Barrier layer effect of titanium-tungsten on the electromigration in sputtered copper films on polyimide

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Titanium-tungsten is employed as the diffusion barrier in a Cu/barrier/polyimide/Si system. The electromigration damage (EMD) of Cu with a TiW barrier is investigated utilizing an empirical formula. Two activation energies are obtained suggesting a surface electromigration mechanism at low temperature (140–190 °C) and a combined migration mechanism at high temperature (190–230 °C). The presence of the TiW barrier layer improves the high temperature electromigration resistance. The effects of the TiW barrier on the microstructure and electrical properties of Cu metallization are discussed.

1. Introduction

Copper has been considered as a substitute for Al interconnects in VLSI devices, due to its low resistivity, high melting point, high mechanical strength, and better electromigration resistance [1, 2]. However, the deficiencies of copper such as poor adhesion to dielectric layers, uncontrollable dry etching, lack of a self-passivation oxide and environmental reactivity limit the usefulness of Cu in IC fabrication. The poor adhesion can be improved by adding a diffusion barrier as an underlying layer.

Tungsten is a good diffusion barrier and is widely used as a plug metal in ICs [3], but its poor adhesion and corrosion properties are major concerns in its use. Adding titanium into tungsten improves the adhesion as well as the corrosion resistance of tungsten. Besides, TiW, as a stuffed barrier, is known as a better diffusion barrier, compared to the sacrificial barrier formed by Ti [4, 5].

In this study, the barrier layer effect of TiW on electromigration in sputtered Cu films on polyimide is investigated. The high thermal stability, ease of planarization, low processing temperature and low dielectric constant render polyimide a good candidate for the dielectric material in multilayer-structure devices. The kinetics of electromigration damage (EMD) are studied by an isothermal resistance change analysis method utilizing an empirical formula [1, 6–8],

$$\frac{\mathrm{d}R}{\mathrm{d}t} \cdot \frac{1}{R_0} = AJ^n \exp\left(-\frac{Q}{kT}\right) \qquad (1)$$

The activation energy Q for EMD and the exponent n of the current density are calculated and discussed.

2. Experimental procedures

Polyimide 2540 (Pyralin®, Du Pont, USA) was dispensed and spun on a p-type (1 0 0) Si wafer. The cleaning of the wafer and the dispersion and curing of polyimide have been described in detail previously [2]. The polyimide-coated Si substrate was processed using conventional photolithography to obtain the test pattern. Samples with positive photoresist patterns were transferred to a vacuum chamber for the sputtering of Cu and TiW films. High purity Ar gas was introduced through a mass flow controller after the vacuum chamber was evacuated to about 1.3×10^{-4} pa. The flow rate of argon was 24 sccm. The sputtering targets were a 99.995% Cu disc (diameter: 15.24 cm, thickness: 0.3 cm, Plasmaterials Inc., USA) and Ti: W = 10 : 90 wt % or a $Ti_{0.3}W_{0.7}$ disc of 99.9% purity (diameter: 15.24 cm, thickness: 0.3 cm, Cerac Inc., USA). Before deposition, the target was pre-sputtered for 1 min to remove any contaminate. The gas pressure was kept at 0.26 pa and the sputtering power employed during deposition was 300 W. The distance between sample and target was 9.5 cm. The deposition rates were 0.14 nm per second and 0.26 nm per second for TiW and Cu, respectively. Copper was sputtered after TiW deposition without breaking the vacuum. The film thicknesses were 650 nm (copper) and 100 nm (titanium-tungsten) on a polyimide coated Si substrate. A lift-off process was carried out after the sputtering of TiW and Cu to leave a pattern for EMD tests. The flow chart for the lift-off is shown in Fig. 1. The advantage of the lift-off process is to give multilayer metal deposition in only one step. After the lift-off process, samples were annealed at 250 °C or 400 °C for 30 min.

The film thickness was measured with a stylus surface profiler. The sheet resistance of the samples was measured with a four-point probe. An X-ray

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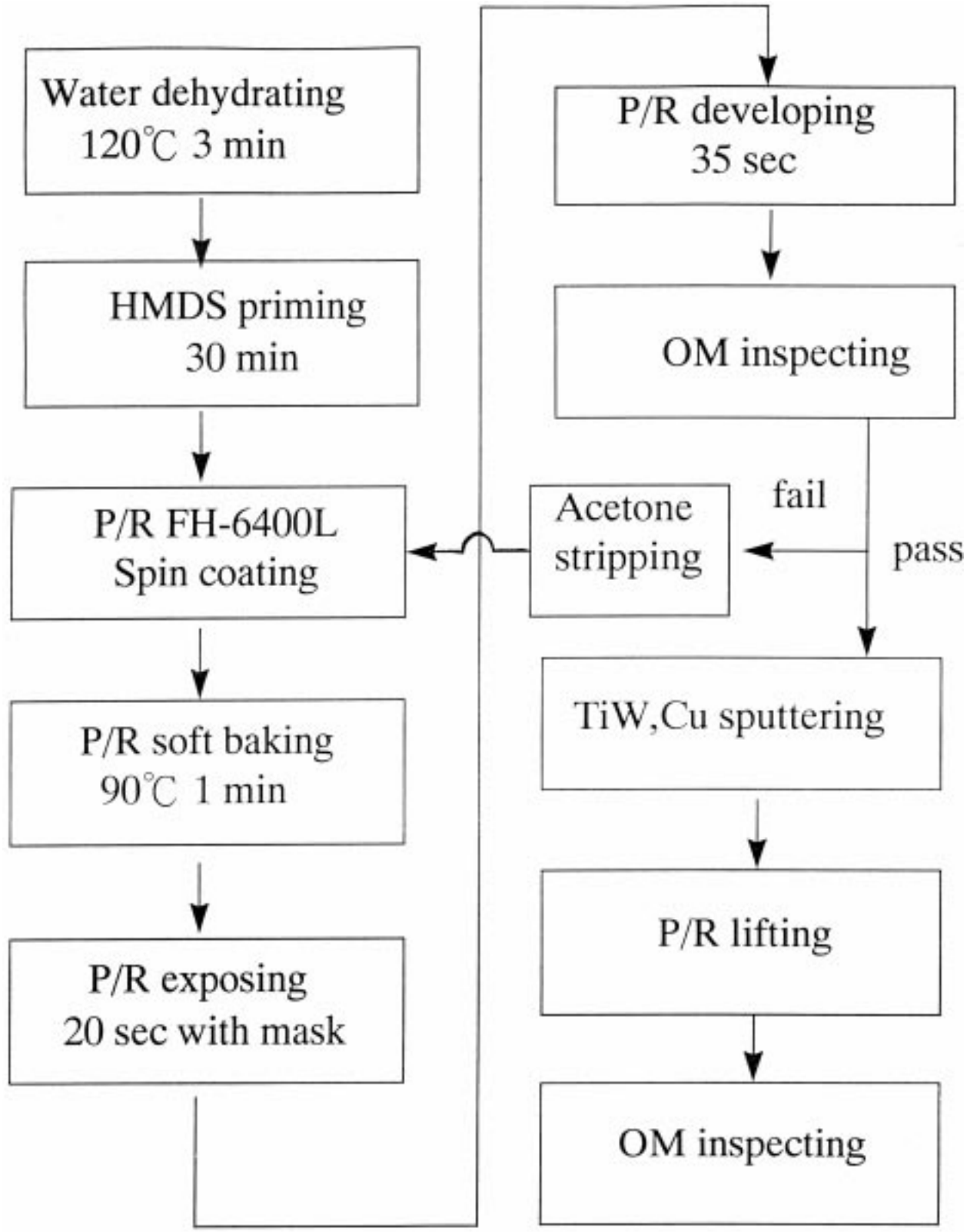


Figure 1 Flow chart of the photolithography and lift-off processes.

diffractometer was used to identify the crystalline phase of the films. The microstructure of the samples was examined with a field emission scanning microscope (FESEM, S-4000, Hitachi, Japan) and a transmission electron microscope. An optical microscope was employed to examine samples after development and lift-off. Auger electron spectroscopy (PERKIN PHI-590AM, Massachusetts, USA) was used to analyze the concentration profile of the films. The electromigration tests were carried out in a quartz tube at temperatures ranging from 110 °C to 230 °C in a N_2 atmosphere. The four I/O pads of the samples were connected to a constant current source (Model 220, Keithley, USA) and a micro-voltage meter (Model 197, Keithley, USA).

The leads between the samples and measurement system were covered with aluminum foil to avoid external electro-magnetic interference. The voltage was acquired once per minute or per 10 min automatically. The resistance was obtained by dividing the voltage by the current.

3. Results and discussion

The sheet resistance and resistivity as a function of annealing temperature are depicted in Fig. 2. Cu/TiW films annealed at 400 °C for 30 min have lower resistivities than those annealed at 250 °C for 30 min and the as-deposited ones. The annealed Cu films have lower resistivity than the as-deposited ones, but no apparent difference is observed for films annealed at 250 °C and those annealed at 400 °C The resistivity of Cu/TiW films is $\sim$ 2.06 μΩ cm which is very close to the bulk resistivity of Cu (i.e., 1.7 μΩ cm at room temperature).

Point defects such as vacancies and interstitial atoms are the main electron scattering sources which increase the resistivity. The decrease of resistivity after annealing is probably due to the decrease in the concentration of point defects. The resistivities of Cu/TiW films decrease with increasing annealing temperature.

The resistivity of the TiW film is $\sim$ 104 μΩ cm and the resistivity of Cu film on TiW is 2.06 μΩ cm as shown in Fig. 2. The film thicknesses of TiW and Cu are $\sim$ 100 nm and $\sim$ 650 nm, respectively. Hence, current flow through the TiW films is negligible (approximately 0.3%). However, the barrier metal TiW lowers the resistivity of the metallization from 2.38 μΩ cm for Cu on polyimide to 2.06 μΩ cm for Cu/TiW on polyimide.

The X-ray diffraction patterns are illustrated in Fig. 3. There is no new compound formation detected in the XRD patterns. The Cu (1 1 1), (2 0 0) and TiW (1 1 0) peaks are apparent after annealing. The full width at half maximum of the Cu (1 1 1) peaks becomes narrower for samples annealed at higher temperatures. A comparison of the Cu (1 1 1) peak between the Cu film on polyimide and Cu/TiW film on polyimide (PI) suggests that the degree of crystallinity in the Cu/TiW film is better than that of the Cu film [9]. This may result from the fact that copper in the former case is grown on an amorphous PI substrate, while in the latter case, it is grown on a polycrystalline TiW film.

The microstructure (from scanning election micro-coppy, SEM) does not reveal any apparent difference between the surface morphologies of Cu and Cu/TiW films. However, the transmission electron micrographs, shown in Fig. 4, suggest that Cu on TiW has a more uniform grain size than Cu on a polyimide substrate. The grain size of Cu/TiW film is about 540 nm, while that of the Cu film ranges from 0.25 μm to 1 μm, as exhibited in Fig. 4. It is argued that higher crystallinity and a more uniform microstructure may result in the Cu/TiW film having a lower resistivity than the Cu film. Metal-dielectric interface stability is controlled not only by chemical reactivity but also by microstructure and mass

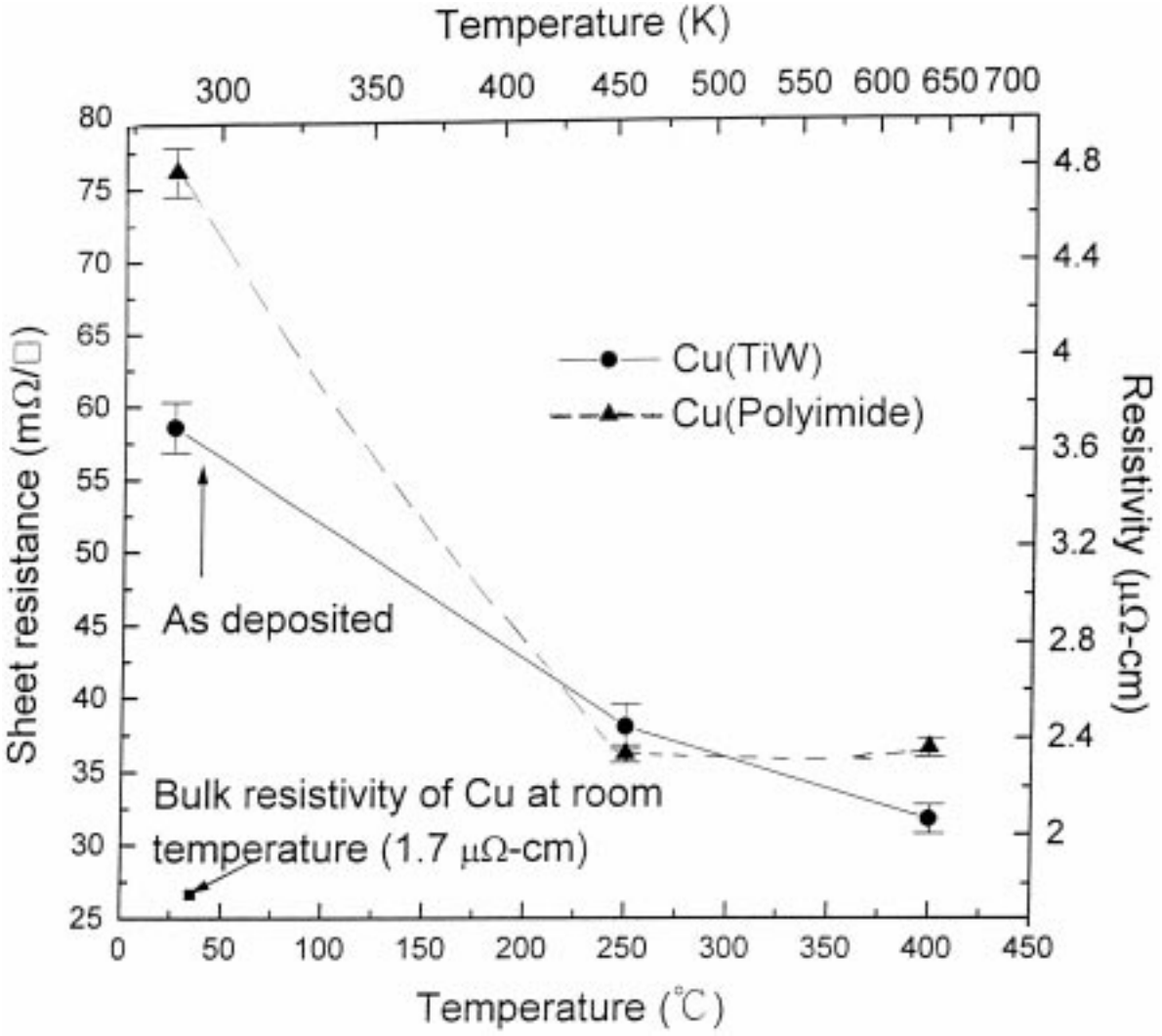


Figure 2 Sheet resistance versus annealing temperature for Cu film with TiW or polyimide underlying layer. Annealing time: 30 min.

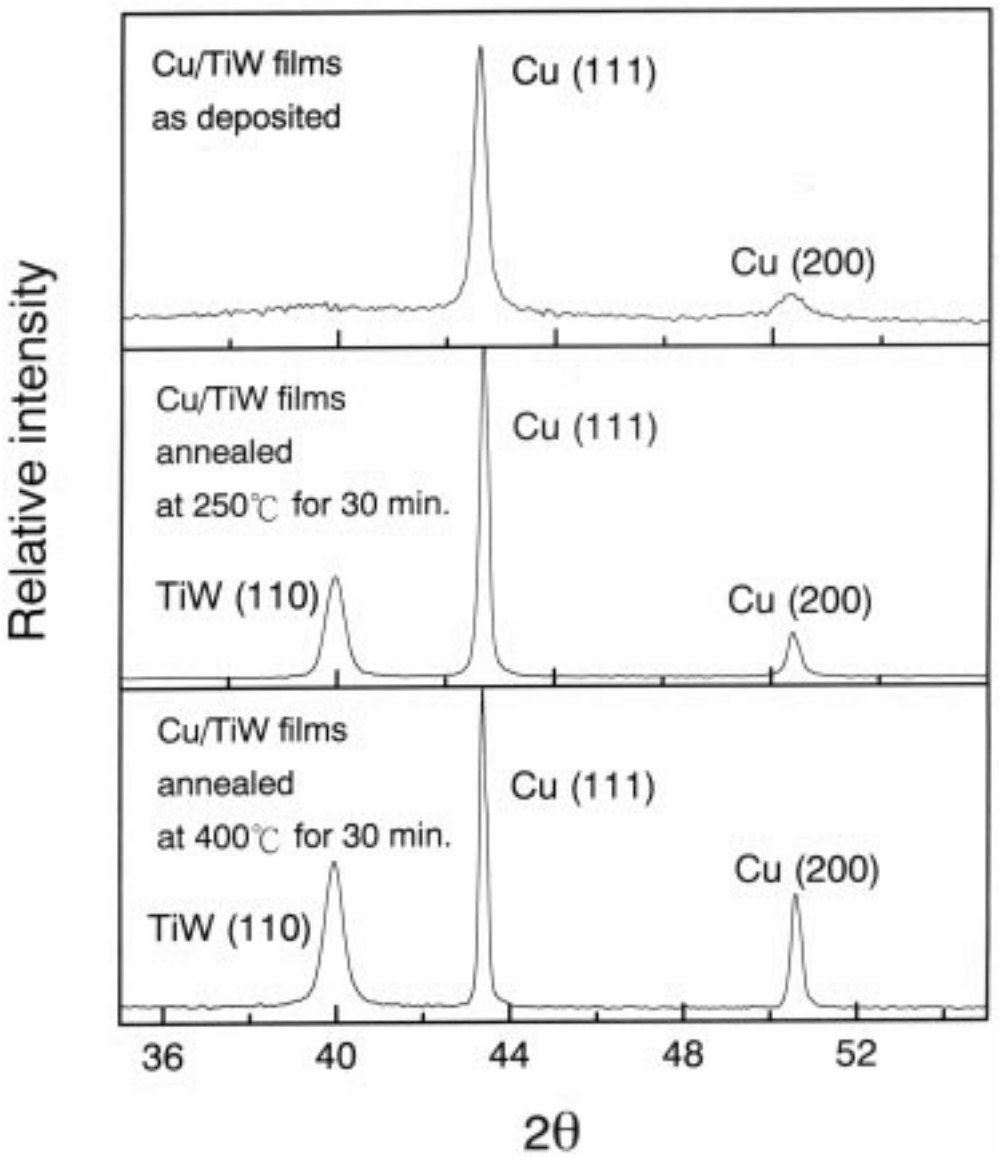
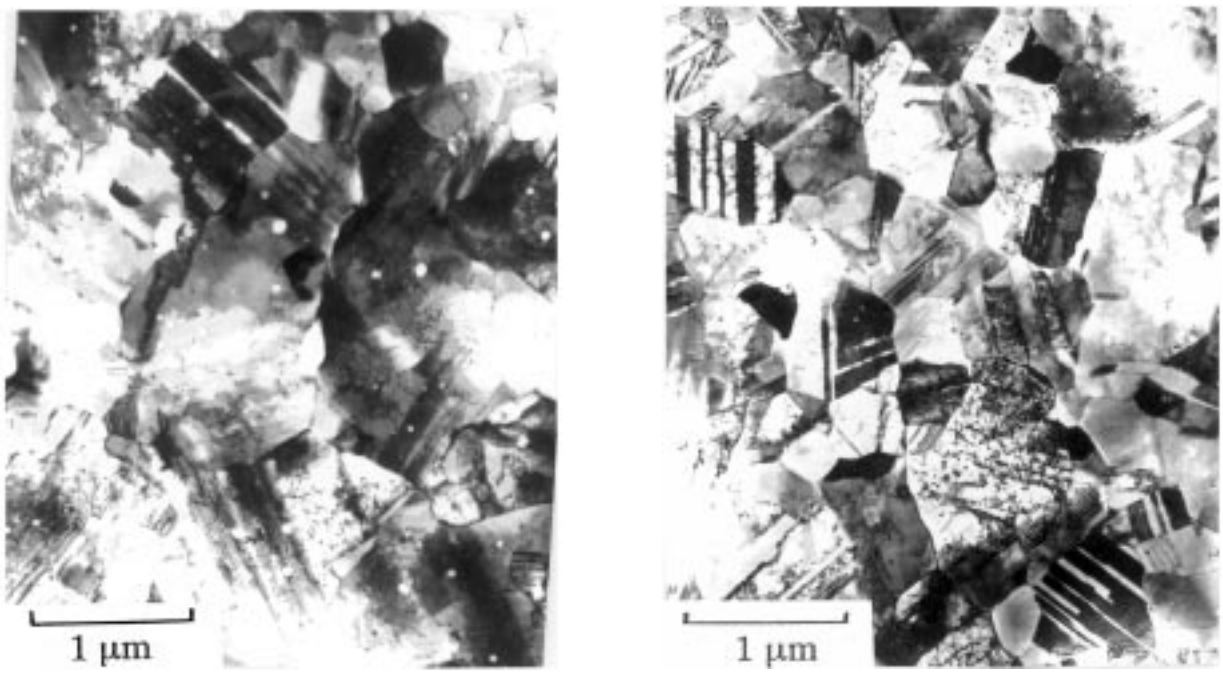


Figure 3 X-ray diffraction patterns of Cu/TiW films on PI 2540 substrate with different annealing temperatures.



(a) (b)

Figure 4 Surface morphology of (a) Cu and (b) Cu/TiW film after thermal annealing at 400 °C for 30 min.

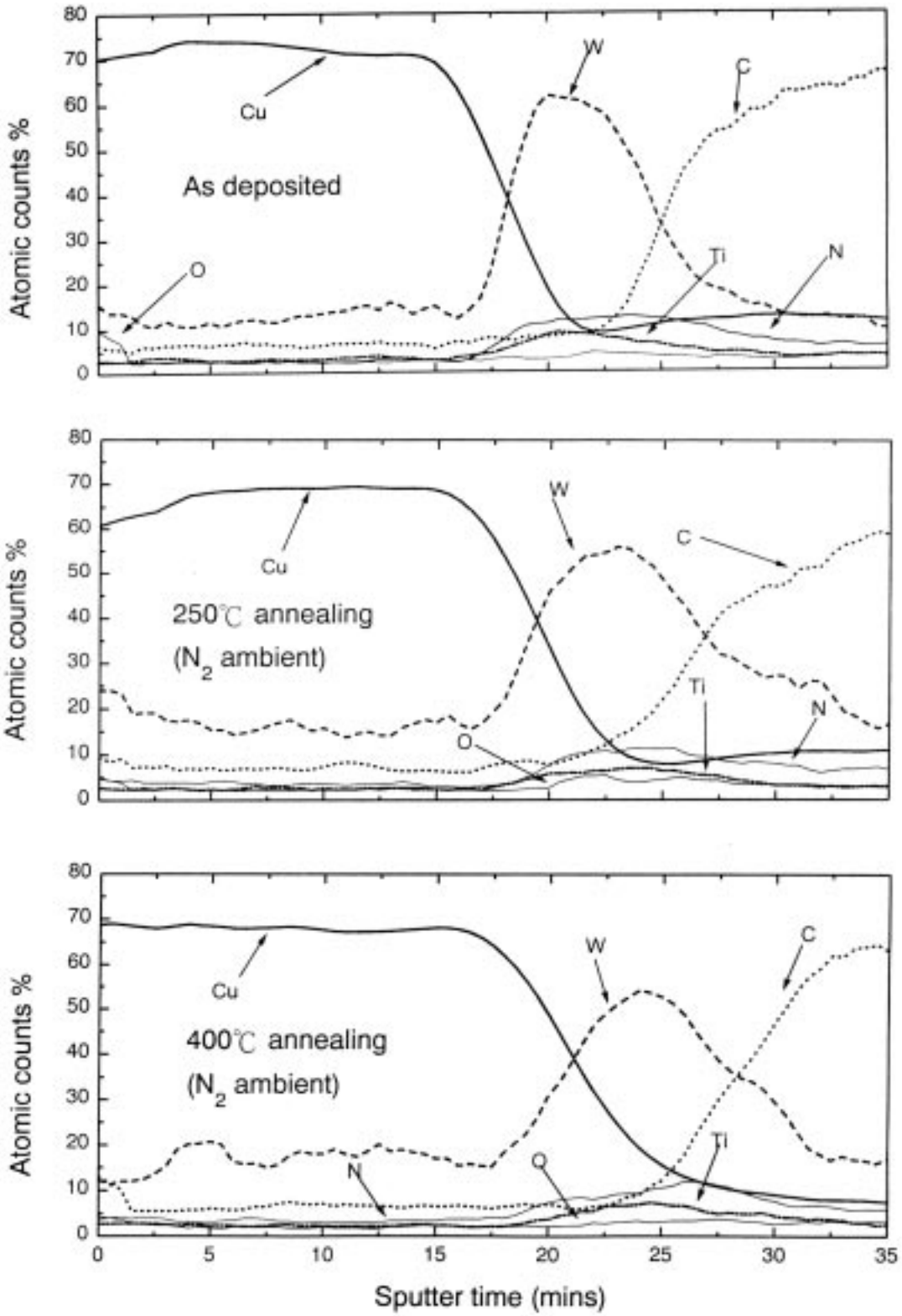


Figure 5 AES depth profile of the sample Cu/TiW films on PI 2540 substrate with different annealing temperatures.

transport properties. For Cu film on polyimide, it has been shown that Cu diffuses into polyimide after 30 min annealing at 400 °C [2]. The diffused copper formed clusters inside the polymer which raised both the dielectric constant and dissipation factor of the polymer, and consequently degraded the properties of the polymer [4]. Auger electron spectroscopy (AES) depth profiling, shown in Fig. 5, indicates that a TiW film can effectively block the diffusion path, as diffusion of Cu into polyimide is not observed when a TiW barrier layer is present.

Since the resistance of metal varies in proportion to temperature, i.e., $R_2 = \alpha(T_2 - T_1) + R_1$, the interconnect temperature can be monitored by measuring the resistance of a test metallization [1]. Fig. 6 gives the resistance of a Cu/TiW film on a polyimide coated Si substrate as a function of temperature. During the EMD experiment, the sample temperature is obtained from the measured resistance of the test metallization. The relative resistance R/R_0 as a function of time at various temperatures is exhibited in Fig. 7. The resistance increases more rapidly at higher soaking temperatures.

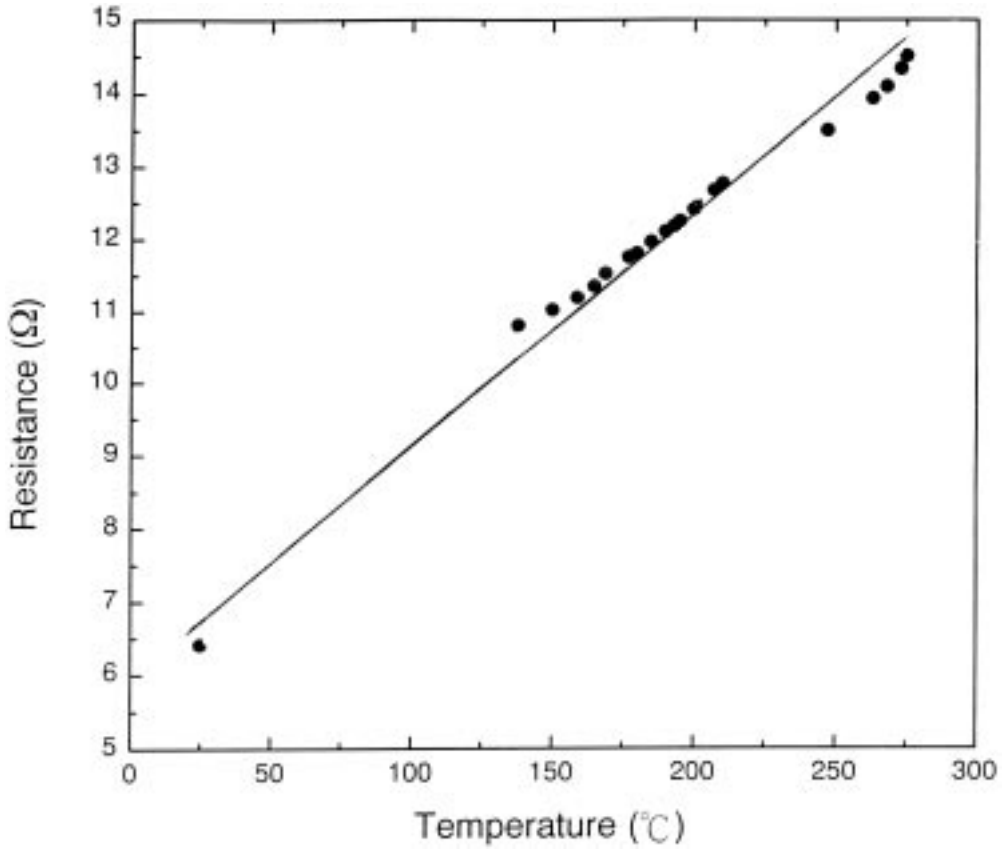


Figure 6 Resistance versus temperature of Cu/TiW film.

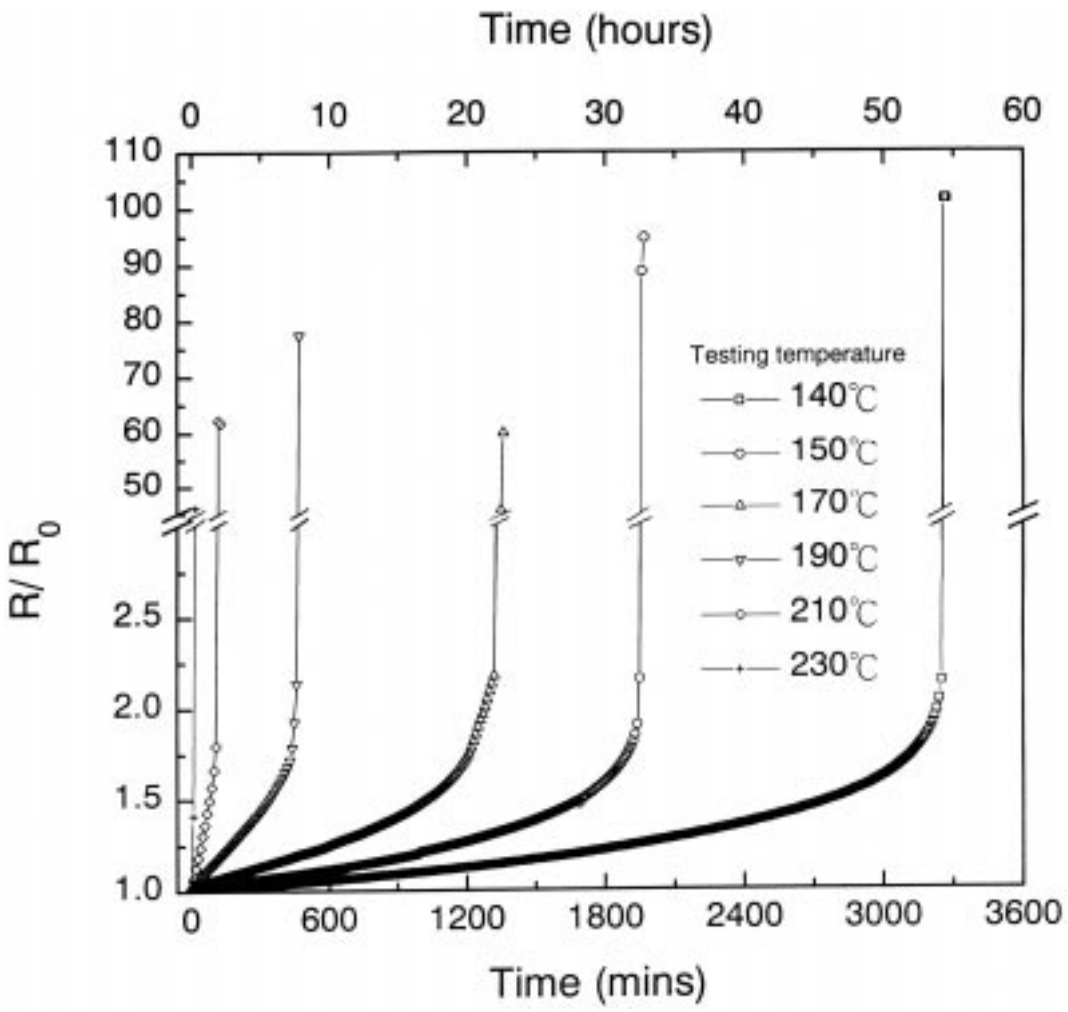


Figure 7 EMD tests of the samples Cu/TiW on PI 2540 substrate at a current density $J = 1.31\,\mathrm{MA\,cm^{-2}}$ at various testing temperatures. Samples annealed at 400 °C for 30 min before EMD tests.

By defining a resistance change of 4.5% as the criterion of early stage failure, i.e., assuming the dimensions of the maximum voids are much less than the line width, the time rate change of electrical resistance $(\mathrm{d}R/\mathrm{d}t)$ due to electromigration damage is thermally activated and can be expressed by the following empirical equation [1, 6–8]:

$$\frac{\mathrm{d}R}{\mathrm{d}t} \cdot \frac{1}{R_0} = AJ^n \exp\left(-\frac{Q}{kT}\right) \tag{1}$$

where R_0 is the initial resistance at a given temperature, A is a pre-exponential factor, J^n is the electron current density raised to the nth power, T is temperature, and Q is the activation energy for EMD. Two activation energies, 1.73 eV (190 to 230 °C) and 0.79 eV (140 to 190 °C), are obtained from the $\ln[(\mathrm{d}R/\mathrm{d}t)(1/R_0)]$ versus $1/T$ plot shown in Fig. 8, compared to an activation energy of 0.77 eV (110 to 220 °C) for Cu film under the same test conditions [2].

Activation energies of 0.5 to 2.3 eV have been reported for Cu electromigration [10, 11]. The large variations in the reported data are probably due to the variations in purity and microstructure of the Cu films and the test conditions, such as ambient temperature and current density. The two activation energies for the Cu/TiW film suggest that there are two migration mechanisms. Hummel *et al*. [12] reported that the activation energy for lattice migration in Cu is of the order of 2.3 eV, while that for grain boundary diffusion is about 1.2 eV. The low activation energy (0.79 eV) obtained at low temperature (140 to 190 °C) suggests that lattice and grain boundaries are not the major paths for electromigration in Cu/TiW. Migration via interfacial diffusion paths, such as surface/interface diffusion, may play an important role in Cu migration. Conversely, at high temperatures (190 to 230 °C), migration through surface, lattice and grain boundaries occurs and results in an activation energy of 1.73 eV. The TiW barrier layer enhances the migration resistance of copper at high temperatures. The activation energies are 0.77 eV and 1.73 eV for Cu and Cu/TiW, respectively.

The current exponent n in Equation 1, calculated from the EMD data is 5.41 for Cu/TiW as compared to 3.58 for Cu, indicating that Cu/TiW is more sensitive to current stressing than Cu. A current exponent of 2 has been obtained by solving a relatively simple diffusion equation where mass transport due to both a concentration gradient and an electromigration force are treated concurrently [12]. Values of n greater than 2 can

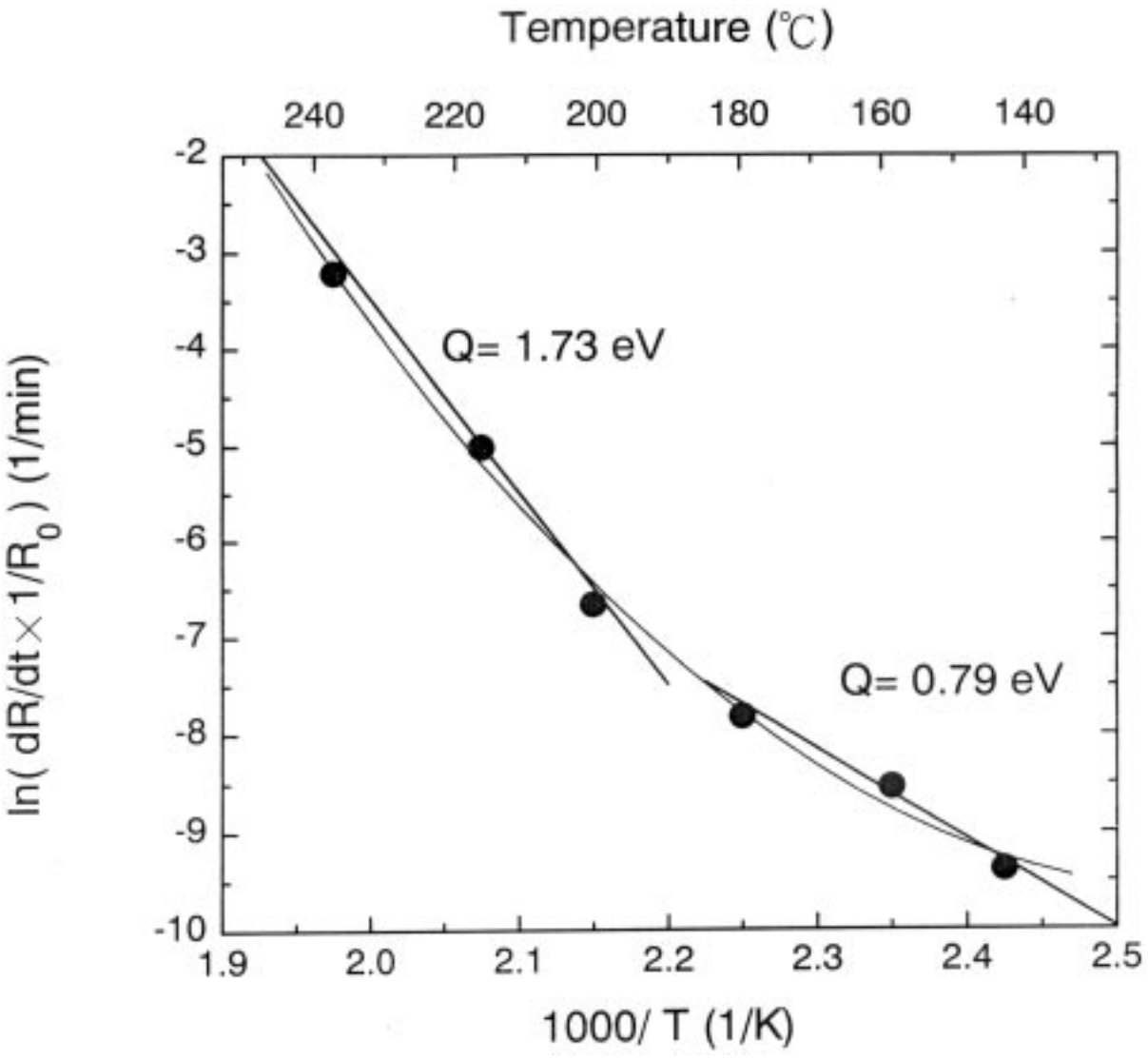


Figure 8 $\ln[(\mathrm{d}R/\mathrm{d}t)(1/R_0)]$ versus $1/T$ for Cu films during EMD test. Current density: 1.31 MA cm^{-2}. Samples annealed at 400 °C for 30 min before EMD tests.

probably be attributed to Joule heating effects which result in a temperature gradient-induced flux divergence. Some models predicted values of 1 to 15 depending on Joule heating [13]. The thermal conductivities of both Ti ($22\,W\,m^{-1}K^{-1}$) and W ($167\,W\,m^{-1}K^{-1}$) are much smaller than that of Cu ($395\,W\,m^{-1}K^{-1}$). One would expect that the introduction of the TiW barrier layer degrades the power dissipation ability of larger Cu films and results in a larger n. However, there are many factors, such as electric field, temperature gradient, residual stress, etc., which would influence the migration of Cu. The root causes for the empirical n are yet to be revealed.

4. Conclusions

The barrier effect of TiW on the electromigration of Cu film is investigated. The Auger depth profile suggests that titanium tungsten is effective in blocking the diffusion of Cu into polyimide. Copper films with a TiW barrier layer exhibit higher crystallinity, more uniform grain size and lower resistivity compared to those without. Samples with $Ti_{0.3}W_{0.7}$ as an interlayer exhibit two migration mechanisms. The activation energies for migration failures are 0.79 eV (140 to 190 °C) and 1.73 eV (190 to 230 °C), suggesting an interfacial diffusion mechanism and a combined diffusion mechanism, respectively. The presence of a TiW barrier layer enhances the high temperature electromigration resistance, however, films with TiW are more sensitive to current stressing than those without.

Acknowledgment

This work is sponsored by the National Science Council, Taiwan, under the contract No.86-2221-E-009-062.

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Received 12 April
and accepted 29 July 1999