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Enhanced diffusion caused by surface reactions in thin films of Sn-Cu-Mn

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ABSTRACT

This paper describes an investigation of low-temperature diffusion in thin films of Sn/Cu, Cu/Mn and Sn/Cu/Mn. The combination of Rutherford backscattering spectroscopy, grazing incidence X-ray diffraction and Auger electron spectroscopy has been used to provide information about the concentration distribution of components and the depth of the various phases and interfaces. The results show that processes that occur on a free surface of thin films can stimulate diffusion of elements in the bulk. It is shown that the element with higher affinity to oxygen tends to move to the surface in order to oxidize and that this oxidation process provides a driving force for further diffusion. Introduction of a third layer to a bilayer system may lead to changes in the surface topography caused by the reactive diffusion between upper layers and it causes the development of fast, ‘short-circuit’ diffusion paths and so increase the diffusion of elements from the bottom to the top. Reactive diffusion between Sn and Cu in the top layers leads to significant changes at the surface with features of the size of 10 to 20 nm appearing. These changes provide shortcuts for the diffusion of Mn atoms from the bottom layer to the free surface. As a consequence of these processes, the sequence of layers of different elements in thin-film structures alters diffusion and results in different sample properties.

1. Introduction

Cu-Mn alloys are widely used because of their electrical and magnetic properties [1, 2]. Re-distribution of the elements may lead to deterioration of these properties and this makes the study of diffusion in this system interesting not only from the theoretical [2] but also from the practical view-point [1]. High temperature diffusion in Cu-Mn alloys was studied by Iijima et al. [3] and faster interdiffusion as the Mn content increased to 30 at.% and then significant reduction with further increases was reported. This non-linear dependence of diffusion coefficients on concentration (Table. 1) makes the system interesting for the current research given that the elemental composition will determine properties of thin films significantly. Special interest lies in diffusion peculiarities in this system at low temperatures (100 - 200°C), that have not been studied earlier.

The Cu-Sn system has a wide range of application in microelectronics and nanoelectronics because of the electrical properties of Cu. Application of Sn solders results in formation of intermetallic compounds of Cu-Sn in a conductive copper layer. These compounds have high electrical resistivity that in return drastically deteriorates electrical properties of the contact. For these reasons, diffusion in Cu/Sn thin films has been studied widely [4–14]. Quantitative diffusion parameters for bulk samples and for films are also listed in Table. 1. If thin films are formed by sputtering, the formation of intermetallic compounds is observed already when condensation occurs. The compounds Cu_6Sn_5 and Cu_3Sn are found when annealing at 200°C [6, 9]. The phase Cu_6Sn_5 is usually formed first and transforms into Cu_3Sn phase as a result of heat treatment [10]. Different features of phase formation are observed in this system that depend on the thickness of films, method of deposition, annealing regimes and other factors [9]. Finally, Cu and Sn are found in thin films that are considered to be promising as components for solar cells [15]. For these reasons, further research on reactive diffusion in Cu/Sn thin films is of great importance, in particular, to understand how to provide thermal stability for such components.

Table 1. Previously reported diffusion in Cu/Mn/Sn

System	Diffusant	Matrix	T °C	Diffusion mechanism	Diffusivity $\text{cm}^2 \text{s}^{-1}$	Ref.
Mn(0.3 ML)/ on crystal Cu (100) face	Mn	Cu	20	surface	5.3×10^{-18}	[28]
Cu-Mn	Mn	Cu	600	bulk	2.1×10^{-12}	[29]
Cu(94 at.%)–Mn(6 at.%)	Cu, Mn	Cu, Mn	850	interdiffusion	0.61×10^{-5}	[30]

Cu(91 at. %)-Mn(9 at. %)	Cu, Mn	Cu, Mn	850	interdiffusion	1.18×10^{-5}	[30]
Cu(71 at. %)-Mn(29 at. %)	Mn	Cu	770	interdiffusion	8×10^{-6}	[3]
Cu(29 at. %)-Mn(71 at. %)	Mn	Cu	898	bulk	0.58×10^{-6}	[3]
Cu-Sn(simulation)	Cu	Cu ₃ Sn	150	bulk	4.13×10^{-12}	[31]
Cu-Sn(simulation)	Sn	Cu ₃ Sn	150	bulk	5.73×10^{-13}	[31]
Cu(40 nm)/Sn(160 nm)	Sn	Cu ₆ Sn ₅	200	grain boundary	2.55×10^{-15}	[11]
Cu(40 nm)/Sn(160 nm)	Sn	Cu ₃ Sn	200	grain boundary	0.8×10^{-15}	[11]
Cu(200 nm)/Sn(400 nm)	Sn	Sn	150	grain boundary self-diffusion	2×10^{-6}	[12]
Cu(560 nm)/Sn(200 nm)	Cu, Sn	Cu ₆ Sn ₅	150	interdiffusion	1.5×10^{-16}	[13]
Cu(9 μm)/Sn(1 μm) electrodeposited layers	Cu, Sn	Cu ₆ Sn ₅	200	interdiffusion	1.0×10^{-13}	[14]
Cu(9 μm)/Sn(1 μm) electrodeposited layers	Cu, Sn	Cu ₃ Sn	200	interdiffusion	2.3×10^{-12}	[14]

This paper presents an investigation of the influence of reactions at a free surface and at interfaces on the behavior of low temperature diffusion and the concentration distribution of elements in thin metal films. In particular, we study bilayer systems where components form solid solutions cover the full range of concentrations (Cu-Mn) or form intermetallic compounds (Sn-Cu). The combination of complete and partial solubility of components was also investigated in one sample of three consecutively deposited layers (Sn/Cu/Mn).

An additional layer of manganese to create Sn/Cu/Mn thin films provides better adhesion to a SiO₂ substrate than Cu due to the high affinity to oxygen of Mn. At the same time, this extra layer influences considerably the properties of the multilayer film as a whole [16]. The system is also of practical interest because it forms Heusler type phases. These are known for their ferromagnetic properties while all the constituent components are not ferromagnetic [17]. Such alloys are very sensitive to slight changes of concentration of the components that are reflected by changes in physical properties. Therefore, establishing how diffusion processes evolve and the various solid state reactions in Sn/Cu/Mn system is of interest. Our study has investigated both three layer and two layer systems Sn/Cu, Cu/Mn. This approach has the advantage that it allows determination of the influence of additional layers on mass transport such as the effect of a Sn layer on top of the Cu/Mn sample and a Mn layer on the Sn/Cu system.

Studying samples under conditions that either stimulate or hinder diffusion of particular elements is valuable in order to understand the requirements for particular conditions or to take precautions so as to preserve desirable properties. One of the major factors that can stimulate interdiffusion in thin metal films is the process of oxide formation at a free surface [18–21]. The free surface pumps material during the initial stages of diffusion, from the bottom layer to the top through the grain boundaries without penetration of material in the bulk of top layer's grains [22]. The driving force of mass transfer that pumps out material from the bottom to the top is the gradient of concentration. If a diffusing element emerges at the free surface and oxidizes then the gradient of concentration does not decrease and the driving force continues for a long time. Thus, in systems with these nanostructures, the gradients of concentration do not disappear in contrast to bulk materials. Homogeneity of concentration is not reached. This effect was observed clearly for thin Cu-Mn films (100 nm) when annealed at 400°C during 30 minutes in a vacuum 10^{-3} Pa [23]. It was seen that Mn atoms segregate on the surface and undergo further oxidation.

Several models can be applied to describe the mechanism of the free surface influence: the 'sink' model considers oxidation of the elements that emerge on the surface as the main driving force [24]; other models consider the surface energy of oxide formation [25] or the surface potential [26]. Sources of oxygen for oxide formation on the surface of thin films systems under annealing in vacuum at different pressures have been studied thoroughly [27]. The process where the free surface pumps material from the bottom layer by diffusion through grain boundaries to the top layer with reactive diffusion occurring to form intermetallic compounds has not been discussed previously.

The present study concerns the basic factors that determine the interdiffusion in metal films and in particular the role of the surface in the evolution of composition changes in the bulk and at interfaces. The combination of a range of experimental techniques is particularly valuable to confirm the composition and phase behavior of materials and how these relate to morphology. The paper describes the application of a range of experimental techniques to thin film samples that were prepared identically, by cutting from a single large piece, and then annealed under a range of different conditions as regards temperature and environment. Annealing both in hydrogen, and for the same temperature and time under vacuum, was performed so as to determine the influence of the free surface and reactions on the evolution of the diffusion.

2. Experiment

Metal films were deposited by magnetron sputtering. The base pressure of the vacuum system was 5×10^{-5} Pa, and high-purity (99.99999%) argon at a pressure of 50 Pa was flowing during sputtering. The substrates were thermally oxidized Si (100) wafers. Thin film systems Sn (60 nm)/Cu (180 nm), Cu (180 nm)/Mn (60 nm) and Sn (60 nm)/Cu (180 nm)/Mn (60 nm) were prepared on top of the SiO₂ on the wafer. The nominal thicknesses of layers were estimated from the sputtering time and the predetermined deposition rate of each target.

Annealing was performed in a vacuum system with a base pressure of 10^{-6} Pa and in hydrogen atmosphere with a pressure of 50 Pa. Annealing temperatures were chosen to be 100°C and 200°C to study low temperature diffusion processes. Annealing time was taken as 20 minutes for each temperature regime. Annealing in hydrogen was performed as it can chemically reduce oxides. The oxide reduction was important in order to study influence of oxidation processes on the surface on the diffusion in the bulk of a sample by excluding it in this way. This phenomenon has also been observed in other studies [15, 32–33]. Annealing in vacuum is not sufficient to prevent oxidation for elements with such a high oxygen affinity as Mn because there is always a source of oxygen from the top oxide layer that has been naturally formed.

The composition of the samples was determined by Rutherford backscattering spectroscopy (RBS). Experiments were performed using helium ions He⁺ with a beam energy of 2 MeV and a scattering angle of 160°. SIMNRA software [34] was used to analyze the RBS data. Auger electron spectroscopy (AES) (Auger microprobe JAMP 9500F, JEOL) with high-spatial resolution imaging (8 nm probe diameter) in secondary electrons and X-ray electron probe microanalysis was also used to investigate the Sn/Cu/Mn system annealed in vacuum. The energy of the primary electron beam was 10 keV. The imaging has been performed using emitted backscattered and secondary electrons. The elemental composition of the derived images has been carried out by means of energy dispersive analysis using an OXFORD INCA PENTA Fctx3 setup. This served as a complement to the RBS experiments to provide more accurate estimates of the concentration distribution of the various elements in the samples. Phase composition was determined by grazing incidence X-ray diffraction using a Siemens D5000 diffractometer with CuK_α radiation in parallel beam geometry with X-ray mirror. X-ray data were obtained in a 2θ scan and the angle of incidence beam was chosen to be 3° in order to penetrate the film but not to reach the substrate. Atomic force microscopy (AFM) (Nanosurf

Mobile S) was used to study the surface topography and the roughness. Measurements were performed in contact mode.

3. Results

3.1. Sn/Cu/SiO₂ system

X-Ray diffraction data for a sample in the as-deposited state showed peaks from the Cu₆Sn₅ phase and pure copper. Annealing at 100°C in vacuum does not influence the phase composition. Annealing at 100 °C under a hydrogen atmosphere, and annealing at 200 °C in both vacuum and hydrogen all lead to complete transformation of the Cu₆Sn₅ phase into Cu₃Sn. Peaks from pure copper remain with a slight decrease of intensity. The position of the copper peaks does not change and this indicates a grain boundary diffusion mechanism. These data are shown in Fig. 1.

Results of analysis of the RBS data are in a good agreement with the X-ray diffraction data. Simulation of RBS data shows transformation of the observed composition Cu₆Sn₅ to that of the Cu₃Sn phase. RBS spectra for the as-deposited sample and the sample after annealing at 200°C in vacuum are shown in Fig. 2. Spectra from other samples are not given because the sample annealed at 100°C in vacuum matches with as-deposited one and annealing in hydrogen shows the same picture as annealing at 200°C in vacuum.

Fig. 1. X-ray diffraction data for the Sn/Cu system: (a) as-deposited sample, (b) annealed at 200°C for 20 minutes. The chart below the measured data indicates where diffraction peaks are expected for the various possible Cu/Sn compounds.

Fig. 2. RBS spectra for Sn/Cu thin films: solid lines represent simulation results. The points are the experimental data.

Simulation of the RBS data shows that the as-deposited (unannealed) sample has a surface layer 17.5 nm thick where the concentration of Sn reaches 37 ± 3 at.% and the Cu concentration is 45 ± 3 at.%. This corresponds to the concentration of Sn in Cu_6Sn_5 phase. There is also about 25 ± 5 at.% of light elements such as O and C at the surface. In subsequent layers below the surface, we observe gradually decreasing Sn concentration. Finally a Cu layer of thickness 53 ± 2 nm with about 1 at.% of Sn is found close to the substrate. Diffusion of Sn atoms into the Cu layer is apparent from the slope on the right side of the Cu spectrum and the overlapping zone between Sn and Cu spectra seen in Fig. 2. The height of the Sn spectra drops after annealing in vacuum at 200°C and in hydrogen at 100°C and 200°C (Fig. 2). The overlap area between the Sn and Cu spectra increases. This indicates that the Cu_6Sn_5 phase has been fully transformed into Cu_3Sn phase together with extensive diffusion of Sn atoms into the Cu layer. The concentration of Sn atoms in the near-substrate layer increases from 1.5 at.% to 7.5 at.%.

Even though X-ray diffraction data do not show the presence of peaks for pure Sn, the RBS data indicate that the Sn concentration decreases gradually from that of the Cu_6Sn_5 phase to 1 at.%. This indicates that Sn is segregated and is found mainly in the grain boundaries and once again suggests a grain boundary diffusion mechanism. Atomic force microscopy does not show significant differences between the samples. The roughness is about 15 nm. This rough structure is inherited from Cu_6Sn_5 phase topography [35–37].

3.2 Cu/Mn/SiO₂ system

X-ray diffraction data showed the presence of Cu and Mn peaks for the Cu/Mn film. Further annealing in vacuum and in hydrogen did not lead to any shift of the peaks from the initial positions. Simulation of the RBS data shows two layers of Cu and Mn being present in the as-deposited state. The top layer that is about 180 nm thick is pure copper. The bottom layer of about 60 nm consists primarily of Mn with a concentration of Cu atoms that is 2 at.%.

Annealing at 100°C in vacuum did not change the distribution of elements in the system. RBS data for the sample annealed at 200°C in vacuum indicates diffusion of Mn atoms to the top of the Cu layer and their concentration at the surface reaches 9 ± 2 at.%. After annealing in hydrogen only 4 ± 2 at.% Mn is found at the surface. The thickness of the layer that contains Mn is about 13 nm in both cases. The RBS spectra for the as-deposited sample and for the samples annealed at 200°C in vacuum and hydrogen are shown in Fig. 3. The increase of the overlap of the signals for Cu and Mn in the sample annealed in vacuum together with the shift of the Cu spectrum towards lower energies, to the left on Fig. 3, indicates interdiffusion of Cu and Mn and the accumulation of Mn atoms at the surface. After annealing in hydrogen at 100°C, the concentration of Mn atoms at the surface reaches 6 ± 2 at.%. This is an intermediate case between annealing at 200°C in hydrogen and in vacuum.

Fig. 3. RBS spectra for Cu/Mn thin films: solid lines represent simulation results. The points are the experimental data.

AFM images for the Cu/Mn films are shown in Fig. 4. The average roughness is about 0.5 nm. The surface topography of the as-deposited state is characterized by the presence of

spikes (Fig. 4a). The lateral average size (diameter) of the base of the spikes lies in the range of 130 to 235 nm and the corresponding height is 3 to 10 nm, shown with an arrow on a Fig. 4a. The surface is expected to be covered by copper oxide after exposure to air and the observed topography will correspond to structures of this material that are formed on top of the Cu film. The spikes are often seen as lines with a lateral separation of about a thousand nanometers on the surface after annealing in hydrogen at 200°C (Fig. 5b).

Fig. 4. AFM images for the Cu/Mn system: (a) as deposited state and (b) after annealing in vacuum at 200°C for 20 min.

Annealing in vacuum at 200°C shows an opposite effect: the formation of cavities. An example is marked with a circle on Fig. 4b. The lateral size of the cavities is the same as for the spikes in the as-deposited state and the average depth of the cavity is of the same magnitude as the height of the spike (Fig. 4a). It is interesting that annealing in hydrogen at 100°C shows the formation of both cavities and scallops (Fig. 5a). Again we see that annealing in hydrogen at 100°C represents an intermediate state between annealing at 200°C in vacuum and hydrogen. Topography roughness profiles were made to estimate the size of features on the surface and are shown in Figs. 5c and 5d. Annealing at 100°C in vacuum did not lead to significant topography changes compared to the as-deposited state.

3.3 Sn/Cu/Mn on SiO₂ samples

X-ray diffraction (XRD) data shown in Figure 6a for the Sn/Cu/Mn system shows the presence of Cu₆Sn₅, Cu and Mn phases in the initial state. The most intense Mn peak is shown magnified in the inset in Fig. 6a and it is clear that the shape is asymmetric and has a step that arises from overlap of separate Cu and Mn peaks. The diffraction angles that correspond to the

(111) peak of Mn and Cu are 43.03° and 43.3° [38] respectively. The step is observed on the right side of the peak at an angle that corresponds to diffraction from Cu (111). Further annealing at 100°C for 20 minutes in vacuum (Fig. 6b) leads to the peak moving to higher 2θ .

Fig. 5. AFM images for the Cu/Mn system: after annealing in hydrogen (a) at 100°C and (b) at 200°C . Topography plots of roughness profiles for the corresponding samples annealed in hydrogen (c) at 100°C and (d) at 200°C .

The intensity of the peak at 43.03° decreases and that can be interpreted as indicating a lower Mn concentration as some of the Mn atoms segregate in grain boundaries. Annealing at 200°C for 20 minutes in both vacuum (Fig. 6c) and under hydrogen (Fig. 6d) leads to a shift of this peak to higher angles so that it corresponds entirely to 43.3° , meaning that the concentration of Mn has dropped further due to the grain boundary diffusion and the Cu diffraction peak is dominant. This is similar to the results for the binary Cu/Sn system where extensive interdiffusion of Cu and Sn occurred and the formation of Cu_6Sn_5 during deposition was observed in thin films of Sn/Cu [4–10]. After annealing at 100°C for 20 minutes, the phase composition remains unchanged. Increasing the annealing temperature to 200°C leads to complete transformation of the Cu_6Sn_5 phase into the Cu_3Sn phase. After annealing at this temperature, diffraction peaks from pure Mn and Cu are also present.

Fig. 6. X-ray diffraction data for the Sn/Cu/Mn system: (a) as-deposited sample, (b) annealed at 100°C for 20 minutes in vacuum, (c) annealed at 200°C for 20 minutes in vacuum, (d) annealed at 200°C for 20 minutes in hydrogen. The chart below the plots of measured data indicates where diffraction peaks are expected for the various possible Mn/Cu/Sn compounds.

X-ray diffraction data presented in Fig. 6d show that annealing in hydrogen leads to formation of a further phase: Mn₃Sn. Auger electron spectroscopy was used in combination with RBS spectroscopy in order to provide a precise depth concentration analysis together with the information about the thickness of constituent layers. AES provides information about the concentration and these data, when combined with the known amount of material obtained from RBS results for the layered structure, which are modelled with constraints to fit the AES concentration profile, are used to derive the thickness. Auger electron spectroscopy data for the unannealed sample and after annealing at 200°C in vacuum are shown in Fig. 7. In the initial state, Cu is observed throughout the entire layer of Sn (Fig. 7a). Sn atoms are also observed through about half the thickness of the Cu layer. There is an overlap between the layer of pure Cu and pure Mn where interdiffusion occurs by a grain boundary mechanism. RBS data are in good agreement with the AES results. The shoulders on the Sn spectrum and Cu spectrum

indicate interdiffusion between the two elements (Fig. 8b). The RBS data also shows that all Sn is involved in the diffusion process. According to the AES data, the thickness of pure tin at the surface is about 8 nm.

Fig. 7. Composition profiles of near surface regions according to the AES data for the initial state (a) and after annealing at 200°C for 20 minutes (b). Composition profiles for the overall sample thickness are shown in the insets labeled a* and b* respectively.

Fig. 8. RBS spectra for Sn/Cu/Mn thin films: solid lines. In (a), the hollow squares correspond to experimental data and black squares represent simulation results to the as-deposited state and the hollow circles and black circles after annealing at 100°C in vacuum. In (b), the hollow squares correspond to experimental data and black squares represent simulation results to the sample annealed at 200°C in vacuum and the hollow circles and black circles to the sample annealed at 200°C in hydrogen.

Although Sn forms Cu_6Sn_5 to a thickness of about 40 nm, some pure Sn remains. Annealing at 100°C for 20 minutes leads to a slight redistribution of the components and the pure Sn at the surface decreases. The thickness of the Cu_6Sn_5 phase remains the same. RBS data suggests the onset of formation of a Cu_3Sn phase, as a layer with a concentration of Sn of

about 25 at.% and thickness 15 nm is detected. The overlapping area between Cu and Mn spectra in Fig. 8a increases and this further indicates interdiffusion at the Cu/Mn interface. This has not been observed for the Cu/Mn bilayer system where annealing at 100°C in vacuum did not lead to interdiffusion of the components.

AES and RBS data clearly indicate the presence of a layer with the composition Cu_3Sn after annealing the Sn/Cu/Mn sample at 200°C for 20 minutes. The thickness of the material with this composition is twice that of the Cu_6Sn_5 phase. Mn atoms diffuse to the surface according to the grain boundary mechanism because no changes in the lattice constants of Cu and Mn were found. The concentration of Mn at the external surface is enhanced with respect to its concentration in the near surface layers and reaches 13 at.%. The similar concentration distribution for oxygen and manganese in the near surface region (Fig. 7b) suggests the formation of manganese oxide on the surface under the conditions of annealing. RBS data for the samples annealed in hydrogen show an extra peak that is marked with a circle in Fig. 8b. This peak results from formation of the compound Mn_3Sn at the surface.

The microstructure and topography for the sample annealed at 200°C for 20 minutes are shown in Fig. 9. The chemical composition was determined using X-ray electron probe microanalysis and the Mn concentration is higher in the dark areas shown in the image. The roughness of the surface of the annealed sample is about twice that of the initial material.

Fig. 9. Secondary electron image (a) and AFM (b) images of the surface the Sn/Cu/Mn sample after annealing at 200°C for 20 min. The composition at the points 1 and 2 are: (1) Sn: 16 at.%, Cu: 72 at.%, Mn: 0.7 at.%. (2) Sn: 7 at.%, Cu: 68 at.%, Mn: 9 at.%, the rest is impurities (oxygen and carbon). The average roughness is 20 nm.

4. Discussion

4.1 Annealing in vacuum

X-ray diffraction and RBS data show extensive interdiffusion of components in the Sn/Cu system that occurs even during the deposition by sputtering. This effect has already been described in previous papers [9, 23]. It was deduced from X-ray diffraction data that the Sn atoms diffuse according to a grain boundary mechanism. Diffusion under the influence of a reaction to form intermetallic compounds is the dominant process in the Sn/Cu thin films and therefore oxidation processes on the surface do not significantly alter the diffusion of the components. The enthalpy of SnO_2 formation is -516 kJ mol^{-1} and Cu_2O is -169 kJ mol^{-1} [39] and therefore there is no driving force for Cu atoms to diffuse to the surface.

The role of oxidation processes becomes significant in Cu/Mn thin films when no formation of intermetallic compounds occurs to drive the diffusion. Interdiffusion of the components in the Cu/Mn system is slower as compared to the Sn/Cu system. Analysis of RBS data shows that annealing at 200° in vacuum leads to diffusion of Mn to the surface where the concentration reaches $9 \pm 2 \text{ at.}\%$.

The Sn/Cu/Mn system represents both cases: diffusion to form compounds in the system Sn-Cu, Sn-Mn and continuous solubility between Cu and Mn. Diffusion behavior in the Sn/Cu mixture is the same as for the bilayer system. Diffusion of Mn in the ternary system occurs more extensively than in the bilayer system as seen from RBS data (Fig. 8). The Mn spectrum completely merged with the Cu spectrum after annealing at 200°C , both in vacuum and under hydrogen, in contrast to the behavior under the same annealing regimes but for the Cu/Mn system (Fig. 3). Even though the Auger data indicates approximately the same amount of Mn atoms to be present on the surface, we observe a higher concentration of Mn in the near surface region ($12 \text{ at.}\%$). Chemical analysis of the different regions visible in the secondary electron image (Fig. 9a) reveals different content of Mn. The light areas have almost no Mn but have $16 \text{ at.}\%$ Sn while the dark spots are characterized by a higher content of Mn ($9 \text{ at.}\%$). The size of these regions is around hundred nm, the size of the Auger probe is 8 nm. Analysis of the AFM images for the Cu/Mn films also showed features with a lateral size of hundreds of nm and these features would correspond to Mn oxide formation. The top layer of the Sn/Cu/Mn sample is an intermetallic compound with a scallop like topography that is inherited from Cu_6Sn_5 phase with a roughness of about 20 nm. This corresponds to about one third of the Sn film thickness. Therefore, since Mn atoms tend to move to the surface in order to oxidize, the shortest path will be between the scallops as shown schematically in Fig. 10. This

explains why there is faster diffusion in the ternary system: the top layer thickness fluctuates a lot due to the roughness and therefore Mn atoms can find a shorter path to the surface. At the same time it was found that minor additions of Mn to the Cu could effectively suppress the growth of Cu_3Sn by reducing Cu diffusion into the Cu_3Sn layer [17]. The diffusion coefficient for Cu into Cu_3Sn in the absence of Mn is $4.6 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ and in the presence of 2 at.% of Mn it decreases to $1.1 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ [26]. Hence, we do not observe changes in mass transfer for the Cu/Sn as compared to the bilayer system. We conclude that Mn does not contribute to the Cu_3Sn phase formation and therefore tends to diffuse to the areas between the grains of this phase that are found at the surface.

The combination of AES, RBS and XRD data allows us to develop a schematic distribution of the concentration and phases present through the depth of Sn/Cu/Mn films that is shown in Fig.11. Mn atoms diffuse over the distance of 240 nm (Sn layer + Cu layer) in 20 minutes. Therefore we can make a rough estimate of the diffusion coefficient of Mn given that $D = x^2 \times t^{-1}$, where x is a diffusion path length and t is time. This suggests that the diffusion coefficient for Mn at 200°C is about $4.8 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$. This value is higher than that calculated by Iijima et al. [3] for the case of bulk diffusion at temperature of 600°C . Given that, we suggest that diffusion occurs via the faster routes, along the surface at grain boundaries or lines of contact between grains. This idea is supported by the XRD data that does not show other phases forming or changes in lattice parameters due to substitution of different atoms.

Fig. 10. Schematic representation of manganese oxide growth on the surface

Fig. 11. Model of composition and phase formation processes in Sn/Cu/Mn systems: (a) – initial state, (b) annealed at 100 °C and (c) 200 °C for 20 minutes in vacuum. The shaded regions correspond to the areas of overlapping composition.

4.2 Annealing in hydrogen

Annealing in hydrogen of the Sn/Cu system does not make a difference as compared to annealing in vacuum. The result of annealing of the Cu/Mn sample at 200°C for 20 minutes in hydrogen indicates concentration of Mn atoms at the surface that is two times lower and less interdiffusion of the components in the bulk 4 ± 2 at.%. This phenomenon can be explained in the following way: for a thin film system with material in the lower layer that has a very high affinity to oxygen, there will be a tendency to diffuse and accumulate on the outer surface so as to oxidize. If atoms of this material react to form an oxide then the gradient of chemical potential between the bottom layer and the surface is unchanged and the diffusion to the surface continues. The outer surface acts as a pump driven by oxygen [33, 23] that forces material from the lower layer to the top providing continuous diffusion. The enthalpy of formation for Mn_3O_4 oxide is $-1390 \text{ kJ mol}^{-1}$ [39].

Therefore, it is thermodynamically favorable for Mn atoms to move to the surface and form an oxide by taking oxygen either from residual gases in the vacuum system or from the Cu oxide. Calculations show that 5 nm of copper oxide is sufficient to form 7.6 nm of Mn_3O_4 if all oxygen from the Cu layer are reduced to oxidize Mn. Koike and Wada [40] have described how Mn atoms in a Cu–Mn alloy film diffuse to the surface and the interface to form oxide. As annealing was performed in good vacuum, we can assume that Mn reduces the Cu oxide that serves as a source of oxygen. The mechanism of this process is described in more

detail in the paper of van Loo et al. [41] where thermodynamics of displacement reactions are discussed. It is suggested that for a system with three components A-B-X, when component A diffuses towards the surface, two possible paths are possible. These paths lead to either a formation of a structure A/AX/B/BX or A/(A,B)/AX/BX. In our experiment, where we have a three component system, Mn-Cu-O, we observe that the structure Mn/(Cu,Mn)/Mn₃O₄ is formed. We do not observe copper oxide because the annealing was carried out in a hydrogen atmosphere that causes reduction of Cu₂O. In the study of Shaffer and McCormick [42] on displacement reactions during mechanical alloying, Cu₂O reduction with Mn was also discussed and the reaction of Cu oxide with Mn is given as follows: $\text{CuO} + \text{Mn} \rightarrow \text{Cu} + \text{MnO}$.

Thus, the oxide formation does not necessarily occur only at the surface but also in the near-surface layer. This process can explain why cavities are observed in the AFM image shown in Fig. 4b and why the diameter of the cavity is the same as the diameter of the base of the spike in the as-deposited sample. As there is copper oxide on the surface, we deduce that features on the surface are related to that material. Another mechanism that can explain cavity formation is that of thermal grooving proposed by Mullins [43]. Development of surface grooves at grain boundaries of a heated polycrystal sample has been described [43]. Initially the grain boundary, γ_{α} , and surface free energies, γ_s are in equilibrium at an angle, 2α , defined as the angle between the two grain surfaces, given by the equation $2\gamma_s \cos \alpha = \gamma_{\alpha}$. When the grain boundary is saturated with the diffusing material, its energy changes and to maintain the equilibrium with the surface the angle must also change and the grooves appear. There is a high possibility that thermal grooving and copper oxide reduction occur simultaneously and lead to the formation of cavities on the surface.

The annealing in hydrogen at 200°C leads to reduction of both Cu and Mn oxides simultaneously. Consequently Mn atoms diffuse to the outer surface in smaller amounts and reside there in the unreacted state. After the sample is removed from the vacuum chamber, Mn atoms are oxidized and we observe stripes on the surface with a pattern that resembles the grain boundaries in Fig. 5b. The X-ray data analysis suggests a grain boundary diffusion mechanism because the peak positions do not indicate changes in lattice constants of Cu and Mn and thus the elements diffuse by a mechanism other than in the bulk of grains. This supports the idea of topographic features appearing on the surface at grain boundaries.

Annealing in hydrogen at 100°C shows an intermediate result between that seen at 200°C in vacuum and in hydrogen. The main question to be addressed is why annealing in hydrogen at a lower temperature causes diffusion of Mn atoms to the surface. This may occur

if the reduction of oxide is controlled by kinetic processes. When annealing at 100°C, less time is spent on heating and cooling the sample, and the total time of heat treatment is less. This may result in incomplete reduction of copper oxide and thus both cavities and scallops are observed in Fig. 5a. As long as Cu₂O remains on the surface, there will be an oxygen source available for the oxidation of Mn and a driving force for diffusion to the surface.

According to the X-ray data, annealing of the Sn/Cu/Mn system in hydrogen at 200°C leads to the formation of a new phase, Mn₃Sn. After annealing at 200°C in vacuum 16 ± 2 at.% of Mn was detected on the surface and about 3 to 5 at.% in the layers below the surface. After annealing at the same temperature in hydrogen, the concentration of Mn atoms at the surface was reduced to 10 at.% and to 1 to 2 at.% in the subsequent layers. Annealing in hydrogen of the three-component system also slows down diffusion of Mn atoms but not so much as observed for the Cu/Mn system. This may be due to formation of another compound at the surface: Mn₃Sn is observed and therefore, in the same way as for oxidation, the concentration gradient does not decrease and diffusion continues.

5. Conclusions

The results show that processes that occur on a free surface of thin films can make significant contributions to the transport in the bulk. The sequence of the layers with respect to the free surface is important. In the Cu/Mn system, it was shown that atoms of the element with higher affinity to oxygen tend to move to the surface in order to oxidize and the process of oxidation provides a continuing driving force for further diffusion. Annealing in vacuum at 200°C gave rise to 9 at.% of Mn at the free surface which is twice that found after annealing in a hydrogen atmosphere. It was shown that the influence of oxidation at a free surface changes depending on the presence of other competitive processes that occur in the near-surface region such as reactive diffusion. Reactive diffusion in the near surface layer of the Sn/Cu system and the thermodynamic preference of SnO₂ oxide formation inhibits enhanced diffusion of Cu atoms towards a free surface. For the Sn/Cu/Mn layers, increases of the Mn concentration on the free surface up to 16 at.% were observed even though the initial layer of Mn was placed further from the surface due to the third layer of Sn in the sample. Formation of specific phases that takes place in the upper layer provides scallops and a rough surface topography, which accelerates diffusion by providing heterogeneity of thickness in the upper layers. The increased amount of Mn at the surface suggests that the diffusion was twice as fast when a source of oxygen was present. Thus, we observe that introducing a third layer to a bilayer film enhances

diffusion processes by altering the surface topography as a result of reactive diffusion between the upper layers.

Therefore, we may deduce that the key factors that enhance diffusion in the system are: thermodynamics that favor formation of specific phases on the surface such as oxides and intermetallic compounds; diffusion that is influenced by topography and formation of structures that are correlated with grain boundaries; the difference in surface energies of elements of thin layers.

The results from this study can guide the selection of the sequence of layers ordering for thin-film structures that will be exposed to thermal treatment so as to prevent degradation of properties that arise from changes in structure.

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