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AES depth profiling of thermally treated Al/Si thin-film structures

A. Zalar[a,*], J.Y. Wang[b], Y.H. Zhao[b], E.J. Mittemeijer[b], P. Panjan[c]

[a] *Institute of Surface Engineering and Optoelectronics, Teslova 30, 1000 Ljubljana, Slovenia*

[b] *Max-Planck Institute for Metals Research, Heisenbergstrasse 3, D-70569 Stuttgart, Germany*

[c] *Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia*

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Abstract

Interdiffusion in sputter deposited bi- and multilayer structures onto smooth silicon substrates consisting of crystalline c-Al and amorphous a-Si layers was studied. The bilayer consisted of c-Al(300 nm) and a-Si(400 nm) layers and the c-Al/a-Si multilayer of four pairs of c-Al(45 nm) and a-Si(85 nm) layers.

Diffusion processes took place in the isothermally heated c-Al/a-Si structures in an argon atmosphere for 20 min at temperatures between 150°C and 270°C, or, at a linear heating rate of 5°C min^{-1} between room temperature and different final temperatures (300–500°C). AES depth profiling of as-deposited and heat-treated samples enabled identification of the main migrating element in the early stage of reaction, which is Si, and observation of new reaction products. In a few annealed multilayers, a mixture of Al–Si solid solutions and precipitates was found with up to 30 at% Si, and in the Si-rich layer up to 10 at% Al. For the multilayer structures annealed at temperatures higher than 250°C, it was found that diffusion processes resulted in the exchange of the Al- and Si-rich layer positions.

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1. Introduction

The aluminum–silicon system forms the basis of a large number of materials for industrial applications [1,2]. The Al–Si system is interesting since the two elements do not form a stable compound and are relatively immiscible [3]. However, in advanced semiconductor thin-film technologies, diffusion barrier layers have to be used to prevent interdiffusion and precipitation of aluminum and silicon in the contacts of electrical circuits [4]. In addition to device applications, there is also basic interest in understanding diffusion processes relevant to the Al–Si system. In the past an unexpected redistribution of the Al and Si layers was observed in an Si/Al/Si sandwich structure after a dynamic heating procedure with a linear temperature increase from room temperature up to 550°C [5]. Recently, the same phenomenon was observed in aluminum-induced crystallization of amorphous silicon on glass substrates at different temperatures [6–8].

Although the precipitation of Si in solid-quenched Al–Si alloys was the subject of several

*Corresponding author. Tel.: +386-61-4264-592; fax: +386-61-1264-593.

E-mail address: anton.zalar@guest.arnes.si (A. Zalar).

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studies [9–11], few investigations were devoted to solid-state reactions in Al/Si multilayer structures. In this work, we studied diffusion processes in sputter deposited c-Al/a-Si thin-film structures (c = crystalline, a = amorphous) from their beginning through the different steps of reactions which were activated during heating processes in a differential scanning calorimetry (DSC) instrument. The diffusion processes, the formation of mixtures of Al–Si solid solutions and precipitates, and the exchange of the Al- and Si-rich layers were investigated in these thermally treated Al/Si thin-film structures using Auger electron spectroscopy (AES) depth profiling. Further, the interdiffusion coefficient was obtained by fitting the calculated AES depth profile to the measured one.

2. Experimental

Al/Si bilayer and multilayer structures were sputter deposited onto smooth silicon (1 1 1) substrates in a Balzers Sputron plasma chamber. The substrate temperature during deposition was below 120°C. The thicknesses of the individual thin films were measured using a quartz microbalance during the sputter deposition. After deposition, the thicknesses of the individual thin films and the total thickness were determined with a measurement error of $\pm 2\%$ by cross-sectional transmission electron microscopy. The bilayer consisted of crystalline c-Al and amorphous a-Si thin films with thicknesses of about 300 and 400 nm, respectively, and the multilayer consisted of four pairs of c-Al and a-Si layers: c-Al (45 nm)/a-Si(85 nm) $\times$ 4.

Diffusion processes in the c-Al/a-Si bi- and multilayers were induced by heating the samples in an argon atmosphere and then quenched at approximately 200°C min^{-1} in a Perkin–Elmer DSC-7 instrument. The c-Al/a-Si bilayers were heated isothermally, 20 min at 180°, 195°C, 210°C, 225°C, 240°C, 255°C and 270°C. The c-Al/a-Si multilayers of the first series were heated isothermally at six different temperatures between 150°C and 225°C for 20 min. The c-Al/a-Si multilayers of the second series were heated at a linear heating rate of 5°C min^{-1}, from room temperature to three different final temperatures of 300°C, 400°C and 500°C, respectively.

The as-deposited and heat-treated samples were characterized by AES depth profiling in a PHI 545 scanning Auger microprobe at a base pressure in the vacuum chamber below 1.3×10^{-7} Pa. A static primary electron beam of 3 keV, 1 μA and a diameter of about 40 μm was used. The samples were sputtered using two symmetrically inclined Perkin–Elmer-PHI Mod. 04-191 ion guns. The ion incidence angle was about 47° with respect to the normal to the sample surface. The stationary samples were sputtered with 1 keV Ar^+ ion beams, rastered across an area between 5 mm $\times$ 5 mm and 10 mm $\times$ 10 mm. AES depth profiles of the samples were obtained by continuous ion sputtering. The Auger peak-to-peak heights of Al(68 eV) Si(92 eV), C(272 eV) and O(510 eV) as a function of the sputtering time were quantified by applying the relative elemental sensitivity factors [12]: $S_{Al} = 0.24$ $S_{Si} = 0.35$, $S_C = 0.18$ and $S_O = 0.50$.

Microstructural investigation of as-deposited Al/Si bi- and multilayer samples were carried out with a JEOL 2000 F transmission electron microscope. The samples were cross-sectioned and then thinned to a thickness transparent for 200 keV electrons by ion milling, using an ion beam thinning unit (Baltec, Balzers) with 5 keV Ar^+ ions at a grazing incidence angle of 78° relative to the surface normal.

As-deposited samples were investigated using a Philips X'Pert MRD diffractometer equipped with a copper tube operated at 1.8 kW, X-ray lens, Eulerian cradle and a secondary monochromator to select Cu K_α-radiation. The samples were irradiated at a grazing incidence angle of 88° (relative to the surface normal).

3. Results and discussion

In order to check the microstructure of the as-deposited Al/Si bi- and multilayers, TEM and grazing incidence XRD analyses were performed immediately after the sputter deposition process. It was found that the Al layers have a weak {111} fibre texture and the Si layers are amorphous (Fig. 1).

The series of AES depth profiles obtained on the same type of heat-treated samples enabled observation and measurement of the increasing reaction width caused by interdiffusion processes at the interfaces of the thin-film structures [5,13]. Because of space restrictions, in this work only the depth profiles of the samples are shown, which are indispensable for the discussion. Fig. 2(a) shows the AES depth profile of an as-deposited c-Al(300 nm)/a-Si(400 nm) bilayer on the smooth silicon substrate with a relatively sharp and clean Al/Si interface. A slight increase of oxygen indicates the a-Si layer-Si(1 1 1) substrate interface. Surprisingly, the sputtering rates of the as-deposited c-Al and a-Si layers are approximately the same. The difference in sputtering rates of as-deposited and heat-treated samples with newly formed reaction products is less than 15%. Therefore, matrix and perferential sputtering effects are not expected to have a marked influence on the quality of the AES depth profiles. The c-Al/a-Si bilayers were heated isothermally for 20 min at six different temperatures between 180°C and 270°C. Generally, the broadening of the interface width increased with temperature. The AES depth profiles of the bilayers annealed at temperatures between 180°C and 225°C showed approximately the same diffusivity for the Si and Al atoms. However, the depth profile of the c-Al/a-Si bilayer heated for 20 min at 270°C (Fig. 2(b)) showed the presence of Al in the entire Si layer and the absence of Si in the surface part of the Al layer. The same was also found for the samples heated at 240°C and 255°C. This indicates that in the

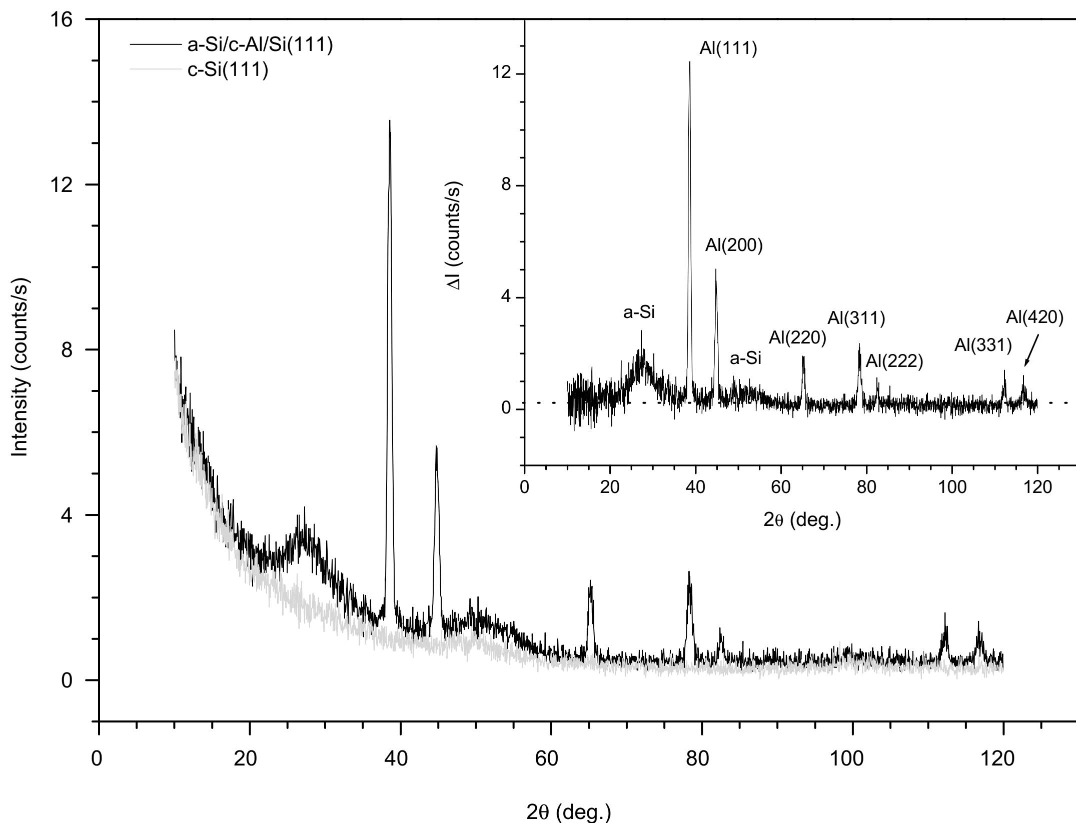

Fig. 1. XRD patterns of the as-deposited c-Al/a-Si /Si(1 1 1) multilayer (black line) and of the Si(1 1 1) substrate (grey line). The XRD pattern (inset) of the as-deposited c-Al/a-Si multilayer after subtracting that of Si(1 1 1).

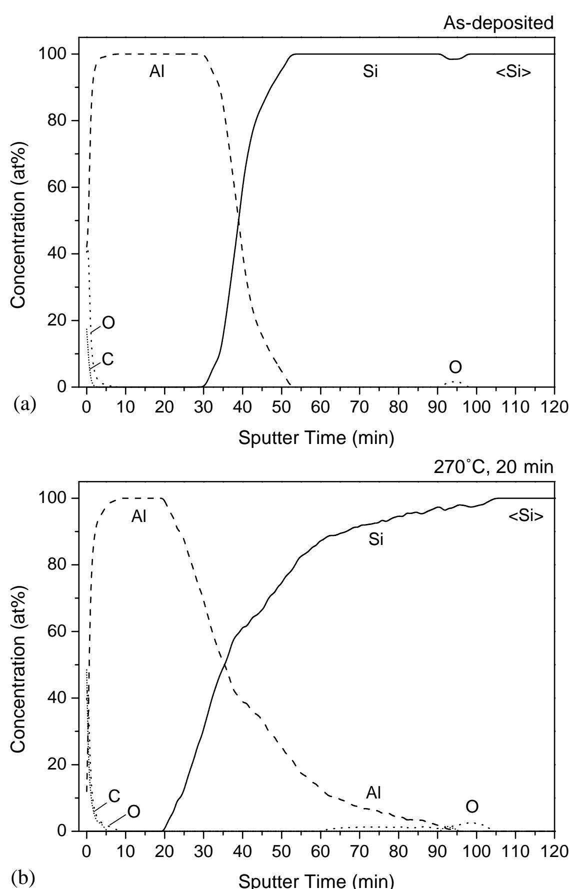

Fig. 2. AES depth profiles of the c-Al(300 nm)/a-Si(400 nm) bilayers: (a) as-deposited, (b) after isothermal heating for 20 min at 270°C.

c-Al/a-Si bilayers heated between 240°C and 270°C, the diffusion rate of the Al atoms in Si is slightly higher than that of silicon in Al.

Fig. 3(a) shows the AES depth profile of an as-deposited c-Al (45 nm)/a-Si(85 nm) $\times$ 4 multilayer. Si is present in the Al thin films even though the substrate temperature during the deposition of the c-Al/a-Si multilayer was less than 120°C. However, despite the high-depth resolution of the depth profile provided by ion etching using two ion beams, it is not possible to exclude topographic effects completely as they might cause a slight loss of depth resolution, especially in Al thin films [14]. Figs. 3(b) and (c) show the depth profiles of the same multilayer after isothermal heating of the samples, 20 min at 165°C (Fig. 3(b)) and 225°C (Fig. 3(c)). As apparent from Fig. 3(b), the concentration of Si in the Al thin films increases but there is no indication of Al in the relatively large middle parts of the Si thin films. Therefore, we conclude that in the early stage of reaction in the c-Al/a-Si multilayer Si is the main migrating element, in accordance with our erlier work which dealt with the a-Si/c-Al/a-Si sandwich thin-film structure [5]. In the c-Al/a-Si multilayers isothermally heated for 20 min at 180°C, 195°C, 210°C and 225°C (Fig. 3(c)), the Al atoms also migrated in the Si thin films. As recognized from Fig. 3(c), the Al atoms from the second Al thin films migrated through the Si thin film and formed a new Al-rich layer on the multilayer surface. On the other hand, in the region close to the silicon substrate it is possible to observe the exchange of Al- and Si-rich layers. In the as-deposited sample (Fig. 3(a)), the Al layer lies on the silicon substrate which is replaced during the isothermal heating procedure at 225°C with the Si-rich layer.

To observe the exchange of layer positions more clearly, the c-Al/a-Si multilayer samples were heated to higher temperature, at a linear heating rate of 5°C min^{-1}, from room temperature to three different final temperatures of 300°C, 400°C and 500°C. As expected, Fig. 3(d) shows that in the sample heated to 500°C the exchange of layer positions again occurs in the surface region of the multilayer and in the region close to the silicon substrate. The diffusion processes during dynamic heating of the c-Al/a-Si multilayer (Fig. 3(a)) to 500°C caused the formation of a new Si-rich/Al-rich $\times$ 4 multilayer structure (Fig. 3(d)). Approximately the same layer exchange phenomena were also observed in the samples heated to 300°C and 400°C.

From the AES depth profiles of the heat-treated c-Al/a-Si bi- and multilayer structures (Figs. 2 and 3), it is possible to conclude that the interaction of the Al and Si layers depends on a number of parameters. Besides the temperature and the heating time, the diffusion processes are dependent on the thicknesses of the Al and Si layers and their structures. In the bi- and multilayer structures, the atoms from the amorphous Si layers have a

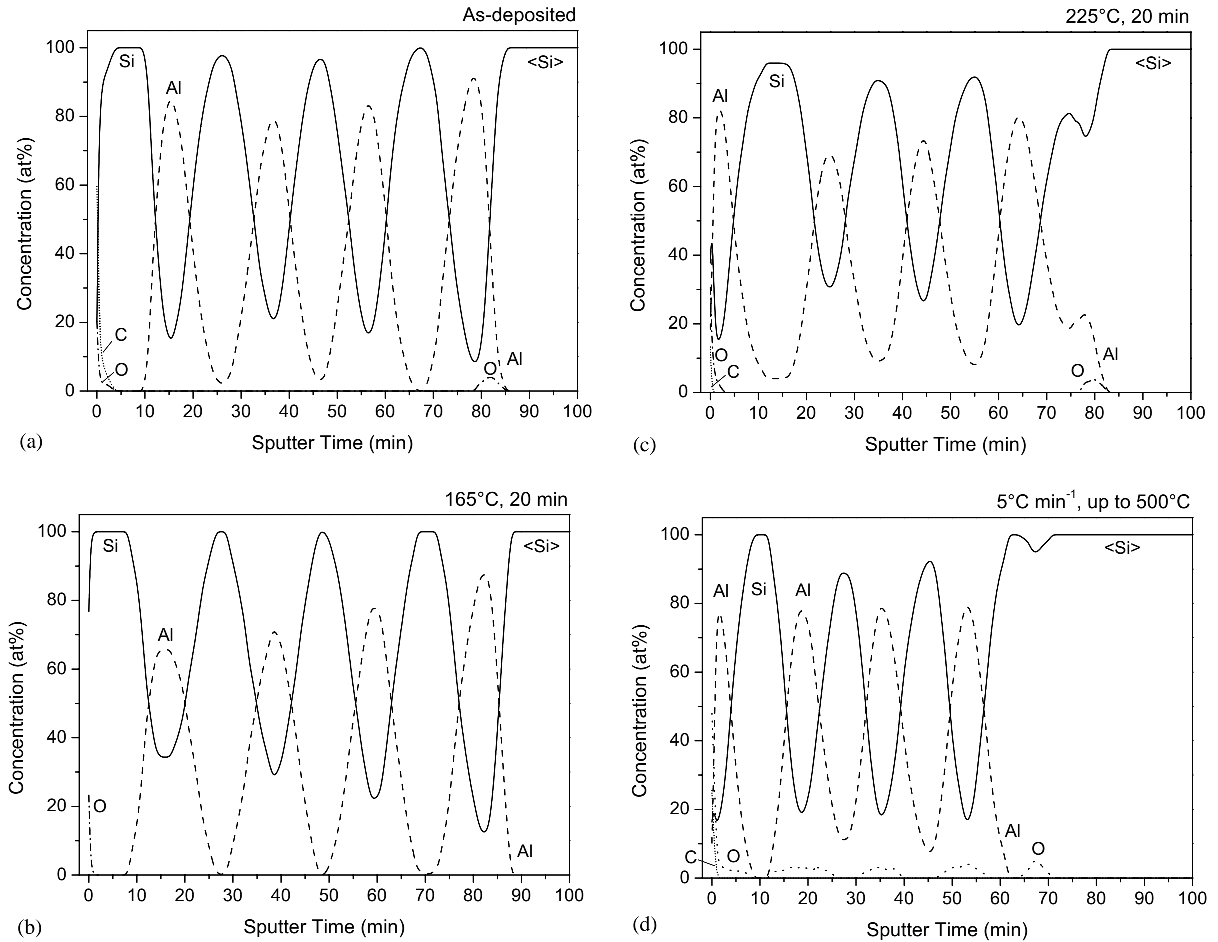

Fig. 3. AES depth profiles of c-Al(45 nm)/a-Si(85 nm) × 4 multilayers: (a) as-deposited; (b), (c) after isothermal heating for 20 min at 165°C and 225°C, respectively and (d) after linear heating at a rate of 5°C min^{-1} from room temperature up to 500°C.

relatively high mobility even at relatively low temperature and migrate into the Al layers, firstly through the grain boundaries, and at higher temperature also through the Al grains [5,7]. In the early stage of reaction, vacancy accumulation should occur on the silicon side of the c-Al/a-Si interface if Si is the main migrating species. With increasing temperature, in the multilayer (Figs. 3(c) and (d)) a marked diffusion of Al atoms in the Si layers was additionally observed, in spite of the low mutual solubility of Al and Si. However, in thin-film structures the solubilities and diffusivities are expected to be considerably higher than in the bulk materials because of the increased number of defects at the interfaces and internal stresses in thin films.

In the c-Al/a-Si multilayer, composed of thinner Al and Si layers, a relatively strong migration of Si (Fig. 3(b)) and Al atoms (Fig. 3(c)) was observed. The large number of interfaces and the smaller grain size in the thinner Al layers enable a high diffusivity of Si atoms in the Al layers. It is surprising that in the Al–Si system with low solubilities (much below 0.1 at% at room temperature), mixtures of Al–Si solid solutions, probably together with fine precipitates, with a

total amount of Si in the aluminum layers up to about 30 at% (Figs. 3(b) and (c)) and Al in the silicon layers up to about 10 at% (Figs. 3(c) and (d)) can be found. Due to the low solubility of Al in the Si layers, the heating and cooling processes induced the migration of Al atoms through the silicon-rich layers located at the multilayer surface and close to the silicon substrate (Figs. 3(c) and (d)). The overall process during the interaction of Si and Al layers leads to precipitation of Al on top of the Si layer and to an exchange of Al and Si layer positions at the silicon substrate.

Recently, Hofmann proposed a model for the quantitative determination of interdiffusion in multilayer structures [15,16]. The depth profiles of the as-deposited c-Al/a-Si and that of the sample annealed for 20 min at 165°C, taking the Al KLL peak intensity as a function of the sputtering time, were evaluated according to that scheme. The apparent interdiffusivity, D_{eff}, was estimated to be about $1 \times 10^{-19}\,m^2\,s^{-1}$ at the first a-Si/c-Al interface beneath the surface and about $2 \times 10^{-20}\,m^2\,s^{-1}$ at the c-Al/a-Si interface close to the silicon substrate. More details of this calculation will be given in our next publication [17].

4. Conclusions

Diffusion processes caused in bi- and multilayer c-Al/a-Si structures by heating were studied using AES depth profiling, XRD and TEM.

A precise measurement of the concentration profiles in the heat-treated c-Al(300 nm)/a-Si(400 nm) bilayers revealed approximately the same diffusivity of Si and Al atoms at temperatures below 225°C. However, in the same bilayer sample heated between 240°C and 270°C, the diffusion rate of the Al atoms was slightly higher than that of silicon. In the c-Al(45 nm)/a-Si(85 nm) $\times$ 4 multilayer composed of thinner layers and heat treated to higher temperatures up to 500°C, silicon was determined to be the main migrating species in the early stage of reaction, followed by aluminum, which is in agreement with our previous investigation of the a-Si/c-Al/a-Si thin-film sandwich structure [5].

The overall process during the interdiffusion of Si and Al layers leads to formation of a mixture of Al–Si solid solutions and fine precipitates with a total amount of Si in the aluminum layers up to about 30 at% and of Al in the silicon layers up to about 10 at%. The precipitation of Al on the Si layers results in an exchange of the Al and Si layer positions on top of the multilayer and in the region close to the multilayer/silicon substrate interface.

The effective interdiffusivity, D_{eff}, for Al in the c-Al/a-Si multilayer sample heated isothermally for 20 min at 165°C was estimated using measured AES depth profiles in combination with the calculated ones; D_{eff} decreases with depth and has a value between $1 \times 10^{-19}\,m^2\,s^{-1}$ in the surface region of the multilayer and $2 \times 10^{-20}\,m^2\,s^{-1}$ in the region close to the silicon substrate.

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