Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Thin Solid Films 433 (2003) 92–96

www.elsevier.com/locate/tsf

Determination of the interdiffusion coefficient for Si/Al multilayers by Auger electron spectroscopical sputter depth profiling

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

[a]*Max Planck Institute for Metals Research, Heisenbergstrasse 3, D-70569 Stuttgart, Germany*
[b]*Institute of Surface Engineering and Optoelectronics, Teslova 30, 1000 Ljubljana, Slovenia*

Abstract

Initial stage interdiffusion processes in Si/Al multilayer structures were studied quantitatively by means of Auger electron spectroscopical sputter depth profiling. The Al sublayers and the Si sublayers were sputter deposited onto a Si(111) substrate. The initial stage of the interdiffusion at the location of the Si/Al interfaces was induced by heating the specimens isothermally in an argon atmosphere at 150, 165 and 180 °C for 20 min, and at 165 °C, additionally, for 10 and 30 min. It was found that, in such sputtering prepared multilayer structures, interdiffusion across interfaces near the surface of the multilayer is faster than across interfaces in the deeper part of the layer. Measured depth profiles of the annealed specimens were compared with that of the as-deposited specimen after quantitative evaluation according to the so-called MRI (mixing-roughness-information depth)-model. As a result, values of the interdiffusion coefficient as a function of the depth beneath the surface were obtained.

Keywords: AES depth profiling; Si/Al multilayer; Interdiffusion; MRI model

1. Introduction

Interdiffusion plays an important role in achieving the desired composition profile and the associated properties of thin films [1]. There is little quantitative information about interdiffusion in thin films as compared with interdiffusion in bulk materials. Auger electron spectroscopy (AES) in combination with ion sputtering could be one of the most powerful methods for the determination of the interdiffusion coefficient for thin films. In the past decades, several more or less approximate methods have been proposed to extract the interdiffusion coefficient from AES depth profiling data. For example: the plateau-rise method [2], the center-gradient method [3], and the interface-width method [4] for a bilayer specimen and a Fourier series method [5] for a multilayer specimen. In these four methods, only parts of the measured depth profile are used for estimating values of the interdiffusion coefficient. Recently, based on the so-called Mixing-Roughness-Information depth (MRI) model [6], a new method of fitting a calculated AES depth profile to the entire measured one has been proposed [7]. The MRI method allows correction for the instrumental smearing effects due to atomic mixing, surface roughness, escape depth of Auger electrons, and preferential sputtering. For cases where concentration profile development can be conceived as Gaussian smearing of an initial concentration profile, it is possible to derive a value of the interdiffusion coefficient from the roughness parameter as determined by fitting depth profiles calculated according to the MRI description, as will be demonstrated here (see Section 3). In this paper this method will be applied in particular to extract the interdiffusion coefficient in a case where the interdiffusivity is depth dependent.

2. Experimental

Si/Al multilayer structures composed of four pairs of Si and Al layers were sputter deposited onto Si(111) substrates in a Balzers Sputron plasma chamber [8]. The substrate temperature during deposition was below 120 °C so that the deposited Si layers are amorphous and the deposited Al layers are polycrystalline. The individual layer thicknesses were determined as 85 nm for the Si sublayers, and 45 nm for the Al sublayers by cross-sectional transmission electron microscopy. The initial

---

*Corresponding author. Tel.: +49-711-689-3479; fax: +49-711-689-3312.
E-mail address: j.y.wang@mf.mpg.de (J.Y. Wang).

0040-6090/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
PII: S0040-6090(03)00284-0

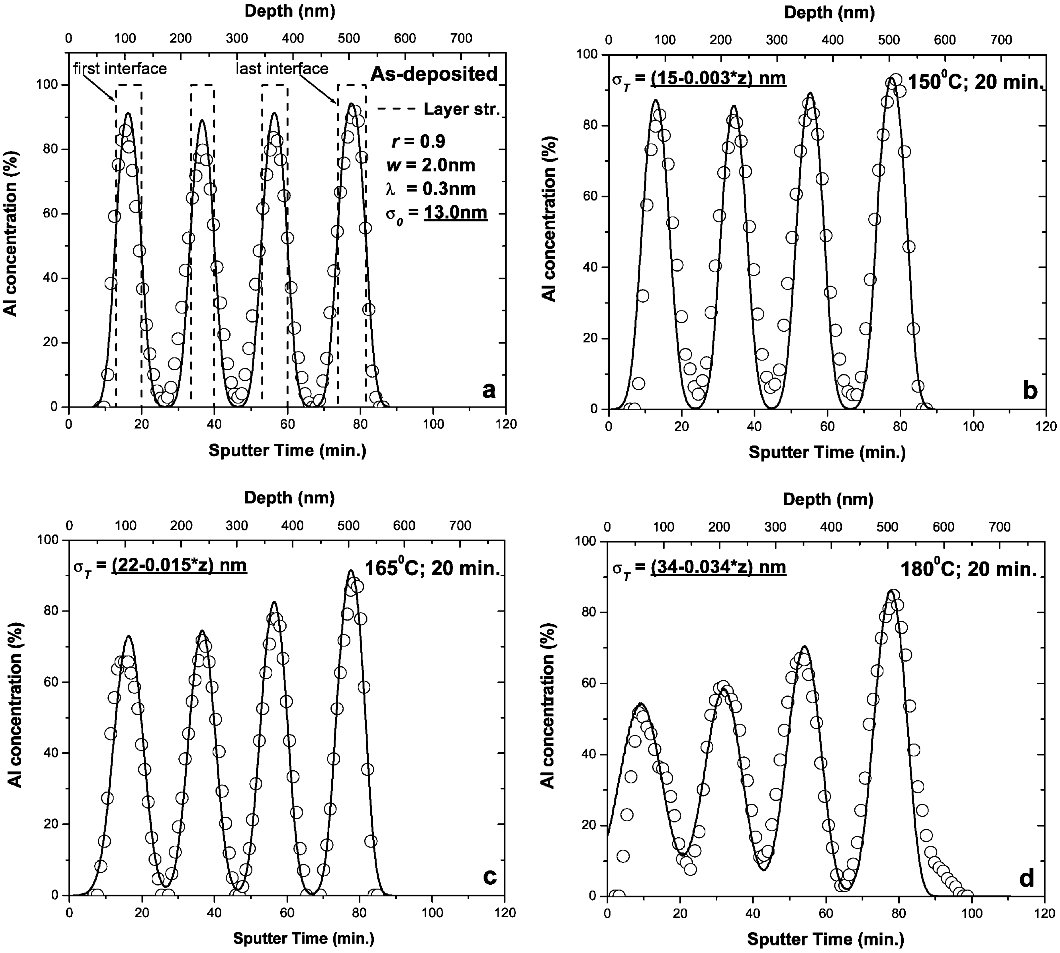

Fig. 1. Measured Al concentration depth profiling data (open circles) and the concentration-depth profiles (solid lines) as calculated by fitting to the measured data according to the MRI description for (a) the as-deposited specimen, and the specimens annealed for 20 min at (b) 150 °C, (c) 165 °C and (d) 180 °C. The dashed line drawn in Fig. 1a represents the as-deposited Al sublayer structure. Values for the ratio of sputtering rates of Al and Si (r), the atomic mixing parameter (w), the escape depth of Auger electrons (λ), and the surface roughness (σ_0) have been given in Fig. 1a. For the annealed specimens, the measured depth profiles were fitted assuming that the roughness parameter σ_T decreases linearly with depth z (see Fig. 1b–d), leaving the other fit parameters as in Fig. 1a.

stage of interdiffusion was realized by annealing multilayer specimens for 20 min at 150, 165 and 180 °C in an argon atmosphere in a Perkin–Elmer DSC-7 instrument. Additional anneals were performed at 165 °C for 10 and 30 min.

The composition-depth profiles of the as-deposited and annealed specimens were measured by AES depth profiling in a PHI 545 SAM at a base pressure below 1.3×10^{-7} Pa. A static primary electron beam of 3 keV, 1 μA and a diameter of approximately 40 μm was used. The specimens were sputtered employing 1 keV Ar^+ ions, rastering an area of 5×5 mm, by using two symmetrically inclined ion guns. The ion incidence angle was approximately 47° with respect to the normal of the specimen surface. The Auger peak-to-peak heights of Al(68 eV), Si(92 eV), C(272 eV) and O(510 eV) as a function of sputtering time were quantified by applying the relative elemental sensitivity factors [9]: $S_{Al}=0.24$, $S_{Si}=0.35$, $S_C=0.18$ and $S_O=0.50$.

3. Results and discussion

Measured Al concentration depth profiling data (open circles) and the concentration-depth profiles (solid lines) as calculated by fitting to the measured data according to the MRI model are shown in Fig. 1a–d for the as-deposited specimen and the specimens annealed at 150, 165 and 180 °C for 20 min. The as-deposited Al sublayer structure has been indicated by the dashed line in Fig. 1a. The fitting according to the MRI model leads to values for four parameters representative for the instrumental smearing upon AES depth profiling [10,11], namely, the atomic mixing parameter (w), the surface roughness (σ), the escape depth of Auger electrons (λ), and the preferential sputtering ratio (r). The values obtained for these parameters by fitting to the measured depth profile of the as-deposited specimen have been indicated in Fig. 1a.

Evidently, upon annealing the measured Al concentration in the near surface Al sublayer decreases faster than that in the deeper Al sublayers. It may be suggested that the apparently faster interdiffusion near the surface is due to a depth dependence of the microstructure of the multilayer. In particular, the interfacial microstructure can affect the rate of interdiffusion in an initial stage. To account for this depth dependence of the extent of interdiffusion, depth profiles calculated on the basis of the MRI model were fitted to the measured Al concentration depth profiling data in Fig. 1b–d assuming, in a first approach, that the MRI roughness parameter σ increases linearly with thickness, taking the other three parameters (w, λ and r) as depth independent and equal to the values determined for the as-deposited specimen (Fig. 1a). The thus determined linear depth dependences of the roughness parameter σ have been indicated in Fig. 1b–d.

Interdiffusion across an interface brings about 'concentration smearing' that can be conceived as a 'roughening' of this interface. Therefore, the roughness parameter, as determined by the fitting described above, not only includes the effect of the intrinsic interface roughness, but also the 'diffusion-induced roughness'. In the MRI model, the interface roughness is described by a Gaussian function ($\sim\exp[-z^2/2\sigma^2]$, where z denotes depth) [6]. Assuming that for an initial stage of diffusion the diffusion-induced concentration profile can be written as the convolution of the initial concentration profile with a Gaussian function of the depth ($\sim\exp[-z^2/4Dt]$, where z is depth and the diffusion length is given by $\sqrt{2Dt}$) [12], then the square of the diffusion length can be expressed in terms of an increase of the 'interface roughness' as follows [7]:

$$2Dt = \Delta\sigma^2 = \sigma_T^2 - \sigma_0^2 \tag{1}$$

where t is the annealing time, and σ_T and σ_0 are the values of the interface roughness parameter after annealing at temperature T and before annealing, respectively. Using the data presented in Fig. 1, the calculated values of the interdiffusion coefficient at two locations, namely the positions of the first (nearest to surface) and last (nearest to substrate) interfaces in the as-deposited Si/Al multilayer (see Fig. 1a), have been given by closed and open circles, respectively, in the Arrhenius plot shown in Fig. 2. The corresponding values of the interdiffusion parameters (pre-exponential factor D_0 and activation energy E_a) as determined from the fit of a straight line to the data in Arrhenius plot have been indicated in Fig. 2, as well as corresponding literature values. The dotted line drawn in Fig. 2 was obtained from the diffusion profile of Si in wrought Al as measured by electron probe micro-analysis [13]; the dashed line was obtained by applying the interface-width method (see Section 1) to the AES sputter depth profiling data obtained for a Si(60 nm)/Al(50 nm)/Si(60 nm) specimen upon annealing at different temperatures [14].

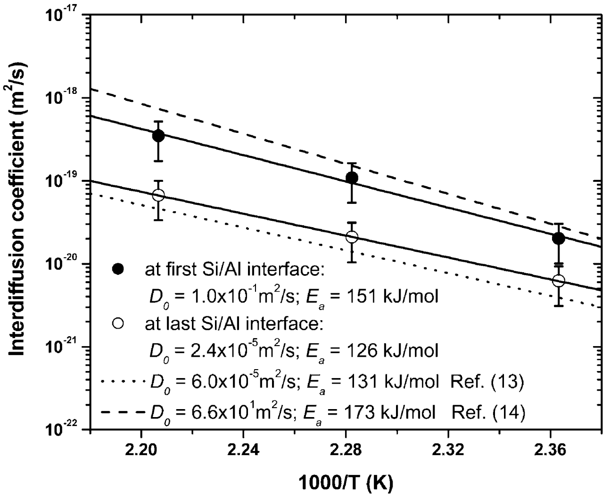

Fig. 2. Arrhenius plot for the interdiffusion coefficient calculated from the annealing time and the depth dependent roughness parameters (see Fig. 1) by applying Eq. (1). The closed and open circles represent the values of the interdiffusion coefficient at the locations of the first and last Si/Al interfaces, respectively. The corresponding interdiffusion parameters (pre-exponential factor D_0 and activation energy E_a) as determined from the linear fit to the calculated interdiffusion coefficients as given in the figure have been indicated, as well as literature values (see details in text).

Using the determined value of the interdiffusion coefficient, the interdiffusion length ($\sqrt{2Dt}$) across the Si/Al interface nearest to the substrate for the specimen annealed at 150 °C for 20 min is calculated as approximately 3 nm. Hence, the current method is very useful to measure very small extents of interdiffusion, i.e. to determine very small (inter)diffusion coefficients.

The values obtained for E_a agree reasonably well with the one determined for Si diffusing into wrought Al (dotted line in Fig. 2), and they are in any case significantly smaller than the one determined for Al diffusing into Si films (255 kJ/mol) [15] or into bulk materials (329 kJ/mol) [16]. It can be concluded that the interdiffusion in the Si/Al multilayer specimen starts with Si atoms diffusing into Al sublayers (see also Ref. [17]).

The interdiffusion at the first interface is more advanced than at the last interface, which is expressed through a relatively large value of D_0 (see Fig. 2). This phenomenon could be related to a depth dependence of the microstructure of the multilayer. In the absence of microstructure data, further discussion cannot be given at this stage.

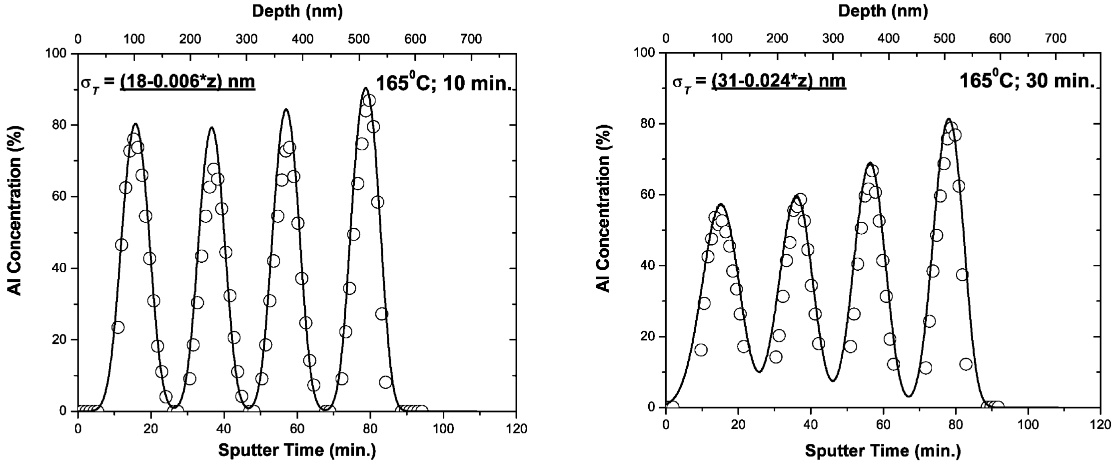

Fig. 3. Measured Al concentration depth profiling data (open circles) and the concentration-depth profiles (solid lines) as calculated by fitting to the measured data according to the MRI description for the specimens annealed at 165 °C for (a) 10 min and (b) 30 min (see also caption of Fig. 1).

Measured Al concentration depth profiling data (open circles) and the corresponding fitted curves (solid lines) are shown in Fig. 3 for the specimens annealed at 165 °C for 10 and 30 min. Again, it is observed that upon annealing the measured Al concentration in the near surface Al sublayer decreases faster than that in the deeper Al sublayers. The depth dependence of the interdiffusion coefficient, as determined on the basis of Eq. (1) with a linear dependence on depth adopted for σ_T (see above), for the three different annealing times at 165 °C investigated here is shown in Fig. 4. It is found that, for the range of annealing time investigated, the interdiffusion coefficient at the depth of the first Si/Al interface varies within the range of 1 to 2×10^{-19} m^2/s; the corresponding decrease of the Al concentration at this depth is larger than 30 at.%. Apparently, the interdiffusion coefficient at this interface and for the initial stage of interdiffusion is not strongly concentration dependent.

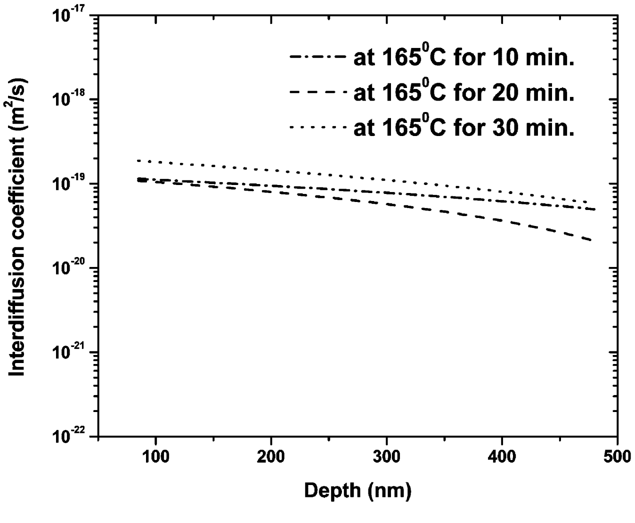

Fig. 4. The interdiffusion coefficient as a function of the depth beneath the surface for the specimens annealed at 165 °C for 10, 20 and 30 min, respectively.

4. Conclusions

- Very small extents of interdiffusion (very small diffusion coefficients) can be determined by Auger electron spectroscopical sputter depth profiling after correction for instrumental smearing due to atomic mixing, Auger electron escape depth, surface roughness, and preferential sputtering.
- The interdiffusion in a sputter deposited Si/Al multilayer occurs faster across interfaces near the surface than across interfaces near the substrate. This may be related to a depth dependence of the microstructure of the multilayer.
- Interdiffusion in the Si/Al multilayer structure starts with the diffusion of Si into the Al sublayers.

Acknowledgments

The authors thank Prof Dr S. Hofmann (Max Planck Institute for Metals Research) for helpful discussion and Mr B. Pracek (Institute of Surface Engineering and Optoelectronics, Ljubljana) for technical assistance. The work was supported by the Ministry of School, Science and Sport of Slovenia, Ljubljana (Project J2-3522-1534-02) and by the Internationales Büro, Deutsches Zentrum für Luft-und Raumfahrt e.V. (Projekt SVN 99/044).

References

[1] R. Pretorius, T.K. Marais, C.C. Theron, Mater. Sci. Eng. Rep. 10 (1993) 1.

[2] A. Bukaluk, Surf. Interface Anal. 5 (1983) 20.

[3] P.M. Hall, J.M. Morabito, Surf. Sci. 54 (1976) 79.

[4] R.J. Highmore, J.E. Evetts, A.L. Greer, R.E. Somekh, Appl. Phys. Lett. 50 (1987) 566.

[5] W. Pamler, Appl. Phys. Part A 42 (1987) 219.

[6] S. Hofmann, Surf. Interface Anal. 21 (1994) 673.

[7] V. Kesler, S. Hofmann, J. Surf. Anal. 9 (2002) 428.

[8] A. Zalar, S. Hofmann, A. Zabkar, Thin Solid Films 131 (1985) 149.

[9] L.E. Davis, N.C. MacDonald, P.W. Palmberg, G.E. Riach, R.E. Weber, Handbook of Auger Electron Spectroscopy, 2nd ed, Physical Electronics Industries, Inc, Eden Prairie, MA, 1976.

[10] S. Hofmann, J. Vac. Sci. Technol. Part B 10 (1992) 316.

[11] S. Hofmann, J.Y. Wang, J. Surf. Anal. 9 (2002) 306.

[12] J. Crank, The Mathematics of Diffusion, 2nd ed, Clarendon, Oxford, 1975.

[13] J.O. McCaldin, H. Sankur, Appl. Phys. Lett. 19 (1971) 524.

[14] A. Zalar, S. Hofmann, P. Panjan, Vacuum 48 (1997) 625.

[15] J.C.M. Hwang, P.S. Ho, J.E. Lewis, D.R. Campbell, J. Appl. Phys. 51 (1980) 1576.

[16] R.N. Ghoshtagore, Phys. Rev. Part B 3 (1971) 2507.

[17] A. Zalar, S. Hofmann, F. Pimentel, P. Panjan, Thin Solid Films 253 (1994) 293.