Dependence of intermetallic compound formation on the sublayer stacking sequence in Ag–Sn bilayer thin films

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ABSTRACT

Intermetallic compound (IMC) formation in thermally-evaporated Ag–Sn bilayer thin films has been investigated employing especially X-ray diffraction (XRD) and (S)TEM methods. The specific IMCs that are present in the as-deposited state depend sensitively on the stacking sequence of the sublayers. In case of Sn on top of Ag, predominantly Ag_3Sn is formed, whereas Ag_4Sn is predominantly present in the as-deposited state for Ag on top of Sn. In the latter case this is accompanied by an extremely fast uptake of a large amount of Sn by the Ag sublayer, leaving behind macroscopic voids in the Sn sublayer. The results are discussed on the basis of the thermodynamics and kinetics of (IMC) product-layer growth in thin films. It is shown that both thermodynamic and kinetic arguments explain the contrasting phenomena observed.

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1. Introduction

The introduction of the European directive ROHS (Restriction of Hazardous Substances Directive) [1] prohibits the further use of Pb-based solders in electrical and electronical equipment. Pb-free solders based on the Ag–Sn, Ag–Sn–In, Ag–Sn–Cu and Ag–Sn–Bi systems are promising candidates for substitution of the classical Pb–Sn solders [2–5], since they have a low melting point and good wettability, as well as mechanical properties comparable to those of the classical Pb–Sn solders [6].

Development of intermetallic compounds (IMCs) upon soldering can greatly influence the properties and lifetime of solder joints [7–10]. Two IMCs have been identified in the Ag–Sn system [11], Ag_3Sn, with a narrow homogeneity range of about 1 at.% (between 24 at.% Sn and 25 at.% Sn) at room temperature (RT), and Ag_4Sn, with a homogeneity range of about 5 at.% (between 13 at.% Sn and 18 at.% Sn) at RT [11]. Ag can dissolve a considerable amount of Sn; the solubility limit at RT is about 10 at.% [12], whereas Sn has practically no solubility for Ag at RT [11]. Ag diffuses in Sn by an interstitial mechanism [13,14], whereas Sn diffuses substitutionally in Ag [15] and thus the diffusion coefficient

for the latter process is relatively small [16]. IMC Interdiffusion coefficients are large at RT: a value of $D = 6.6 \cdot 10^{-16}$ cm^2 s^{-1} has been obtained for the Ag_3Sn phase [17]. This diffusion coefficient is much larger as compared to the diffusion coefficient for substitutional Sn diffusion in Ag [16] and comparable to the diffusion coefficient for interstitial Ag diffusion in Sn [13]. Therefore, it may be expected that interdiffusion can lead to IMC formation even at RT. Consequently, knowledge of the evolution of IMCs and the corresponding microstructure at RT is of particular importance in view of a possible long-term stability of Ag–Sn based solder joints.

A few papers on the RT aging of evaporated Ag–Sn bilayers have been published [17–20]. In these early works only the formation of Ag_3Sn was reported.

The main goal of the present study is the investigation of IMC formation in Ag–Sn thin films in the as-deposited state in more detail. In particular, it will be shown that the stacking order of the sublayers controls which IMC is formed.[1] This peculiar observation is discussed and explained in terms of the thermodynamics and kinetics associated with phase formation in this system.

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[1] In case of IMC formation in Au–Sn bilayers a similar dependence on sublayer stacking sequence was observed [21], which was explained as a consequence of oxide formation. Such trivial origin, for the effect observed, can be excluded in the present case (see Section 2.1).

2. Experimental procedures

2.1. Specimen preparation

Thermally evaporated Sn–Ag bilayer films were prepared using a Lesker Nano 36 machine. The materials Ag (purity: 99.99 wt.%, Lesker) and Sn (purity: 99.999 wt.%, Heraeus) were placed in separate evaporation boats, made of Mo in the case of Sn evaporation and made of W in the case of Ag evaporation. Single crystalline Si (100) wafers, covered with an amorphous 50 nm SiO_2 layer, were used as substrates for all evaporated bilayers. The substrates were ultrasonically cleaned in acetone and subsequently in isopropanol; cleaning was done for 20 min in each solvent. Next, the substrates were placed in a solution of 1 part of 32 wt.% H_2O_2 and 2 parts of 96 wt.% H_2SO_4 [22]. The solution was heated until the boiling point was reached, and kept at this temperature for about 20 min. Afterwards, the substrates were rinsed with demineralized water and dried in a flow of nitrogen gas. As last step of the cleaning procedure, the substrates were cleaned in an oxygen plasma for 10 min. The substrates were fixed on a rotatable substrate holder. The substrates on the holder were placed at a distance of approximately 35 cm from the evaporation sources. Rotation speed of the substrate holder was about 30 rpm. Depositions were carried out at pressures between 0.6×10^{-5} Pa and 2.6×10^{-3} Pa. The Sn layers as well as the Ag top layers were deposited at RT. The Ag bottom layers were deposited at 200 °C, which was done to increase the Ag grain size in order to decrease the amount of (grain boundary) interdiffusion and IMC formation (cf. Section 3.1), thereby preserving the as-deposited state for a longer period of time. Thicknesses of the sublayers varied from 50 nm to 500 nm. The subsequent depositions of the sublayers were carried out without breaking the vacuum; Auger electron spectroscopy, done with a Jeol Jamp 7830 F, revealed that no oxide layer was present between the bottom and the top sublayers.

Thicknesses and deposition rates of the films were monitored with a quartz crystal balance (Lesker), which was separately calibrated for Ag and Sn. A deposition rate of 8 Å s^{-1} was generally used for all Ag layers; in two cases deposition rates of 4 Å s^{-1} and 16 Å s^{-1} were used. A deposition rate of 12 Å s^{-1} was used for Sn, if Sn was the bottom layer. A higher deposition rate of 23 Å s^{-1} was used for Sn, if Sn was the top layer, in order to decrease the roughness of the Sn top layers. Thickness and roughness of the single- and bilayers were measured with a Dektak 8 profilometer (Veeco).

For each material and deposition rate, the substrate-surface temperature was measured with a type-k thermocouple during deposition of single layers. The maximum surface temperatures reached during deposition of the Ag top sublayers at 4 Å s^{-1}, 8 Å s^{-1} and 16 Å s^{-1} were 33 °C, 38 °C and 39 °C, respectively. For Sn deposition rates of 12 Å s^{-1} and 23 Å s^{-1} the maximum surface temperatures were 45 °C and 49 °C, respectively. The indicated temperature for the deposition of the Ag bottom sublayer (200 °C) corresponds to the average temperature as measured with the thermocouple. An overview of all bilayers prepared for this work is given in Table 1.

The present study is focused on bilayers in the as-deposited state. However, interdiffusion and phase formation proceed rapidly in the Ag–Sn samples, even at RT (Cooling the samples is no option in view of the β-Sn to α-Sn transition at 13 °C). Therefore, first measurements after bilayer preparation, unavoidably taken some time after bilayer deposition, represent a starting stage of aging already; this especially holds for the TEM measurements.

Table 1
Overview of the stacking sequence, thicknesses, depositions rates and deposition temperatures of the Ag and Sn sublayers in the investigated bilayers.

Stacking sequence	Thickness [nm]	Dep. rate [Å/s]	Dep. temp. [°C]
Ag on top of Sn	Ag: 500	Ag: 4	Ag: room temp.
	Sn: 500	Sn: 12	Sn: room temp.
Ag on top of Sn	Ag: 500	Ag: 8	Ag: room temp.
	Sn: 500	Sn: 12	Sn: room temp.
Ag on top of Sn	Ag: 500	Ag: 16	Ag: room temp.
	Sn: 500	Sn: 12	Sn: room temp.
Ag on top of Sn	Ag: 75	Ag: 8	Ag: room temp.
	Sn: 500	Sn: 12	Sn: room temp.
Ag on top of Sn	Ag: 500	Ag: 8	Ag: room temp.
	Sn: 100	Sn: 12	Sn: room temp.
Sn on top of Ag	Sn: 500	Sn: 23	Sn: room temp.
	Ag: 500	Ag: 8	Ag: 200
Sn on top of Ag	Sn: 50	Sn: 23	Sn: room temp.
	Ag: 500	Ag: 8	Ag: 200

2.2. X-ray diffractometry (XRD)

Phase analysis of the thin films was performed on the basis of $\theta - 2\theta$ scans (2θ = diffraction angle) recorded with a Bruker TXS D8 Discover diffractometer using Cu–K$_\alpha$ radiation from a rotating anode X-ray tube. The tube was operated at 50 kV and 24 mA. A Xenocs Fox 2D collimating mirror was placed in the incident beam path in order to obtain a parallel X-ray beam. The radiation emerged from a 100×100 μm^2 spot under a take-off angle of 6°. A VÅNTEC-500 2D detector was used with a recording time of typically 120 s per frame. It covers a 2θ range from 29.8° to 47.0°. The illuminated area on the sample was restricted by cylindrical collimators with diameters of 0.5 mm or 1.5 mm. The intensities recorded by the 2D detector were converted to conventional XRD diffractograms by integrating over a χ range from 73.8° to 106.6°, where χ is the Eulerian tilt angle.

To investigate the textures of the bilayers, Ag {111} and Sn {100} pole figures were recorded with a Philips (PANalytical) MRD Pro diffractometer utilizing {111} Ag and {200} Sn reflections, respectively. The diffractometer was operated in a parallel-beam geometry with a polycapillary X-ray collimator in the incident beam. The spot size of the incident beam was approximately 4×4 mm^2. Co–K$_\alpha$ radiation from a conventional X-ray tube, operating at 40 kV and 40 mA, was used. K$_\beta$ radiation was removed by a graphite monochromator in the diffracted beam. Intensities were recorded using a proportional counter.

2.3. Electron microscopy (SEM and TEM)

In order to investigate the microstructure of the thin films, cross sections of the bilayers were prepared and investigated with a FEI Nova Nanolab 600 Dual-Beam (Focussed Ion Beam (FIB)) instrument. Before cutting the cross section, a Pt capping layer was deposited in order to obtain a sharp interface to the surface in the cross section, as well as to protect the individual layers. Images were recorded with the electron beam mode of operation (SEM) as well as with the ion beam mode of operation (FIB) using a secondary electron (SE) detector.

Transmission electron microscopy (TEM) specimens were also prepared with the Dual-Beam instrument using the in-situ lift-out technique [23]. Typical thickness of the TEM specimens was about 100 nm. For the TEM investigations a Philips CM200 instrument equipped with a double tilt stage and a LaB$_6$ cathode operating at an acceleration voltage of 200 kV was used. A Gatan CCD camera, attached to the microscope, was used to capture bright field (BF) and dark field (DF) images and selected area diffraction patterns (SADPs).