AES and XRD study of In/Cu thin films deposited onto SiO_2 by electron beam evaporation

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Abstract. In order to investigate the diffusion of indium (In) when an In thin film is coated with a copper (Cu) thin film, thin In/Cu films were grown on a silicon dioxide (SiO_2) substrate. Both the In and the Cu layers were grown by electron beam evaporation. The temperature during evaporation of the films ranged between 27 and 38 °C. The In films (500 Å) were coated with Cu films (500 Å and 1000 Å). The films were characterized with X-ray diffraction (XRD) and Auger electron spectroscopy (AES). The In/Cu layers interdiffused during evaporation and formed intermetallic $CuIn_2$ and $Cu_{11}In_9$ phases. The In layer completely reacted with the Cu layers during the deposition process. The In layer was effectively coated with a Cu layer (1000 Å). The In (500 Å)/Cu (1000 Å) films were annealed at temperatures ranging between 150 and 300 °C for 49 min. The diffraction data of the annealed films showed peaks for Cu, $CuIn_2$, $Cu_{11}In_9$ and Cu_2In. The AES depth profiles illustrate phase formation and segregation of the In to the surface of the films. The results of this work provide insight information towards the In doping of Cu crystals at temperatures higher than the melting point of In (156.6 °C).

1. Introduction

Due to copper's excellent electrical properties, it is widely used in the electronic industry and it appears to be a promising material for integrated circuit interconnections. However, Cu cannot form a self-passivation layer under oxidizing conditions and adheres poorly to glass. Experimental studies [1, 2] have shown that In on a Cu surface of Cu/In thin films improves the adhesion of Cu on glass and provide Cu with a self-passivation layer under oxidizing conditions. Thus making Cu/In thin films a potential material for application in thin-film transistor liquid-crystal display (TFT-LCD) and in ultra-large-scale integrated (ULSI) devices.

Previous studies on the Cu/In system focused more on the reaction and formation of intermetallic compounds in Cu/In thin films at room temperature [4-7]. In these studies, it was shown that the first compound ($CuIn_2$) that formed, formed directly from the starting metals (In and Cu), the second compound ($Cu_{11}In_9$) that formed, formed through a reaction of the first compound with the excess of the high-melting metal (Cu).

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Each time the compound that has formed will react with the excess high melting point metal forming the next meta-stable compound, this process will continue until the final stable compound is formed. This phenomenon is a promising phenomenon to be used in a method to dope Cu (a high melting point metal) crystals with In (very low melting point metal).

This project focused on In/Cu films that were grown on SiO_2 substrate by electron-beam evaporation and the intermetallic phases that formed during annealing.

2. Experimental details

SiO_2 substrates were prepared by wet oxidation at 1000 °C for 1 hour. The substrate was cooled to room temperature and a In film of 500 Å was grown on the SiO_2 substrate by means of electron beam evaporation. The In films were then coated with Cu films that range in thickness from 500 Å to 1000 Å as shown in figure 1 (the insert). The Cu films were also grown by means of electron beam evaporation. During evaporation of the films the base pressure in the vacuum chamber was 2.5×10^{-5} Torr. The temperature of the substrate during evaporation was between 27 °C and 38 °C. The films thicknesses were monitored during the evaporation with an Inficon Leybold Heraeus XTC thin film monitor.

The In films coated with a 500 Å and 1000 Å Cu layer were annealed in a vacuum tube furnace with a base pressure of 8.0×10^{-5} Torr. The annealing temperatures were, 150 °C, 200 °C, 250 °C and 300 °C for 49 minutes.

X-Ray diffraction (XRD) measurements were used to characterize the samples after evaporation, annealing and indentifying the compounds that formed. Auger electron spectroscopy (AES) depth profiles were also obtained for each sample utilizing Ar^+ ion etching with a 2.0 keV ion beam with an ion current density of 0.113 A/m^2. The AES measurements were performed with a 10.0 keV electron beam with a beam current of 4.8 μA.

3. Results and Discussion

Figure 1 shows the XRD data of the as-prepared (un-annealed) films for both the 500 Å and 1000 Å Cu cover layers. From the XRD data it is clear that two phases namely $CuIn_2$ and $Cu_{11}In_9$ form at room temperature (between 27 °C and 38 °C) during the evaporation. The XRD peaks corresponding to the two phases are shown in figure 1. The formation of the two phases ($CuIn_2$ and $Cu_{11}In_9$) at a low temperature is consistent with observation found in literature [8]. According to Keppner [8] $CuIn_2$ form at low temperatures and is only stable below 150 °C. For the un-annealed sample with the 1000 Å Cu layer, a larger Cu peak is seen at 43.262° that indicates that more unreacted Cu is left for the thicker Cu layer after the formation of the $CuIn_2$ and $Cu_{11}In_9$ phases, as expected. For both samples there are no In peaks visible in the spectra, suggesting that all pure metallic In was consumed in the phase formation process. This has been confirmed by the Auger depth profiles (Figure 3).

The standard XRD peak positions (2θ) for Cu, In, $CuIn_2$, $Cu_{11}In_9$ and Cu_2In are summarised in table 1. The XRD standards for Cu, In, $Cu_{11}In_9$, Cu_2In are from the Joint Committee on Powder Diffraction Standards (JCPDS) data files number 04-0836, 05-0642, 41-0883, 42-1475 respectively while $CuIn_2$ XRD data are those used by Keppner *et al.* [8] and Başol *et al.* [9].

Table 1. The values of 2θ obtained from figure 1 and 2. The phases indexed to the data are shown with JCPDS data (intensities are in parentheses).

Obtained data	**JCPDS data**				
	Cu	In	$CuIn_2$	$Cu_{11}In_9$	Cu_2In
2θ (degrees)	2θ (degrees)	2θ (degrees)	2θ (degrees)	2θ (degrees)	2θ (degrees)
33.453	-	-	-	32.979 (80)	-
33.641	-	-	-	32.979 (80)	-
34.455	-	-	34.454 (100)	-	-
41.796	-	-	-	41.478 (100)	-
42.142	-	-	-	-	42.160 (100)
43.262	43.297 (100)	-	-	-	-
54.399	-	-	-	54.983 (50)	-
56.171	-	-	-	57.256 (60)	-

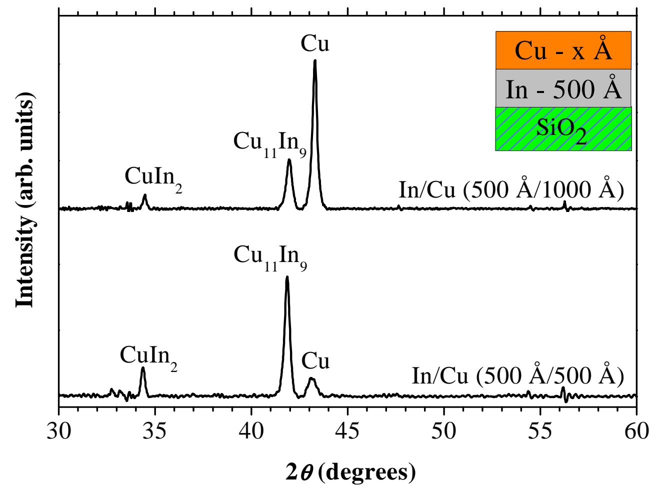

Figure 1. XRD data of the as-prepared In/Cu thin films on SiO_2 substrate.

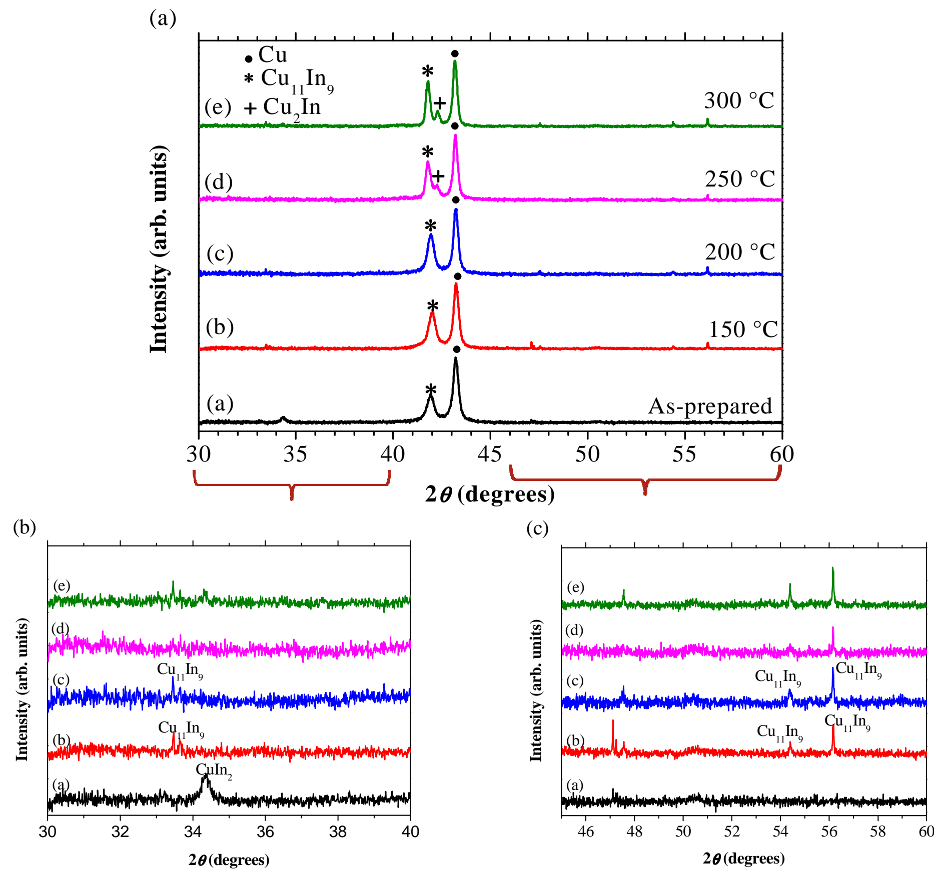

Figure 2. XRD data of the annealed In (500 Å)/Cu (1000 Å) thin films for 49 minutes.

The XRD data of the annealed In (500 Å)/Cu (1000 Å) thin films are shown in figure 2. The thin films were annealed for 49 minutes at 150 °C, 200 °C, 250 °C and 300 °C. When annealing the thin film at 150 °C for 49 minutes the $CuIn_2$ peak at 34.455 ° disappeared from the XRD spectrum while the 41.796 ° peak of $Cu_{11}In_9$ increased relative to the 43.262 ° peak of Cu. There also appeared new peaks at 33.453 °, 33.641 °, 54.399 ° and 56.171 ° corresponding to the $Cu_{11}In_9$ phase. Annealing the thin film at 200 °C for 49 minutes all the $Cu_{11}In_9$ peaks grew in size relative to the 43.262 ° peak of Cu. A new peak at 42.142 ° appeared in the spectrum for the thin film annealed at 250 °C for 49 minutes. This new peak corresponds to the 42.160 ° peak of the Cu_2In phase.

Figure 3 shows the AES depth profiles of as-prepared (un-annealed) (a) and annealed ((b) to (e)) In/Cu thin films. From the depth profile of the In (500 Å)/Cu (1000 Å) un-annealed film it is noticeable that the Cu have diffused through the In layer. This is in agreement with the XRD, where no pure metallic In peaks were measured. It can be seen from the film annealed at 150 °C for 49 minutes that the In have diffused deeper into the Cu layer. This is clearly seen by looking at the 5 % In concentration marker. For the un-annealed sample the marker is at 440 Å while for the annealed (150 °C) sample the marker is at 300 Å clearly showing that In diffused deeper into the Cu layer.

When the samples were annealed at 200 °C for 49 minutes the In diffused throughout the Cu layer. But instead of having a classical diffusion shape the depth profile had two plato regions indicating the formation of a new phase. This is in agreement with the XRD and the phase was identified as $Cu_{11}In_9$.

For the samples that were annealed at 250 °C and 300 °C for 49 minutes the plato regions grew more prominently and clearly indicating the formation of more phases. It was also clear from the 200 °C, 250 °C and 300 °C AES depth profiles that In was enriched on the surface. This suggests that In segregated from a Cu matrix during a heat treatment.

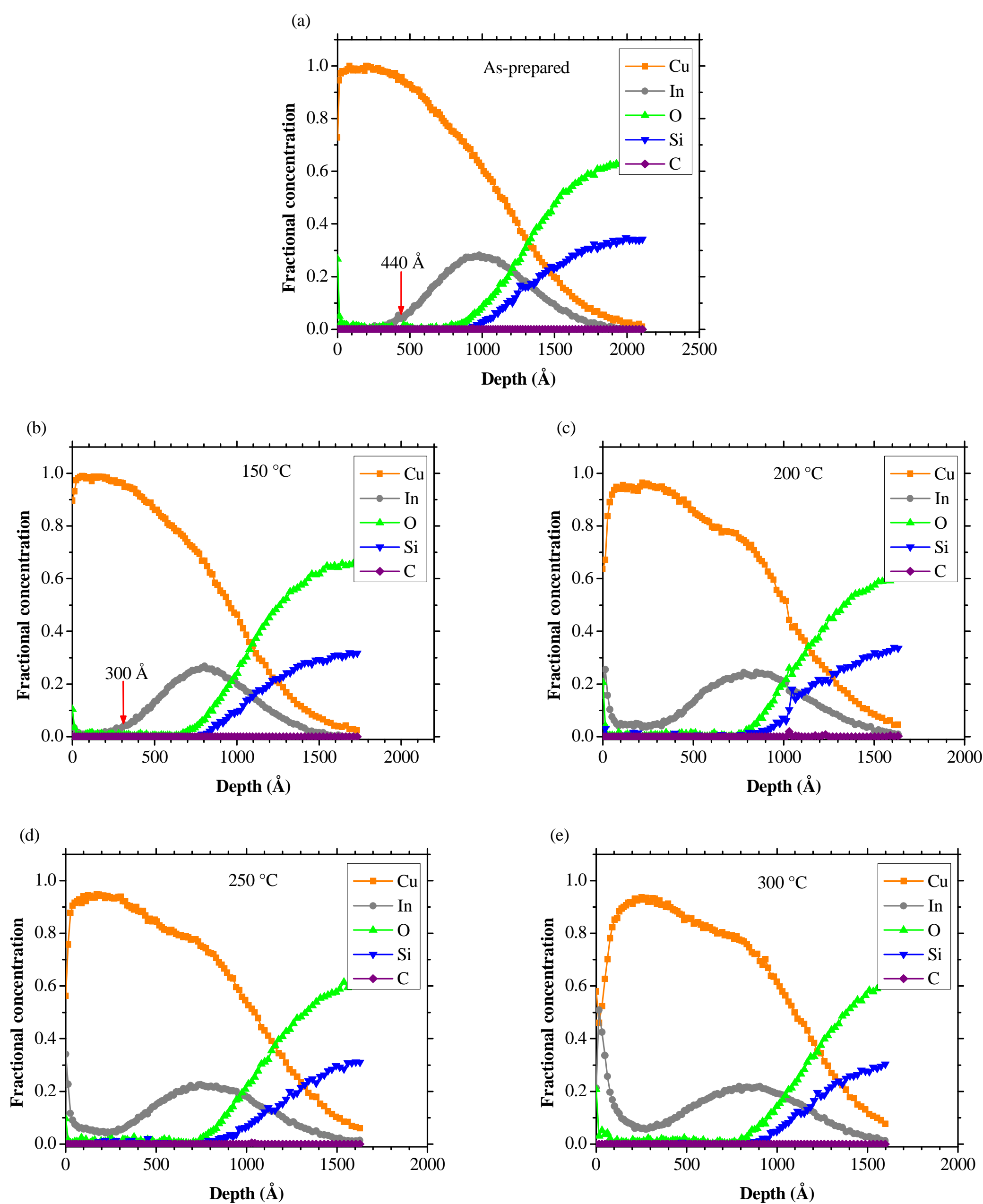

Figure 3. AES depth profiles of the as-prepared (a) and annealed (b-e) thin films.

4. Conclusion

The In layer reacted with the Cu layer during deposition to form two intermetallic phases namely $CuIn_2$ and $Cu_{11}In_9$. The XRD data of the annealed thin films showed that in the temperature range between 150 and 300 °C the phases that formed, were $CuIn_2$ followed by $Cu_{11}In_9$ and lastly the formation of Cu_2In. AES depth profiles also showed that In segregated to the surface, enriching the surface with In. This suggests that In will segregate from a Cu matrix during a heat treatment.

Acknowledgments

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