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XRD and ToF-SIMS study of intermetallic void formation in Cu-Sn micro-connects

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ABSTRACT

An identified reliability challenge of significant importance to Cu–Sn bonding for 3D integration is Cu–Sn intermetallic void formation. Voids, often referred to as Kirkendall voids, form within the inter-diffusional zone between Cu and Sn, more specifically within the intermetallic compound Cu_3Sn. The root-cause(s) of void formation is not well understood, therefore this study is designed to understand under what conditions voids form. The two main hypotheses for the root-causes of void formation are (i) the imbalance of diffusion rates between Cu and Sn during the formation of Cu–Sn intermetallic compounds and the resulting residual stresses and (ii) the co-deposition of impurities during Cu electroplating to void formation. Therefore, an *ex-* and *in-situ* x-ray diffraction (XRD) study is used to probe the material state as a function of thermal annealing, and a time-of-flight mass spectroscopy (ToF-SIMS) study is used to detect impurities co-deposited during Cu electroplating and to understand the effects of thermal annealing on the impurities' kinetic behaviour.

1. Introduction

Micro-connects, including small volume interconnects (or microbumps) and Solid Liquid Interdiffusion (SLID) bonds for Micro- or Nanoelectromechanical Systems (MEMS and NEMS) are functionally far superior compared to traditional large volume interconnects, and enable novel integration techniques for the miniaturisation of complex integrated systems [1,2].

For the successful implementation of micro-connects, critical reliability challenges need to be addressed. As micro-connects have smaller volumes than traditional forms of interconnects, they become more susceptible to microstructural defects. Such defects can lead to catastrophic and costly failures within integrated systems. Although micro-connects are promising as a 3D integration tool, without a thorough investigation into microstructural defects, implementation could prove to be costly.

Cu–Sn intermetallic (IMC) void formation (often referred to as Kirkendall voids) in micro-connects is one such defect that has been shown to negatively affect reliability [3–5]. Although void formation has been studied for some time, the root-cause(s) of void formation is currently not well understood and can cause an interconnect to appear to void sporadically for no apparent reason; therefore a study is required to understand under what conditions void formation occurs. Voids form preferentially at the interface of Cu and Cu_3Sn or within Cu_3Sn [6].

The electroplating parameters used in the deposition of Cu have been shown to influence void formation. Parameters include, electroplating current density, electroplating agitation rate, purity of the electroplating solution and the additives used in electroplating. All these parameters influence not only the micro-structural properties but also the chemical composition of the deposited Cu, as impurities are co-deposited during electroplating [7,8]. Therefore the microstructural and chemical compositional behaviour of a voided Cu–Sn micro-connect is critical in understanding the root-cause(s) of void formation.

To understand under what conditions voids form an x-ray diffraction (XRD) analysis of samples with different voiding propensities was undertaken. XRD data provides information on the crystallinity of the metallic samples, including crystalline size and texturing as a function of thermal annealing. Such information can provide an insight to what microstructural conditions cause a higher voiding density (*i.e.* samples under a specific type of texturing).

In addition to the XRD analysis, a time-of-flight secondary ion mass spectroscopy (ToF-SIMS) analysis was performed to understand (i) the types of impurities co-deposited during electroplating and (ii) the impurity segregation behaviour as a function of annealing. Previous studies [9,10] have shown that organic and non-organic impurities are co-deposited during Cu electroplating and that these impurities contribute to void formation. If this is the case, the behaviour of the impurities over a thermal lifetime can provide an insight as to which impurity or combination of impurities contributes to void formation. Furthermore, the approach provides a kinetic insight into how impurities behave within the Cu–Sn system as a function of thermal annealing.

2. Experimental procedure

Samples were prepared on a 100 mm Si wafer. The XRD samples had a 40 nm Cr film and 100 nm Cu film deposited by magnetron sputtering.

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The ToF-SIMS samples had 120 nm SiO_2 that was deposited using PECVD followed by 100 nm of Pt, 40 nm of Cr and 100 nm of Cu by magnetron sputtering. The Cr functions as a barrier/adhesion layer and the Cu is the electroplating seed layer. The wafers were diced into 50 mm × 80 mm rectangles designed to fit into a 267 ml small electroplating cell. The cell was designed so that the cathode was placed parallel to the anode. Before Cu electroplating, the rectangles were pre-treated with oxygen plasma for 3 min using a PVA Tepla 400 plasma system at a power of 100 W and an O_2 flow rate of 3 ml/min.

To evaluate the electroplated Cu with different voiding characteristics, a range of electroplating chemistries were used. In addition, a PVD sputtered Cu sample that, in contrast to the electroplated samples, showed no voiding was used as a reference. An overview of the samples is given in Table 1. All electroplated samples were produced using a DC current at a current density of 10 mA/cm^2 with a magnetic stirring rate of 30 RPM. Directly following the Cu electroplating, Sn was deposited electrochemically using a commercial solution (NB Semiplate Sn 100) at a DC current density of 10 mA/cm^2. For the XRD samples, a target thickness of Cu and Sn was 2 μm and 1 μm respectively, designed to limit X-ray absorption in the Sn to improve the intensity. For the ToF-SIMS samples, a target thickness of Cu and Sn was 1 μm and 5 μm respectively, designed so that the Cu and Cu_3Sn interface was as close to the sputter surface as possible for improved depth resolution.

The wafer rectangles were finally diced into two sets of squares, 20 mm × 20 mm and 10 mm × 10 mm for XRD and ToF-SIMS respectively. Additionally focused ion beam (FIB) prepared cross-sections were made of the XRD samples to evaluate both the Cu–Sn IMC growth and grain behaviour. An overview of the sample structures can be seen in Fig. 1.

As the Cu–Sn samples are thermally annealed, the dissolution of Cu into Sn occurs. This process allows for the formation of the Cu–Sn IMCs. The two IMC that form at the temperatures used in this work are the othorhomibic-Cu_3Sn (ε) and the low temperature monoclinic-Cu_6Sn_5 (η′).

2.1. XRD

The XRD analysis was carried out using the Rigaku SmartLab X-ray diffractometer operating in the focused incident beam configuration with a 2D-detector. The focused beam mode was chosen as it provides a high intensity over a small illumination footprint (0.4 mm × 0.4 mm). This comes at the cost of x-ray parallelism and subsequently the peak resolution (medium resolution). Two acquisition modes were used in this work, (i) θ/2θ scan where the acquired 2D image was then collapsed into a diffractogram and (ii) wide-area reciprocal space map (RSM) providing sample texturing information as a function of chi (χ) angle. Indexing of the diffractograms was made with the ICSD (Inorganic Crystal Structure Database) database, the following PDF-numbers were used: 4-836, 65-5721, 45-1488 and 4-673 for Cu, Cu_3Sn, Cu_6Sn_5 and Sn respectively.

The diffractometer was operating with a Cu Kα radiation source with a wavelength of 0.154 nm and at a tube voltage of 45 kV at 200 mA. The 2θ range that was collected was from 20° to 90°. For the *in-situ* XRD a linkam heating stage was used at a temperature of 175 °C for 4 h under standard atmospheric conditions. The θ/2θ scan was continually looped with a duration of 30 min during the annealing process.

Table 1
List of the sample names, electroplating chemistries and suppliers used in this study.

Sample	Concentration	Chemical	Formula	Supplier
Sputtered	-	-	-	-
Basic	0.25 M	Copper Sulphate	$CuSO_4 \cdot 5H_2O$	Aldrich 209198
Solution	1.8 M	Sulphuric acid	H_2SO_4	Aldrich 258105
	1.92 mM	Hydrochloric acid	HCl	Aldrich 40304
SPS	0.25 M	Copper Sulphate	$CuSO_4 \cdot 5H_2O$	Aldrich 209198
Solution	1.8 M	Sulphuric acid	H_2SO_4	Aldrich 40306
	1.92 mM	Hydrochloric acid	HCl	Aldrich 40304
	0.01 mM	SPS	$C_6H_{12}Na_2O_6S_4$	Raschig RALU®PLATE SPS

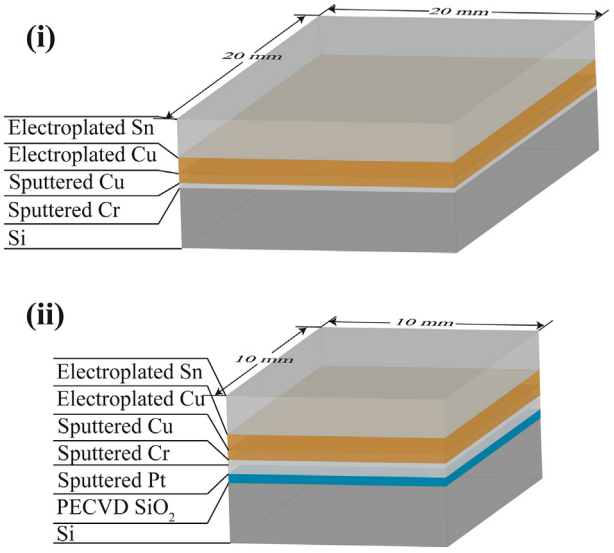

Fig. 1. An overview of (i) XRD samples and (ii) ToF-SIMS samples.

2.2. ToF-SIMS

The ToF-SIMS samples, as seen in Fig. 1, were delaminated at the SiO_2 and Pt interface. The film was exfoliated by applying Loctite EA 9492 epoxy adhesive to the Sn surface and mounted onto a brass substrate. The purpose of this was to achieve an initially smooth sputtering surface for the ToF-SIMS that is close to the region of interest. This increases the depth resolution by reducing the effects of preferential sputtering rates that occurs as deeper into the sample is probed. The sample analysed was fabricated using the SPS chemistry and isothermally annealed for 4 h at 150 °C.

The ToF-SIMS was undertaken using an Iontof ToF-SIMS^5−100 instrument. The mode was a high-current bunched mode for high mass resolution. The primary ion species used was Bi_1+ at 25 keV with a cycle time of 80 μs. The measurement was done in a negative polarity mode with a sputtering species of Cs^+ at 2 keV. The species further analysed were C^-, O^-, F^-, S^- Cl^-, Cr^-, Cu^-, Sn^- and Pt^-. All the signals have been normalised by the total intensity.

3. Results and discussion

3.1. Cu–Sn cross-sections

This section considers the cross-sectional behaviour of the XRD samples. FIB cross-sections and scanning electron microscope (SEM) secondary electron (SE) micrographs were taken of the samples before and after thermal annealing and the results can be seen in Fig. 2. The three samples exhibited different voiding behaviour. The sputtered sample experienced little to no voiding (sub figure i), the basic solution sample experienced moderate levels of voiding (subfigure ii) and the SPS sample experienced dense levels of voiding (sub figure iii), with all voids located within the IMC phase of Cu_3Sn (ε).

In addition to the voiding behaviour, the grain-structure of the samples is presented in Fig. 3, both before (i–iii) and after thermal annealing (iv–vi). There are three different characteristic grain growth behaviours occurring in the samples. The sputtered Cu exhibits large grain sizes that

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