

On diffusion-controlled interface microstructure of vapor deposited bilayer thin film of Sn/Cu

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Abstract. Depth dependent concentration profiles for bilayer film of Sn (500 Å)/Cu (500 Å) are determined at different temperatures by X-ray photoelectron spectroscopy (XPS). Although the nature of the diffusion profile for the sample studied immediately after deposition could be explained by the existing laws, the profiles for others are found to be distinctly different and are not explained by the theories of nucleation and growth of the inter-metallic phases. Measured value of the inter-diffusion coefficient for Cu points out to the grain boundary as well as interstitial diffusion processes. It is also observed that the compositions across the bulk of the films become uniform on annealing at higher temperatures and the width of this region increases with annealing. However, the composition close to the surface is found to be entirely different from that of the bulk even on prolonged heating. The findings possibly demonstrate the importance of physical surface in influencing the solid-state reactions.

Keywords. Diffusion; solid-state reaction; surface; X-ray photoelectron spectroscopy.

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1. Introduction

The process of inter-diffusion of Cu and Cu alloy films are of interest for the application in micro-electronic device interconnections. Extensive studies have so far been made to explain the formation of inter-metallic phases and their stability [1–5]. It is now well-established that η (ordered Cu_6Sn_5) phase is formed first. By heating within 115–150°C, ε (Cu_3Sn) phase is formed from a reaction between Cu and η phase. Finally, by heating to 650°C, formation of δ (Cu_4Sn) has been reported [1], which remains upon cooling to room temperature. Tu [3] measured the inter-diffusion coefficient of Cu in Cu_6Sn_5 . From the estimated value of the coefficient, Tu [3] inferred that the grain sizes of inter-metallic phase formed was small. Because of the experimental difficulties it had not been possible to measure the grain sizes at the interface. Most of these studies report the structure of interfaces for thick sample when a stable phase is formed. Recently, formation of a two-dimensional

alloy at the surface of Cu (Sn) (111) has been reported by Contini *et al* [6]. In an attempt to explain the diffusion mechanism at atomic level, Bukaluk [7,8] has studied the diffusion couples of Pd/Cu and Ag/Cu by Auger electron spectroscopy. It has been shown that Fourier series solution described the shape of the experimentally determined diffusion profiles. Coloration of tin-coated copper cable has been shown to be due to the diffusion of Cu in Sn [9]. Recently, Dhabal and Ghosh [10] reported the compositional variations across the cross-section of bilayer films of Sn/Cu without giving any physical basis for such variations. The present study is an attempt to explore the physical basis for such variations.

2. Experimental

Experimental details of sample preparation and instrumental settings are described elsewhere [10]. Prior to recording the spectra, each sample is sputtered cleaned for possible surface contamination during transport to the UHV chamber for analysis. For quantitative analysis, areas under the photoelectron peaks are estimated using Shirley's background subtraction technique [11]. Atomic per cent compositions are determined using the published values of the sensitivity factors [12]. No attempt has been made to correct for the depth-dependent composition variation [13]. Under the experimental conditions employed, the quantitative XPS results are expected to be accurate within 10–20 at% [11–13]. Atomic per cent values less than 10% are ignored. Microstructural parameters like crystallite size and rms strain are obtained from the best-fit profile of Cu (200) using single-line technique [14]. The errors in these parameters are subjected to the assumptions made as regards to the shape of the distribution functions. Validity of these assumptions is checked by evaluating these parameters for different orders of reflections which coincides for correct assumptions [15]. However, in the present studies no higher order reflections could be recorded. The reported values of the crystallite size and rms strain are the volume average parameters.

To determine the composition at different depths across the film thickness, surface layers are removed by low-energy Ar⁺ ion sputtering. Thickness of the layers removed is obtained by calibrating the time of etching at a given Ar⁺ ion gun settings. This is done by measuring the time required to remove completely a given thickness of Sn/Cu film (estimated by SEM/stylus) on glass substrate for a particular Ar⁺ ion gun settings. Removal of the layer is ascertained by the appearance of the Si 2p signal from the substrate. Thus the etch rate for the film is measured. Assuming the thickness removed linearly depends on the time of etching, thickness of the layer removed is estimated from the time of etching.

3. Results and discussion

Figure 1 gives the wide-scan spectra of a sample of Sn/Cu film at room temperature at four different depths. The Cu 2p signal appears on removing the surface layers and the signal strength increases at greater depths. Figures 2a and 2b give

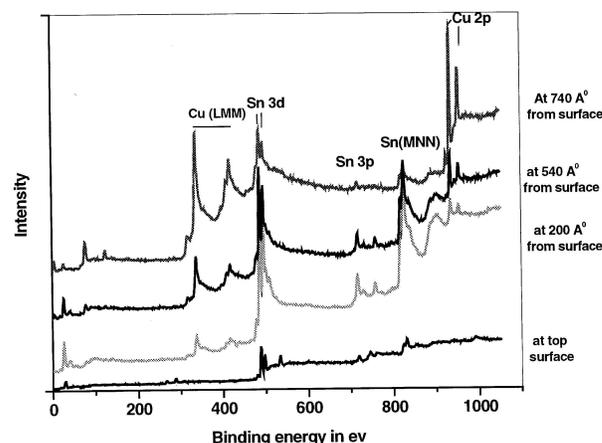


Figure 1. Wide-scan XPS spectra of Sn/Cu thin film at different depths from the surface at room temperature.

the atomic per cent composition variation with depth for samples at room temperature and room temperature sample measured after one month. The quantitative results are obtained after recording the high-resolution lines of Cu $2p_{3/2}$ and Sn $3d_{5/2}$. The conventional method of quantification has been used to determine the atomic per cent composition of Cu and Sn with depth. The nature of variation of Cu concentration with depth could be represented by a sinusoidal variation (sinusoidal fit: $y = A + B \cos(cx + d)$, where $A = 0.42843319$, $B = 0.43290524$, $c = 0.0040171879$, $d = 2.9261985$) for sample at room temperature (figure 2a). Bukaluk [8] in his studies with multilayer systems of Ag/Cu and Pd/Cu showed that the diffusion profile could be represented by a sinusoidal variation. Bukaluk used depth-dependent Auger electron spectroscopic technique. He reasoned that the diffusion in these systems is through grain boundary migration as opposed to lattice diffusion because of limited mutual solubility of Cu in Ag, and Cu in Pd. In the present studies, observed concentration variation of Cu, for samples at room temperature is described by sinusoidal function. Since the sinusoidal function is the first term of the Fourier series solution of the Fick's law for isothermal diffusion with a constant diffusion coefficient [16], the observed diffusion of Cu in Sn and vice versa at room temperature is described by isothermal diffusion process. However, it has been pointed out [3,8] that atomic diffusion is primarily through grain boundary migration provided the grain sizes of the phases are small. X-ray diffraction measurements have been done to determine the crystallite size, which is an equivalent parameter to grain sizes measured under microscopes. Because of the overlapping X-ray diffraction lines of the different phases present in Cu-Sn system, it is difficult to estimate the crystallite sizes of the phases with precision. Assuming the contribution to the X-ray diffraction pattern from intermetallic phase Cu_6Sn_5 to be negligibly small, pseudo-Voigt [14] single line analytical technique is used to determine the crystallite sizes for Cu and Sn. The average value obtained by the crystallite size is of the order of 400 \AA and rms strain is of the order of 3×10^{-3} . Since the overall thickness of the bilayer film is only of the order of 1000 \AA , presence

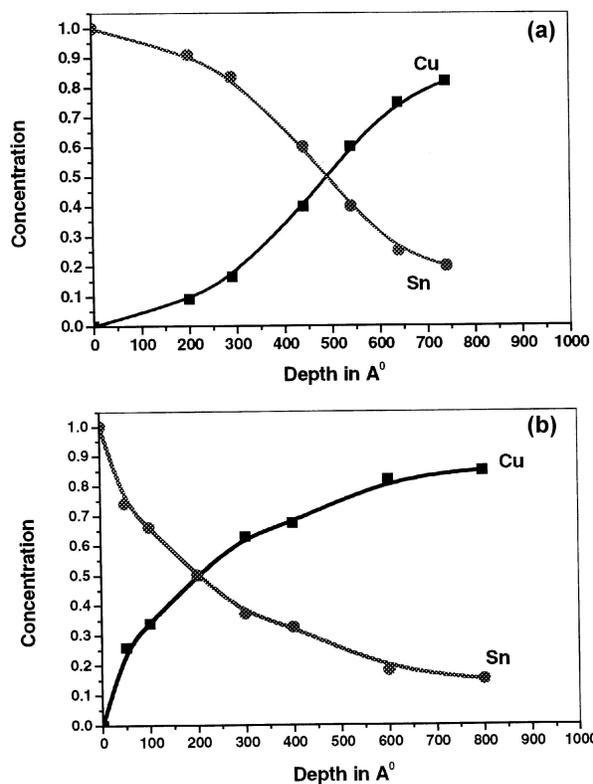


Figure 2. Variation of concentration of Sn and Cu with depth from the top surface at room temperature (a) for fresh sample and (b) for sample measured after 1 month (best fit with $b = 0.004$).

of such large crystallite across the bulk of the film seems unrealistic. This is further supported by the smooth nature of the experimentally determined concentration profiles across the cross-section of the film (figures 2a, 2b). As the sampling depth of the XPS technique is of the order of 50 \AA [12,17] and the area (circular with radius $\sim 0.3 \text{ cm}$) of the sample exposed to the X-ray beam for XPS analysis is large, the smooth variation of concentration could be explained provided the crystallites are thin (less than 50 \AA) in cross-section and are oriented parallel to the interface. Thus the concentration profile across the cross-section could be due to the variation in the concentration of individual phases (in this case Cu and Sn) along the depth with a depth resolution of 50 \AA .

The inter-diffusion coefficient for Cu at room temperature is measured from the profiles (figure 2a and 2b), assuming the cross-over point as the reaction front. The coefficient is found to be of the order of $1.5 \times 10^{-18} \text{ cm}^2/\text{s}$. The higher value of this parameter when compared with the value reported by Tu [3], could be due to very small crystallites as has been reported for nano-crystalline materials [18]. This could also be due to the interstitial diffusion which according to Tu [3] gives an additional degree of freedom for the diffusion process. Since at room temperature intermetallic

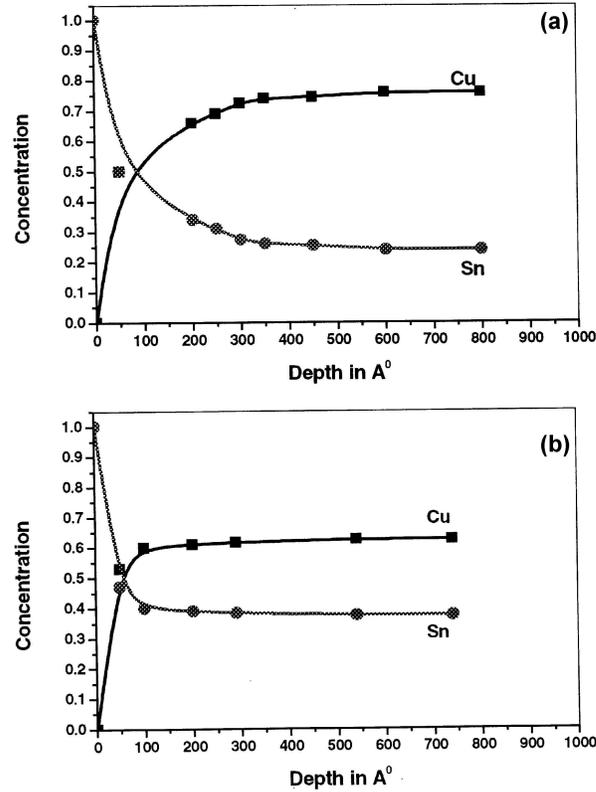


Figure 3. Variation of concentration of Sn and Cu with depth from top surface (a) for a sample at 100°C and (b) for a sample at 200°C (best fit with $b = 0.02$ and $b = 0.04$ respectively).

phase Cu_6Sn_5 (a long period superlattice of its high-temperature ordered hexagonal lattice [3]) is formed, diffusion of Cu is more crucial than that of Sn for the formation of the superlattice as this phase has excess of vacant sites for Cu. It has been observed that both mass transports along grain boundaries and interstitial diffusion at the growth front are sufficiently fast at room temperature and hence there is no lattice barrier for the growth of the superlattice phase. However, this may not be the same for high-temperature phases. This is due to the kinetic difference in the formation of the phases and is attributed to the diffusion of Cu in Sn but not vice versa [3]. Hence the inter-diffusion coefficient determined refers to Cu only.

Figures 2b, 3a and 3b show the concentration variation across the cross-section of the films for samples at room temperature for one month, for samples heated at 200 and 300°C respectively for 2 h. Best fits could be represented as

$$C_{\text{Cu}} = C_0(1 - e^{-bX}), \quad (1)$$

where C_0 and b are constants and X is the distance measured from the surface of the film. Again, for grain boundary diffusion it has been shown that concentration

variation across the thickness is represented for a given time as [16]

$$C(X, t) = C_0[1 - \operatorname{erf}(X/2(\sqrt{Dt}))], \quad (2)$$

where D is the diffusion coefficient. To a first-order approximation in such cases the depth (X) dependence of the concentration profile for a given time could be represented as

$$C(X, t) = \text{Const.} [\exp(-kX^2)]/X, \quad (3)$$

where, k is a constant. Thus, the observed concentration profiles (figures 2b, 3a and 3b) could not be described by the grain boundary migration of the atomic species.

For sample at 200°C (figure 3b), the Cu concentration nearly remains constant for depths above 100 Å and Cu distribution is described by eq. (1) with $b = 0.04$. Similarly for sample annealed at 100°C, constancy in Cu concentration could be assumed for depths above 300 Å for $b = 0.02$. However, for sample studied after one month (figure 2b) Cu concentration is found to change across the cross-section of the film ($b = 0.004$). From XRD studies [10] and also from the ratio of the atomic concentrations measured from XPS, formation of intermetallic phases like Cu_3Sn and Cu_6Sn_5 in the bulk of the samples annealed at 100 and 200°C is evident. However, for thickness within 100–300 Å from the surface, distributions of Cu and Sn (figure 3b) indicate some kind of non-equilibrium distribution. The concentration profile (figure 3b) gives the average value of the ratio of the atomic concentrations of Cu and Sn as 1.5 which indicates that the phases (Cu_3Sn and Cu_6Sn_5) formed are in equal proportions. However, no such conclusions could be drawn for samples annealed at 100°C (figure 3a) and the one studied after one month (figure 2b). This is because the diffusion-controlled solid-state reaction is yet to reach equilibrium.

The different values of the parameter b obtained for the three samples may be interpreted as follows: The regions, over which the concentrations of Cu is varying before being nearly constant (e.g. in case of 200°C it is nearly 100 Å), are defined as the interfaces. For the sample annealed at 100°C, where the solid-state reactions are to reach equilibrium, the interface is of the order of 300 Å. In the case of one-month-old sample the interface (initially it was at 500 Å from the surface) extends throughout the bulk of the sample. X-ray measurements for these samples indicate the presence of Cu, Sn phases [10], indicating incomplete reactions. Thus the parameter b gives a measure of the inverse of the width of the interface. These findings possibly point out the importance of the physical barrier like surface which influences the solid-state reactions. Although the best fits shown are empirical in nature, the present approach describes an attempt to incorporate the surface effect. One of the approaches could be by adding additional terms to eq. (3) to obtain the best fit which needs further investigations.

Finally, it may be concluded that the above studies have experimentally demonstrated the importance of surface in influencing the solid-state reactions and the near-surface compositions are different from that of the bulk.

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