JOURNAL OF MATERIALS SCIENCE 35 (2000) 3655 – 3658

Electric field induced interfacial reaction of Au-Ag bimetal film on SiO_2 surface

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Interface evolution of nanometer scale Au-Ag bimetal film on SiO_2 substrate surface during electromigration was investigated by angle resolved X-ray photoelectron spectroscopy (ARXPS). ARXPS spectra showed that a chemical reaction between Au-Ag film and SiO_2 layer occurred at interface, which caused Au, Ag and Si having different distribution and chemical states across the film. This result as well as previous observation by atomic force microscopy (AFM) demonstrate that electromigration of Au-Ag bimetal film on SiO_2 surface is accompanied with strong interfacial chemical reaction rather than a simple lateral physical diffusion process. © *2000 Kluwer Academic Publishers*

1. Introduction

The growing miniaturization tendency of electronic devices leads to an increase of their surface to volume ratio [1], therefore surface diffusion exerts an significant influence on the stability of device performance due to the surface diffusion coefficients to be much larger than that of bulk [2]. In the past decades, the structures of metal/Si interface have been intensively studied using many techniques, and it has become evident that the electrical properties of metal/semiconductor contact are strongly affected by microscopic structural defects of the interface. Recently, study of mass transport of metal adsorbates on Si or SiO_2 substrate surface under the action of d.c. electric field, which is called surface electromigration, attracted much interest both for technological interest and for basic understanding of these complex phenomena [2–6]. Although the evolution of interface upon deposition and subsequent thermal annealing which involve chemical composition and electronic structure change of Au, Ag on Si (111) surface have been reported in a series of papers [7–9], the similar studies for electromigration is still rare, since the electromigration taking place on semiconductor surface is usually considered as two dimensional lateral diffusion. We have studied the diffusion kinetics and surface morphology change of Au-Ag bimetal film on SiO_2/Si surface due to d.c. current passing through the substrate by using Auger line scan analysis and AFM observation [10]. In this paper, we present the results of interfacial interaction and corresponding chemical structure change of the Au-Ag/SiO_2 system by means of ARXPS.

2. Experimental procedure

The experiments were carried out in an ultra high vacuum (UHV) chamber ($\sim 1 \times 10^{-7}$ Pa) which is connected with a Perkin-Elmer PHI 5300 ESCA system. The substrate used was cut from a mirror-polished SiO_2 wafer (which is prepared through thermal oxidizing method to form a 100-nm-thick SiO_2 layer on the surface of a p-type Si (111) wafer with resistivity of 100 Ω·cm), the size of the sample is $20 \times 5 \times 0.5$ mm^3. It was cleaned in alcohol, rinsed in deionized water, dried by blowing with high purity nitrogen and then put into UHV chamber. The substrate was mounted between two Ta electrodes and the resistance was prechecked in order to assure the good electrical conductance for applying d.c. current. Au and Ag were deposited from two separate tungsten basket evaporation sources onto SiO_2 surface in turn, during deposition the pressure of the chamber was kept below 8×10^{-7} Pa. The thickness of bimetal film (4 nm Au + 5 nm Ag) was estimated by evaporation amount and calibrated by a separate depth profiling analysis. In situ electromigration experiment was performed by applying a constant d.c. current onto substrate along its longer side to drive the surface mass transport in UHV condition. After electromigration the sample was transferred into the XPS analysis chamber. The chemical composition and states of Au-Ag/SiO_2 system were measured using a normal Al K_α X-ray source. The electron energy analyzer was operated at a constant pass energy of 37.25 eV. ARXPS measurement was carried out by setting the take-off angle (TOA) of photoelectrons at 5°, 30°, 45° and 90° respectively. The energy scale was calibrated to reproduce the binding energy of Au $4f_{7/2}$ (84.00 eV), Cu $2p_{3/2}$ (932.66 eV), and Ag $3d_{5/2}$ (368.00 eV), the standard deviation of the analyzed result is less than 0.02 eV. The energy shift coming from the charge effect during XPS measurement is calibrated by the binding energy of C 1s (285.00 eV).

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3. Results and discussion

Fig. 1 shows the core level spectra of Au-Ag bimetal film in as-deposited state and after electromigration, these XPS spectra were measured at TOA, 30°. It displays that the binding energy of Au $4f_{7/2}$ and Ag $3d_{5/2}$ core level in as-deposited film is 84.00 eV and 368.00 eV respectively, which accurately correspond to pure elemental state of Au and Ag [11], and demonstrates the as-deposited bimetal film having a uniform continuous structure as observed by AFM [10]. Fig. 2 shows the summary of binding energy shifts of Au and Ag after electromigration for 5 min and 30 min. From Fig. 1 and Fig. 2, it could be noted that after d.c. current stressing for 5 min, both the core level of Au $4f_{7/2}$ and Ag $3d_{5/2}$ shift to high binding energy side by ~1.0 eV simultaneously. In the meantime, the full width at half maximum (FWHM) increased. We suggest that such binding energy shifts are caused by differential charge effect due to the structural change of film from continuous configuration to isolated islands [12, 13]. However, when the current stressing time extends to 30 min, the notable feature is that the core level of Au and Ag shift to low binding energy side by ~0.2 eV simultaneously, this suggests the decrease of differential charge effect of film surface due to the film structure converting from isolated islands to corrugated sheets as described by AFM observation. On the other hand, with the current stressing time increased, the peak intensity of Au 4f and Ag 3d spectra reduced obviously, and their *S*/*N* ratio decreased either. It reflected that during electromigration process the Au-Ag film was thinned down to less than 3 λ (mean free path of inelastic scattering) which is observed by AFM [10]. Fig. 3 shows the Si 2p ARXPS spectra in Au-Ag/SiO_2 system obtained after electromigration for 5 min. It should be indicated that for an as-deposited film, there is no any Si 2p peak can be found within the binding energy range of 95–115 eV, which proved that SiO_2 substrate surface was completely covered by uniform Au-Ag film. After heating sample by d.c. current for 5 min, two apparent characteristic peaks of Si 2p appear at the binding energy of 103.86 eV and 99.60 eV, which correspond to SiO_2 and elemental Si, respectively. The interesting is that the intensity ratio of these two peaks change definitely with the take-off angle. At the TOA, 5°, elemental Si signal is stronger than that of SiO_2, but at TOA, 90° only SiO_2 signal can be detected, which shows elemental Si mainly present at vertical boundary of grains. This result not only reveals the interfacial reaction between Au-Ag film and SiO_2 in existence during the electromigration of Au-Ag bimetal film but also shows the reaction product silicon having segregated up to surface. Thus the

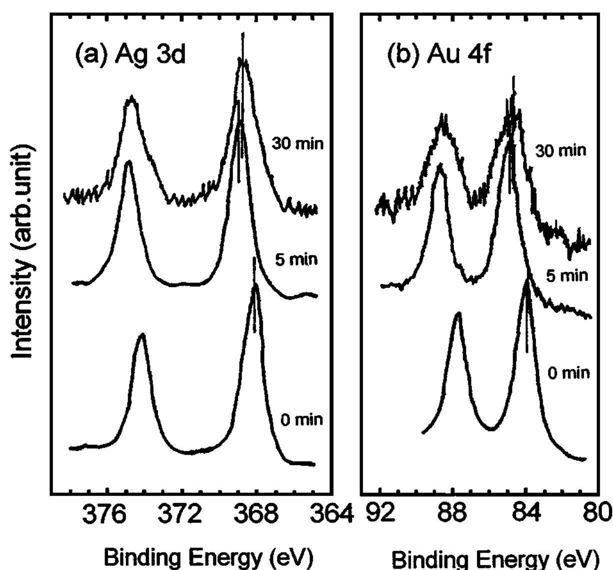


Figure 1 XPS spectra of as-deposited Au-Ag film and after electromigration collected at photoelectron take-off angle $\theta = 30°$. (a). Ag 3d and (b). Au 4f. Current density $J = 2.0$ A·cm^{-2}, $T = 140$°C.

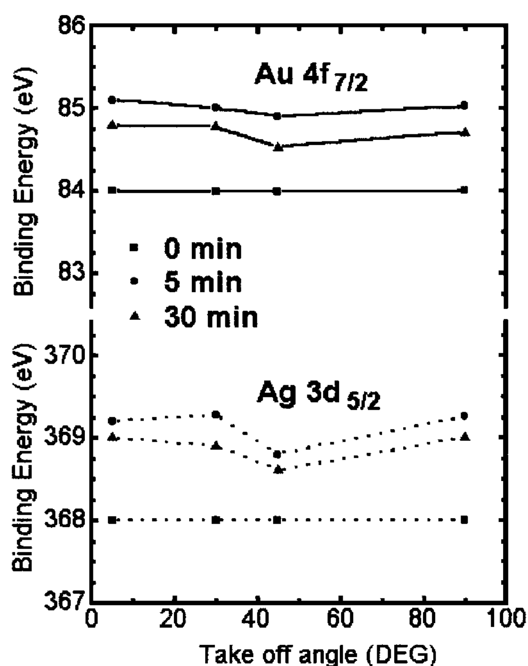


Figure 2 Summary of core level shifts of Au and Ag in Au-Ag bimetal film on SiO_2 surface during electromigration.

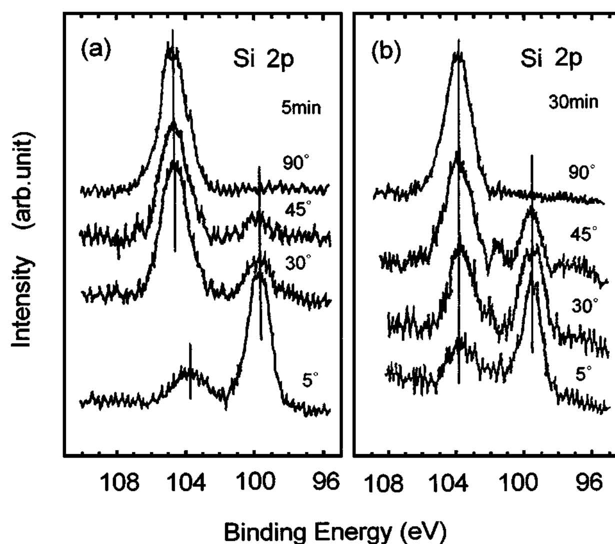
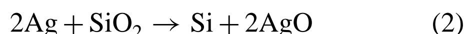


Figure 3 ARXPS spectra of Si 2p in Au-Ag/SiO_2 system after electromigration for 5 min with current density $J = 2.0$ A·cm^{-2}, $T = 140$°C.

plausible interfacial reaction formula can be expected as follows:

$$Ag + SiO_2 \rightarrow AgSi + O_2 \quad (1)$$



$$2Ag + SiO_2 \rightarrow Si + 2AgO \quad (2)$$

Since the Si 2p core level binding energy of elemental Si is very close to that of AgSi, none of the above two reactions can be absolutely excluded. However, considering a weak shoulder feature appears at low binding energy side of the Ag $3d_{5/2}$ XPS spectra with the d.c. current stressing time increase, which probably corresponds to AgO, we suggest that interfacial reaction (2) will mostly occur in present experiment condition. The ARXPS spectra of Si 2p in Au-Ag/SiO_2 system for a 30 min electromigration has a similar behavior with that of the 5 min electromigration. In Fig. 3, the characteristic peak of elemental Si is stronger than that of SiO_2 at the topmost layer of the film. The intensity ratio change of two characteristic Si peaks versus take-off angle imply Si having a certain distribution of the concentration and chemical state throughout the film, i.e., Si produced from interfacial reaction diffuses towards the top layer, and mainly exists at the boundaries of islands or corrugated sheets. Therefore, when the spectra were acquired at $\theta = 90°$, only substrate SiO_2 signal can be detected. Fig. 4 shows Ag 3d ARXPS spectra ob-

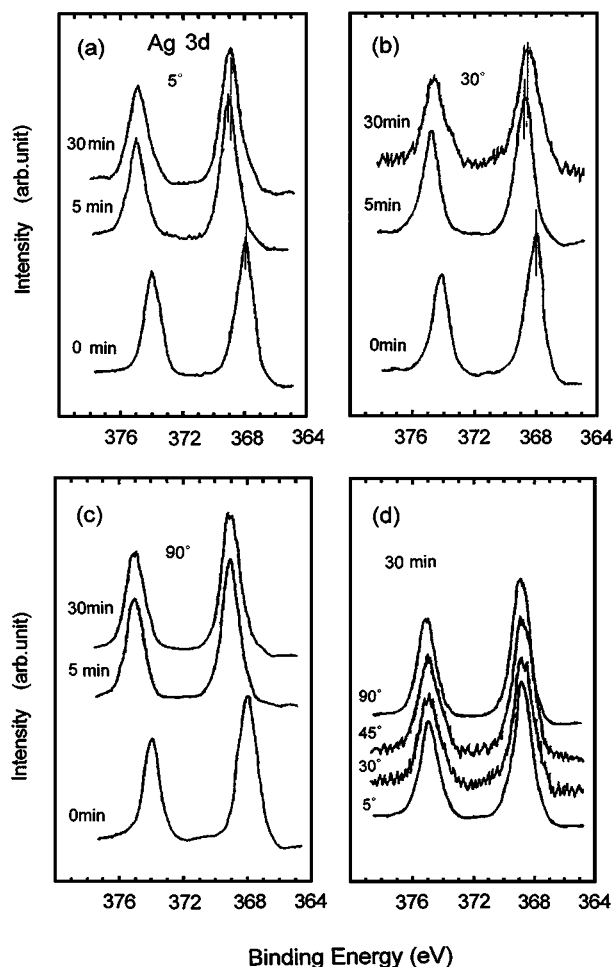


Figure 4 XPS spectra of Ag 3d orbital. (a)–(c). Before and after electromigration measured at TOA of 5°, 30° and 90°. (d). After electromigration for 30 min measured at TOA of 5°, 30°, 45° and 90°.

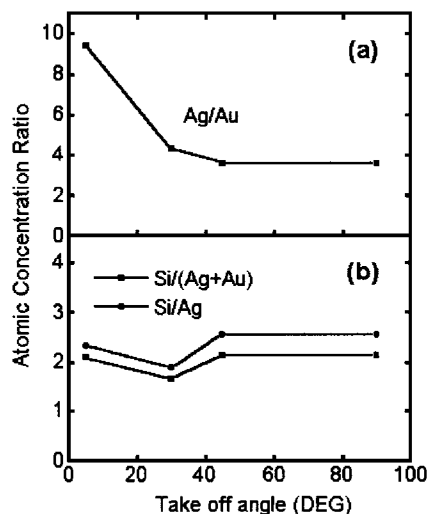


Figure 5 Atomic ratio variation of Au, Ag and Si with respect to the photoelectron take-off angle after electromigration.

tained at different TOA, it reveals the characteristics of Ag atoms migration under the action of electric field for 30 min. Comparing the signal intensity of Ag 3d XPS spectra collected at TOA, 5° and 90°, it is easy to find that there is a very little change. But the signal intensity at TOA, 30° or 45° is obviously weaker than that of 5° or 90° TOA. This result demonstrates Ag segregate at the topmost layer of Au-Ag film, and the distribution of Ag along the vertical direction across the film is inhomogeneous. In order to describe the distribution of each species in Au-Ag/SiO_2 system after electromigration more clearly, Fig. 5 shows atomic ratio variation of Au, Ag and Si with respect to the photoelectron take-off angle θ. Fig. 5a clearly indicates that segregation of Ag towards top layer of the film was enhanced by d.c. current heating, although such segregation already exist during the growth of Au-Ag film due to the lower surface free energy of Ag. Similarly, the atomic ratio of Si/(Au + Ag) and Si/Ag shown in Fig. 5b reveal the distribution feature of Si across the film in vertical direction. Based on the XPS results as well as our previous study on diffusion kinetics and morphology change to the same system, the effect of d.c. electric field on this Au-Ag/SiO_2 system is clarified. Au-Ag/SiO_2 system simultaneously undergo two aspects of physical and chemical changes: Au-Ag bimetal film spread out with its structure transforming from fine-grained continuous islands to isolated islands, leaving the SiO_2 substrate partially bared, and then with the current stressing time extend further, isolated Au-Ag islands combine with each other and form a corrugated sheets with large size. Meanwhile, Ag reacts with SiO_2 surface at a substrate temperature of 140°C, produces AgO and elemental Si. The product Si continuously diffuses to the grain boundary and is slightly oxidized. Eventually, upon such physical and chemical effect, a complex Au-Ag alloy islands structure with Ag segregating at top layer and Si segregating at the grain boundaries was formed.

4. Conclusion

In summary, the measurement of surface core level spectra of Au, Ag and Si in Au-Ag/SiO_2 system under

the effect of d.c. electric field was performed by using ARXPS technique, and the XPS results were correlated with our previous AFM observation. It is suggested that electric field can not only altered the metal atoms aggregation states of Au-Ag film which caused a continuous islands structure transform to isolated islands and further to a corrugated sheets structure but also lead to a notable chemical reaction occurred at the interface between Au-Ag film and SiO_2 layer. This process result in the product Si and Ag segregate towards the surface of the film through grain boundary diffusion, and finally formed a complex configuration of Au-Ag film in nanometer scale.

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Received 18 February
and accepted 17 November 1999