Surface Segregation of Substrate Al in the Cr/Al/Al System

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(Received November 19, 2001; accepted March 18, 2002)

Surface segregation of Al in the Cr/Al/Al thin film system was observed at 813K. The film was deposited by rf magnetron sputtering. The segregation phenomenon and the depth profile of the segregated layer were monitored by XPS. Cr 2p and Al 2s photoelectron peaks were analyzed in detail to investigate the chemical interaction of the segregated layer (Al) with the film material (Cr).

1.Introduction

When a metal film on a metal substrate is heated, the substrate material may accumulate on the film surface either by bulk diffusion or by grain boundary diffusion leading to the segregation of the substrate element on the film. The segregation of the substrate material depends upon the free energy of the film surface. In the process of segregation, the substrate atoms break the bond at the interface when activated and reach spontaneously on the film surface to minimize the free energy. This process finally leads to the formation of an over layer of the substrate material on the film. Surface modification by such process may have many implications in microelectronics and catalysis fields.

Substrate segregation onto the film surface was studied for a large number of metal/metal combinations [1] and the observations are summarized as, (i) the concentration of the substrate element saturates on the film surface and the saturation concentration depends on the adsorption site and not on the temperature, (ii) the thickness of the segregated layer is limited within few mono-layers and after sputtering the segregated layer out, segregation can be observed on re-heating the system, and (iii) the segregation phenomenon occurs through the defect sites like grain boundary.

The surface segregation phenomenon in transition metal alloys was predicted by calculating surface segregation energy [2] that is the difference of total energy of the system with segregate in the surface layer and in the bulk of the alloy. In thin film case, the surface segregation was predicted by using adsorption energy [1]. In the calculations [1], it was shown that the adsorption energy of Al on Cr is higher (377 kJ/mol) than the adsorption energy of Al on Al (270 kJ/mol) and hence from the prediction, Al can segregate through Cr film in Cr/Al system. However the Al segregation was not observed experimentally [1] for such system due to a stable oxide layer formed on the Al substrate, which might have prevented its diffusion through the film.

In this report, segregation of Al through Cr film as observed by XPS, is presented. The formation of the aluminum oxide between Cr and Al was avoided by developing Cr/Al/Al system.

2. Experiment

Al film was deposited on polished and degreased Al substrate (10 mm x 10 mm x 1 mm) and Cr film was deposited successively on the Al film using a dual magnetron sputtering system. The Al and Cr film thickness was approximately 1 μm and 2μm respectively.

The XPS characterization and in-situ heating were done in a separate chamber using Mg K_α as x-ray source (PHI Model 5400 series). The pass energy of the analyzer was 22 eV during data collection. The Cr film surface was covered with oxide layer and was cleaned by Ar ion sputtering prior to the segregation study of the system. Ar ion beam of 3 keV with 25 mA emission current was used to get the depth profile of the segregated film.

3. Results and discussion

Al was seen on Cr surface on heating at 813K and the surface composition monitored by XPS is shown in Fig. 1. The heating of the system was stopped as soon as the Al signal was seen on the surface. The layer of Al on the surface was removed completely by sputtering.

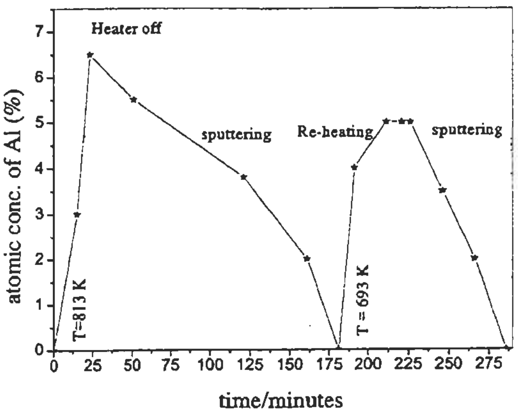

Fig1. Surface concentration change by heating, sputtering and reheating of Cr film on Al substrate.

Re-heating of the system showed the appearance of Al on the surface and that at a lower temperature (693 K), which was again removed by sputtering. The corresponding XPS spectra of the Cr film surface at different stages are shown in Fig. 2.

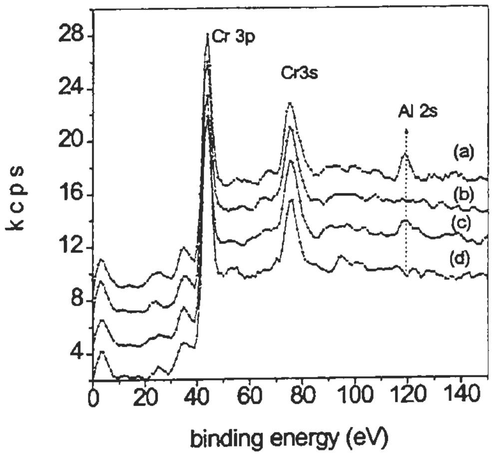

Fig.2. XPS of (a) segregated Al on Cr film, (b) removed Al by sputtering, (c) re-appearance of Al on heating and (d) removed by sputtering.

Aluminum seen on the surface was approximately 6.5% atomic concentration, which was probably, much less than the saturation. Al on Cr surface was removed completely, which proves that Al segregated on the film. On reheating at a lower temperature Al appeared again and saturation was seen at around 5% that was less than the amount seen in the first heating.

The film was sputtered further at a higher sputtering rate (approximately 77.6 Å/minute for SiO_2) in a separate chamber to see the interface of the Cr/Al film after the segregation and the depth profile is shown in Fig. 3. Although a sharp Cr/Al interface is observed, there is an Al-Cr reaction layer with almost uniform composition from about 4-7 minutes. Al was not observed in side the Cr film (0-3 minutes) suggesting the surface enrichment of Al was due to segregation process.

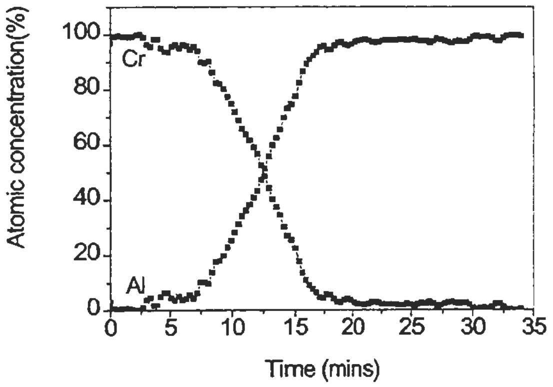

Fig. 3. Depth profile of the post-segregated film showing a sharp interface between Cr/Al substrate.

From the above results it appears that Al diffused through the grain boundary of the film to form the segregated Al layer on the surface and as the heating was stopped before saturation, some amount of Al was trapped at the grain boundary. When the system was reheated, Al came to the surface at lower temperature and saturated to the amount available at the grain boundary.

A new Cr/Al/Al system was heated at a lower temperature (793 K) in the XPS system and Al was found on the surface of the Cr film. It is obvious that lower temperature reduces the bulk diffusion and provides a better situation to get the saturation segregation of Al on Cr. The system was heated until the saturation of Al content (Fig. 4). The saturation concentration was seen to be around 43% (atomic concentration) as calculated by XPS quantification method. But the surface of the Cr film was seen heavily damaged due to Al diffusion. The film was sputtered to remove Al but Al was found diffused inside the Cr film. This was due to the bulk diffusion of the substrate material and consequently mixing of Al with Cr took place. From the Al-Cr phase diagram, the phase is likely to be a Cr rich (Cr_2Al) compound.

From Fig. 4, the diffusion coefficient of Al through Cr film was calculated by using the formula, $D=x^2/2t$ (where D= diffusion coefficient, x = film thickness and t = diffusion time for the segregation), and was found to be 1.5×10^{-15} m^2/s, whereas the bulk diffusion of Al through Cr at 793 K was seen to be 2.8×10^{-13} m^2/s [4]. Although these two values differ by about a factor of 200, the bulk diffusion of the substrate took place almost simultaneously with the grain boundary diffusion on prolonged heating as observed in Fig. 4.

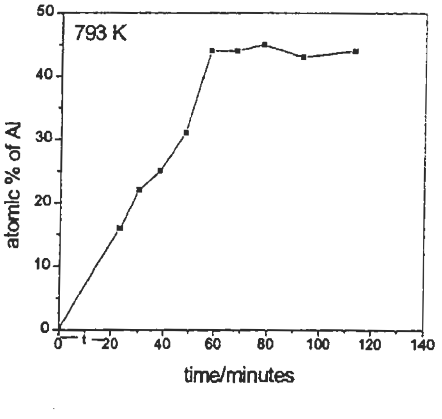

Fig.4. Bulk diffusion of Al on Cr film when heated at 793 K for longer duration.

Thus it was required to prevent the bulk diffusion of Al and further heating of the film was stopped in order to establish the segregation phenomenon in the system.

In a similar study for M/Ti (M = Nb, Zr, Cr, Cu) combination, it was shown [3] that the bulk diffusion coefficient for Ti is 10^{10} order less than the diffusion coefficient in films. So in such cases the saturation of segregation was seen very distinctly, as bulk diffusion of the substrate element could not take over the segregation process.

Binding energy analysis: Al 2s photoelectron peaks from pure Al, Al in segregated case and Al in intermetallic compound are shown in Fig. 5.

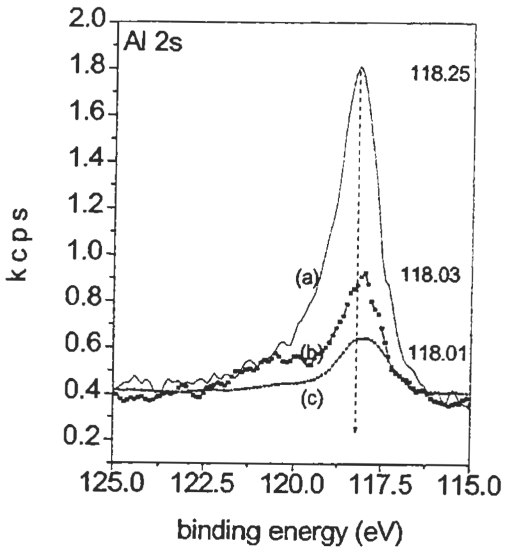

Fig. 5. Al 2s photoelectron peak for (a) pure Al at 118.25 eV, (b) Al in intermetallic compound of Cr, at 118.03 eV and (c) segregated Al on Cr surface at 118.01 eV.

Al 2p peak (73 eV), which is the most sensitive peak of Al, overlaps with Cr 3s peak

(75 eV) and hence not suitable for the analysis.

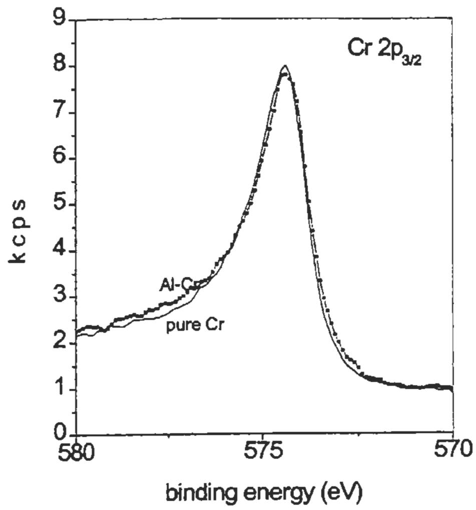

Fig. 6. Cr 2p$_{3/2}$ photoelectron peak for pure Cr and reacted with segregated Al.

In case of segregated Al, 2s-binding energy was seen reduced by 0.25 eV from that of pure Al. From the chemical shift of Al 2s peak it is evident that electron was transferred from Cr to Al.

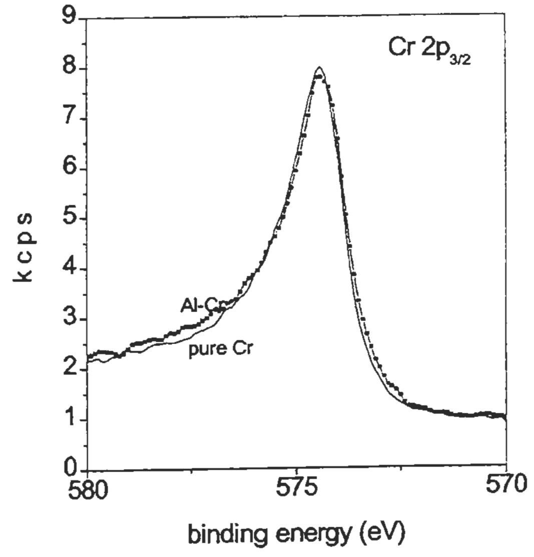

Fig. 6. Cr 2p$_{3/2}$ photoelectron peak for pure Cr and reacted with segregated Al.

The electronic configuration of Cr is [Ar]$3d^5 4s^1$ and that for Al is [Ne] $3s^2 3p^1$. As the Cr 3d orbital is half filled, it is very stable and the 4s electrons are easily donated to Al p orbital for stable configuration. Similar results were observed in case of Ni for photoelectron study of Ni-Al compound [5], where it was explained that Ni donated sp electrons to Al, which effectively reduced the binding energy of Al 2s peak. Cr 2p photoelectron peaks were also compared for pure and segregated ones (Fig. 6). No significant change in the peak was observed as the small amount of Al adsorbed on the surface could react with a small amount of Cr, and the signal from reacted Cr was too small to show any change in the Cr signal. However a small change in the background in the segregated ones might be due to reaction of surface Cr with Al.

4.Conclusions

Segregation of Al by grain boundary diffusion through Cr film was studied by XPS. Al was observed to segregate on the Cr film when the Cr/Al/Al system was heated in vacuum. The depth profile of the segregated film showed no Al in the Cr film. This implies that the segregation of Al occurs by grain boundary diffusion. But the saturation segregation of Al on Cr surface is not observed as bulk diffusion of Al takes place on longer heating resulting in formation of intermetallic compound.

The chemical interaction of the segregated Al layer with Cr film was monitored from the binding energy shift of Al photoelectron peak. The binding energy value of Al 2s peak is found reduced by 0.25 eV after the segregation.

5. References

[1] M. Yoshitake and K. Yoshihara, Surf. Interface Anal. **30**, 337 (2000).

[2] A. V. Ruban, H. L. Skriver and J.K. Norskov, Phys. Rev. B, **59**, 15990 (1999).

[3] M. Yoshitake and K. Yoshihara, J. Japan Inst. Metals, **55**(6), 727 (1991).

[4] *CRC Handbook of Chemistry and Physics*, 68th Edition, Editor R.C. Weast, CRC Press Inc., Florida (1987-88).

[5] S. -C. Lui, J. W. Davenport, E. W. Plummer, D. M. Zehner and G. W. Fernando, Phys. Rev. B,**42**, 1582 (1990).