn oxide film. The left side whisker of (a) does not have a shadow, which indicates that it formed after sputtering.

After the Auger analysis, the sample had been stored at 2×10^{-9} Pa for 9 days, and it was exposed to the atmosphere less than 30 min just prior to the SEM analysis. Thus, we do not expect that the oxide film formed due to the 30-min atmosphere exposure caused the growth of the observed Sn whiskers without shadows. The results, illustrated in Fig. 3, suggest that whiskers can grow regardless of the presence or absence of a Sn surface oxide film. An alternative explanation must be found for the localization of stress relief and whisker nucleation and growth.

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