Experimental report

19/09/2016

Proposal:	**1-04-95**	**Council:**	4/2015
Title:	Inter-diffusion in electrodeposited metal bilayer films		
Research area:	Materials		

This proposal is a new proposal

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Samples: quartz/MPTS/Au/Cu/Ag
quartz/MPTS/Au/Ag/Cu
quartz/MPTS/Au/Cu/Sn
quartz/MPTS/Au/Sn/Cu

Instrument	Requested days	Allocated days	From	To
FIGARO	3	0		
D17	0	3	18/09/2015	21/09/2015

Abstract:

We propose time-resolved specular neutron reflectivity measurements on Cu/Ag and Cu/Sn bilayers (each deposited on Au in either configuration). Electrochemical and AFM imaging data indicate substantial inter-diffusion of the two components, but cannot provide the dynamics or quantify the spatial profiles of the components. We propose to use specular neutron reflectivity to monitor inter-diffusion of the components in Cu/Ag and Cu/Sn bilayers (in both configurations) and the influence, if any of inter-diffusion involving the Au substrate. Modelling suggests diagnostically distinct evolution of reflectivity profiles for different mechanisms, in the extreme represented by (i) vertical diffusion of under laterally uniform conditions and (ii) rapid vertical transport followed by slow lateral diffusion. The outcomes should contribute to the development of coatings for Cu conductors on printed circuit boards with improved solder wetting characteristics, alleviating solder joint failure.

ILL Experiment 1-04-95   18th – 21st September 2015

Inter-diffusion in Electrodeposited Metal Bilayer Films

Experimental team – A. R. Hillman, V. Ferreira, E. Smith and A. Ballantyne

Background

Printed circuit board (PCB) design and manufacture uses copper tracks to enable electrical conduction between electronic components. It is necessary to protect the surface of the copper in order to ensure consistent solderability during electronics assembly. Typically, protection is achieved through the deposition of a thin film of metal on the surface of the copper that is either less prone to oxidation or produces oxides that can be readily removed from the surface. Two of the most common surface finishes are immersion silver (ImAg) and immersion tin (ImSn) and at Leicester we have led efforts to develop plating processes for these metals from Deep Eutectic Solvents (DESs). We have established protocols for the efficient deposition of single layers of each component metal (Cu, Ag, Sn) for study by neutron reflectivity.

Where thin metal films are present in contact with each other, inter-diffusion will occur. This is mixing between the two metal films at the boundary between the two, leading to the formation of intermetallic species, consuming the individual metal films.

Proposed

We proposed to study metal/metal inter-diffusion processes for bilayer systems of Cu/Ag and Cu/Sn systems deposited from DES media. Through this we aimed to investigate:

i) Timescale of inter-diffusion of electrodeposited bilayer metallic components
ii) Extent of inter-diffusion of first layer with Au substrate and possible incorporation of Au into the second substrate
iii) Inter-metallic growth mechanism. i.e. does intermetallic growth preferentially occur uniformly across the boundary between the metallic films or have rapid penetration down grain boundaries prior to lateral expansion

Performed Measurements

Six Au coated quartz blocks with a (3-mercaptopropyl)trimethoxysilane binding layer were used to study a series of different metal films. We performed electrochemical growth of a series of metal films as detailed in **Table 1**. Metal films were deposited *ex situ* from 10 mM solutions of the metal in Ethaline 200 (a 2:1 molar mixture of choline chloride and ethyleneglycol) at a fixed potential of -0.4 V (w.r.t. Ag/AgCl). Ag was deposited for 2 hrs whereas Cu and Sn were deposited for 3 hrs. After growth kinetic NR measurements were recorded at one incident angle due to the desire to visualise low timescale change in film composition. Adequate statistics to ascertain fringe positions and film thicknesses were obtained in tens of seconds from data in the range of $0.009 < q\ (\text{Å}^{-1}) < 0.08$. Data was acquired in 50 s slices. Subsequently, longer timescale measurements at two angles (offering full q-range) measured periodically enabled measurement of longer timescale changes in film composition. In the case of Cu/Ag and Ag/Cu films inter-diffusion was slower and thus the blocks were placed in an oven at elevated temperatures (80 °C and 94 °C) to accelerate the ageing process. Ageing measurements with Sn films were performed at room temperature.

Outcomes and findings

There are six individual metal multilayer systems in this study Cu, Ag, CuAg, AgCu, CuSn and SnCu. We have previously observed for Sn coatings on Au that inter-diffusion occurs rapidly as the Au surface onto which Sn was deposited changed from a gold colour to one which was silvery, when viewed through the quartz block. This is indicative of rapid diffusion between the Au and deposited Sn layers. CuAg and CuSn are both interfaces present within commercial PCB surface finishes with shelf-lifetimes of greater than six months and thus are inferred to involve slower inter-diffusion. CuAu interdiffusion is also known to be a relatively fast process as this is the resulting interface when the “skip plating” phenomenon occurs.

Table 1: Metal films grown and measurements recorded on each film.

Block	Film (s)	Measurements
2.2	Cu	Au dry in air Kinetic ageing 4 dry measurements with ageing
2.4	Sn	Au dry in air Kinetic ageing 4 dry measurements with ageing
1.1	Cu/Ag	Au dry in air Kinetic ageing 4 dry measurements with ageing @ high temp
1.3	Ag/Cu	Au dry in air Kinetic ageing 4 dry measurements with ageing @ high temp
1.4	Cu/Sn	Au dry in air Kinetic ageing 6 dry measurements with ageing
2.3	Sn/Cu	Au dry in air Kinetic ageing 5 dry measurements with ageing

Based on prior perceptions of rapid mixing of thin metal films each of the electrodeposits had their NR profiles recorded under kinetic mode for at least 2 hrs. Measurements were obtained at low q range, where the high neutron flux enabled rapid measurement times (as short as 50 s). As such, changes in film composition can be visualised at short time scales. **Figure 1** shows reflectivity profiles recorded at 50 s intervals at both CuAg and CuSn films grown *ex situ* with every 50th trace plotted. In each case, little variation can be observed in the reflectivity profiles with any variations occurring within the error of measurement. The absence of observed variation in the neutron reflectivity profiles suggests inter-diffusion may either:

- occur over much longer timescales than is studied during kinetic NR measurements (ca. 3 hours). This is likely the case for Cu, CuAg and AgCu metal films.
- occur prior to the beginning of kinetic measurements but reached a steady state. This could be the case in “fast” diffusion processes such as those for Sn, CuSn and SnCu.

After kinetic NR measurements were recorded, the NR profiles were measured over a wider Q range with measurements at two angles followed by subsequent ageing steps. The CuAg and AgCu coatings were aged at elevated temperature a number of times with NR profiles recorded after each measurement as shown in **Figure 2 (a)** CuAg and **(b)** AgCu. In each case some marked changes in the profile can be observed. At high values of Q (>0.06 Å) there was a shift in fringe start from 0.061 $Å^{-1}$ to 0.069 $Å^{-1}$. This is consistent for both of the metal films.

For the AgCu film (**Figure 2 (b)**) high Q had the most pronounced difference in the NR profile. In the case of CuAg however there was additional variations in the reflectivity profile at a Q of c.a. 0.023 $Å^{-1}$ with a reduction in reflectivity intensity and the fringe shifting to higher Q. In both cases, the largest variation in reflectivity profile occurred after the coatings had been through successive heating cycles as well as having been aged for a day at room temperature. This suggests that there is little difference in the inter-diffusion rate of Cu and Ag films at the different temperatures studied and the largest influence on the extent of inter-diffusion of the metals was the time this process has had to occur.

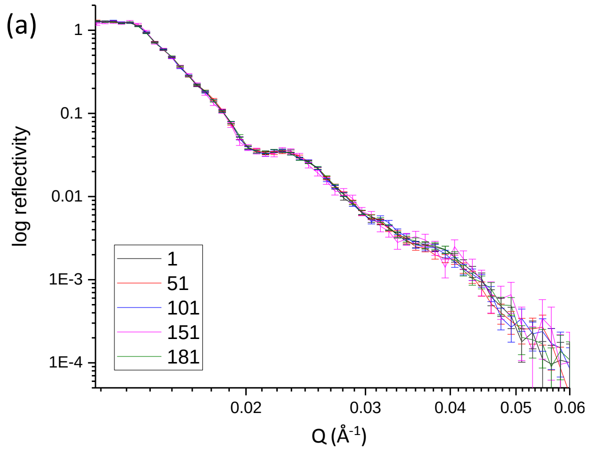

Figure 1 R(Q) profiles showing short term variations of **(a)** CuAg and **(b)** CuSn films. R(Q) profiles were recorded for 50 s with every 50th profile (approx. every 50 mins) displayed; see inset for run numbers).

Where Cu and Sn films were investigated, there was an evolution of the NR profile with increased time between measurements. For example, **Figure 2 (d)** shows the reflectivity profile for the CuSn system. Between 0.02 and 0.025 Å^{-1} a reduction in fringe intensity was observed and there was also an increase in fringe spacing above 0.03 Å^{-1}. At high Q (> 0.05 Å^{-1}) any variation in NR profile was within experimental error.

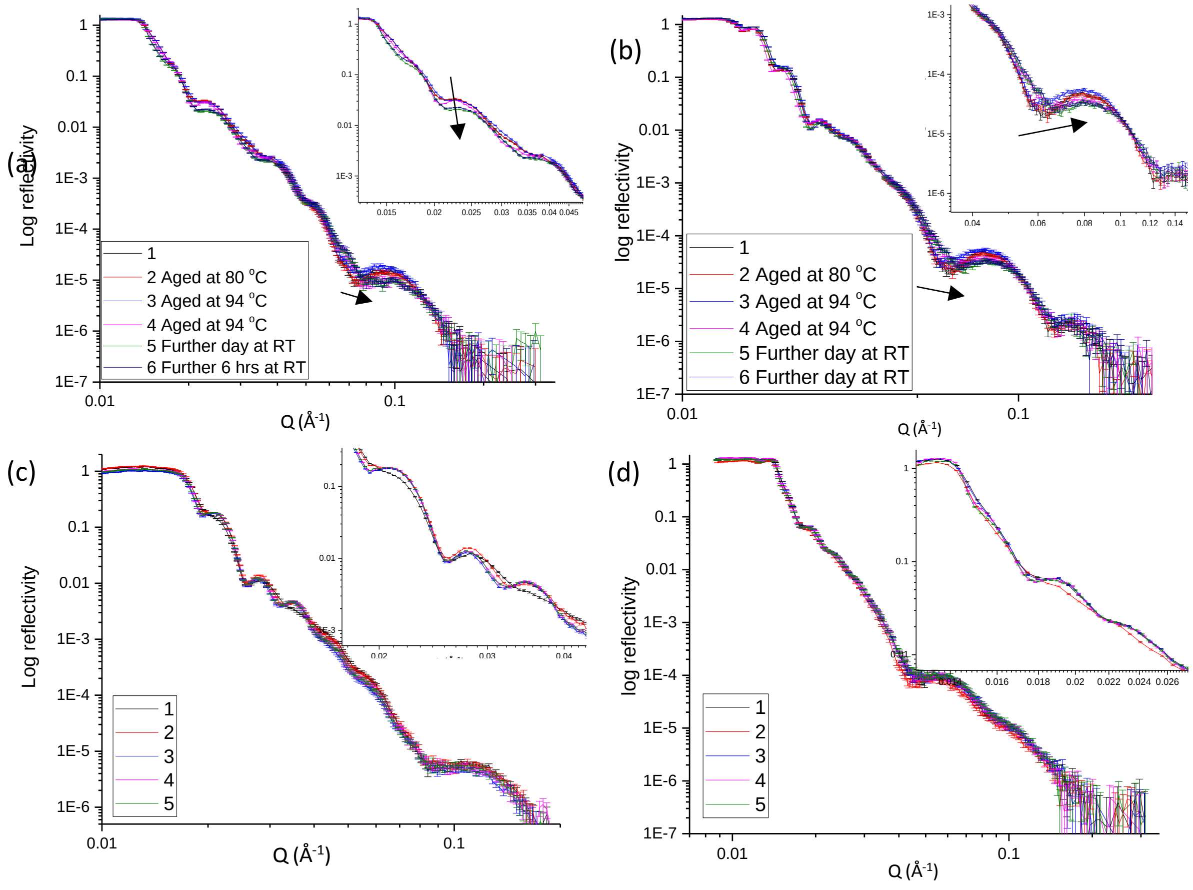

Figure 2 NR profiles of metal films of **(a)** CuAg, **(b)** AgCu, **(c)** CuSn and **(d)** SnCu. CuAg and AgCu films were aged in a convection oven for 9 hours at either 80 °C or 94 °C whereas CuSn and SnCu films were aged at atmospheric temperature

The above data shows that there are clear and observable differences in the fresh and aged coatings that were investigated. Present efforts are focused on converting these to variations in the scattering length density profiles, and thence information on the rate of interpenetration of the metals within each other.