

Passivation of copper films with magnesium doping using recoil ion implantation

Zhen-Cheng Wu*, Yu-Lin Liu, Mao-Chieh Chen

Department of Electronics Engineering and the Institute of Electronics, National Chiao-Tung University, 1001 Ta Hsueh Road, Hsinchu 300, Taiwan

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Abstract

This work investigates the effects of Ar⁺ ion implantation through a multilayer structure of SiO₂(100 nm)/Mg(20 nm)/Cu/SiO₂/Si on the oxidation resistance of Cu films. Experimental results indicate that implantation at 130 keV to a dose of $5 \times 10^{15} \text{ cm}^{-2}$ significantly enhances the oxidation resistance at temperatures up to 375°C. At this energy, a small number of Mg atoms are knocked out, leading to formation of an impervious MgO barrier layer on the Cu surface, which effectively suppresses the oxidizing diffusion paths. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Copper; Ion implantation; Magnesium; Oxidation

1. Introduction

Copper is a highly promising alternative metallization material to Al-based alloys for the next generation ultra large scale integrated (ULSI) circuits owing to its low electrical resistivity (1.67 $\mu\Omega \text{ cm}$ for bulk) and superior electro/stress-migration resistance [1–3]. However, copper easily oxidizes on its exposed surfaces at low temperatures in the ambient normally used in the ULSI back-end process. This characteristic is compounded for integration with a high temperature (>400°C) metallization process. Related investigations have proposed various methods to improve the oxidation resistance of copper films, among which, the most useful ones are to incorporate in copper a small amount of dopants, such as B, N, Ti, Mg, Al, and Cr, using ion implantation [4–12], co-deposition, or successive deposition of layered structures followed by annealing at 300–800°C [13–19]. Doing so not only modifies its surface properties, but also retains its inherent bulk benefits. Among these additives, Mg has received increasing attention owing to its ability to enhance oxidation resistance and electromigration resistance. Ding et al., reported that thermally annealing the co-sputtered Cu-(2 at.% Mg) alloy film in Ar ambient at 400°C for 30 min would lead to formation of a thin protective layer of magnesium oxide on the

surfaces and curtailment of further oxidation of Cu films [20]. Moreover, according to Takewaki et al., the Cu-Mg film exhibits a resistivity of 1.81 $\mu\Omega \text{ cm}$ and the Cu-Mg interconnect exhibits a migration resistance three times larger than the giant-grain Cu interconnection [21].

In this work, we use Ar⁺ ion implantation through magnesium to knock a small number of Mg atoms (<3 at.% Mg) into Cu films. The sputter deposition scheme can not always precisely control such a small content of Mg. Correspondingly, this work explores the feasibility of controlling the amount of recoiled magnesium atoms by simply varying the implantation energy and dosage used. It is interesting to investigate the oxidation resistance and the electro/stress-migration resistance of the Cu(Mg) alloy films prepared by this scheme. Particular emphasis is made on the ability of optimal implantation condition to improve the oxidation resistance of copper films.

2. Experimental details

The experimental samples used in this study were prepared on p-type (100) oriented Si wafers of 4-inch diameter. After initial RCA cleaning, a 2000 Å thick SiO₂ was thermally grown at 1050°C in a dry oxygen atmosphere. Copper films with a thickness of 3000 Å were sputter deposited on the SiO₂ covered substrate. The base pressure for the Cu deposition was 1.5×10^{-6} Torr, and the Cu films were

* Corresponding author. Tel.: +3-571-2121; fax: +3-572-4361.

E-mail address: u8511503@cc.nctu.edu.tw (Z.C. Wu)

sputter deposited using a pure Cu target (purity 99.99%) in Ar ambient at a pressure of 7.6×10^{-3} Torr. After the sputter deposition of Cu films to complete the structure of Cu/SiO₂/Si, a 200 Å thick magnesium (Mg) film was sputter deposited on the Cu surface of the Cu/SiO₂/Si substrate in the same sputtering system without breaking the vacuum. The Mg film was then sputtered using a pure Mg target (purity 99.95%) in Ar ambient also at a pressure of 7.6×10^{-3} Torr. This was followed by sputter deposition of a 1000 Å thick capping oxide layer; the oxide layer was RF sputter deposited using an SiO₂ target in Ar ambient at a pressure of 7.6×10^{-3} Torr. This capping oxide was used to prevent the underlying Mg and Cu films from contaminating the implantation chamber and to avoid other unwanted contamination, such as hydrocarbon, which might adhere to the surface from the environment before the oxidation proceeded with. Next, the SiO₂/Mg/Cu/SiO₂/Si samples were implanted with Ar⁺ ions through the Mg layer at an energy ranging from 100 to 140 keV to a dose of 5×10^{13} to 1×10^{16} cm⁻². The implantation energy was determined by simulation using a TRIM program [22] such that the implanted Ar⁺ ions are projected near the copper surface. Following implantation, RIE was used to remove the capping oxide, followed by removal of the Mg layer by dipping the wafers in a 2% acetic acid solution for 5 s. The wafers were cut into pieces with a sample size of 1.5×1.5 cm² for each oxidation study. For comparison, control samples were prepared by implanting Ar⁺ ions into the samples of SiO₂/Cu/SiO₂/Si structure without a Mg layer on the Cu surface, followed by removal of the capping oxide. Table 1 summarizes the ion implanted samples studied herein, where samples D and E are control samples of the samples B and C, respectively.

To investigate the oxidation resistance of the ion implanted Cu films, samples of Cu films were thermally treated at various elevated temperatures in air for 30 min. Next, measurements were made via various techniques to characterize the oxidation behavior of the Cu films. A four-point probe was then used to measure the sheet resistance (R_s) of the samples. Moreover, the crystallinity of the films was studied using X-ray diffraction (XRD) analysis. Secondary ion mass spectroscopy (SIMS) was used to measure the elemental depth profiles, and X-ray photoelectron spectroscopy (XPS) was employed to study the elemental chemical states.

3. Results and discussions

Fig. 1 shows the typical XRD spectra for 3000 Å thick Cu films (on SiO₂/Si substrates) as well as samples A, B, and C thermally treated in air at various temperatures. The diffraction peak of cuprous oxide (Cu₂O) appeared after the samples were thermally treated at a certain temperature, which is referred to hereinafter as degradation temperature (T_d). The degradation temperatures (T_d) were found to be 175°C for the sample of pure Cu film (Fig. 1a), 225°C for sample A (Fig. 1b), 375°C for sample B (Fig. 1c), and 200°C for sample C (Fig. 1d). Fig. 2 shows the sheet resistance change as a function of thermal treating temperature for samples A, B, and C; data for the sample of pure Cu film are also included for comparison. The sheet resistances (R_s) of the as-prepared fresh samples A, B, and C were determined to be 103, 90, and 102 mΩ/□, respectively, which are lower than the R_s value of 150 mΩ/□ measured for the as-deposited Cu film of the same thickness. The reduction of sheet resistance for the fresh samples A, B, and C compared with that of the as-deposited pure Cu film is attributed to the self-annealing because the temperature of the implanted samples was raised to about 100°C during the ion implantation process. We believe that self annealing occurs also for the control samples D and E, which do not contain any Mg atom and whose R_s values were determined to be 87 and 101 mΩ/□, respectively. Notably, the temperatures at which the R_s value revealed a significant increase were found to be fairly consistent with the degradation temperature T_d for all the samples observed. Moreover, according to Fig. 2, the sheet resistance of sample B revealed a relatively smaller change up to a temperature of 350°C than the other samples. Obviously, sample B has a much better resistance to oxidation as discussed later.

Fig. 3 shows the degradation temperatures (T_d) for the Mg doped Cu films processed by Ar⁺ implantation at various energies to a dose of 5×10^{15} cm⁻². According to this figure, the implantation energy of 130 keV resulted in a Mg doped Cu film of the best oxidation resistance. Fig. 4 shows the SIMS depth profiles of sample B. The Mg atoms were located basically at the Cu surface in an extremely shallow region; this Mg-rich layer immediately formed a native layer of magnesium oxide (MgO), as confirmed by XPS analysis to be shown later in Fig. 5. This finding differs from that in literature that the MgO

Table 1
Summary of ion implanted samples studied in this work^a

Sample identification	Samples structures for Ar ⁺ ion implantation	Implantation energy (keV)	Implantation dose (cm ⁻²)
A	SiO ₂ /Mg/Cu/SiO ₂ /Si	130	1×10^{16}
B	SiO ₂ /Mg/Cu/SiO ₂ /Si	130	5×10^{15}
C	SiO ₂ /Mg/Cu/SiO ₂ /Si	140	5×10^{15}
D	SiO ₂ /Cu/SiO ₂ /Si	130	5×10^{15}
E	SiO ₂ /Cu/SiO ₂ /Si	140	5×10^{15}

^a The capping SiO₂ and Mg layers were removed after ion implantation.

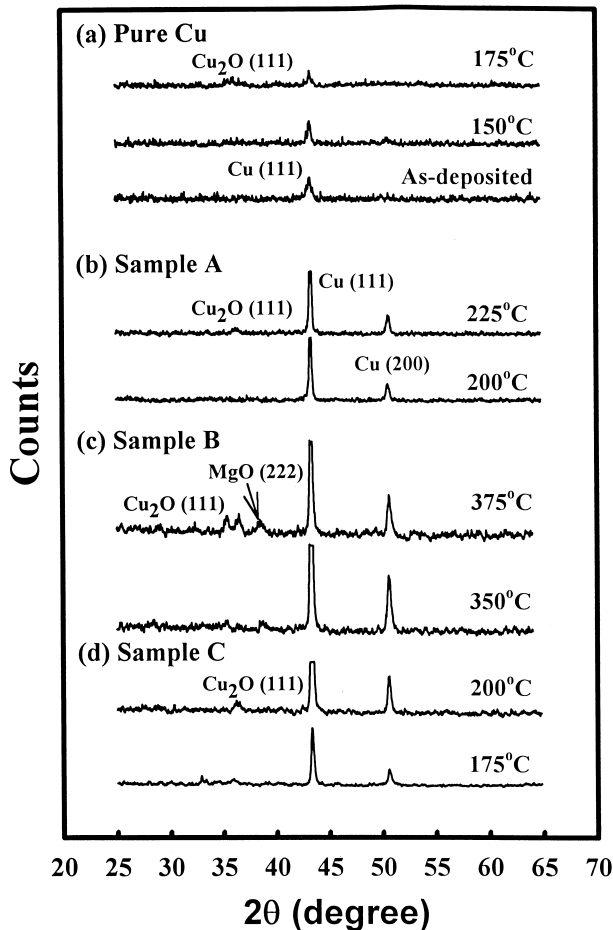


Fig. 1. XRD spectra for (a) pure Cu films, (b) sample A (Ar^+ 130 keV/ $1 \times 10^{16} \text{ cm}^{-2}$), (c) sample B (Ar^+ 130 keV/ $5 \times 10^{15} \text{ cm}^{-2}$), and (d) sample C (Ar^+ 140 keV/ $5 \times 10^{15} \text{ cm}^{-2}$) thermally treated in air at various temperatures.

oxide layer was formed on the Cu surface during a 30 min thermal annealing at 400°C in Ar ambient [19,20]. We believe that the rapid formation of this native MgO surface

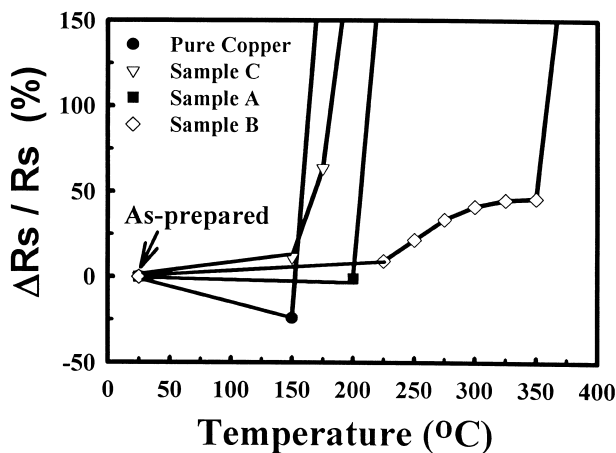


Fig. 2. Sheet resistance change as a function of thermal treating temperature for samples A, B, and C as well as pure Cu films.

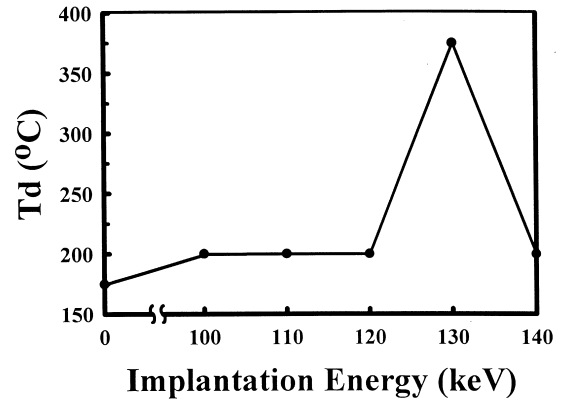


Fig. 3. Degradation temperature (T_d) of Mg-doped Cu films vs. implantation energy of Ar^+ ions; the implanted dose is $5 \times 10^{15} \text{ cm}^{-2}$.

layer is related to the enhanced chemical reactivity induced by the energetic ion bombardment of Ar^+ implantation. As expected, the surface MgO oxide layer prevents the copper surface from oxidizing. Fig. 5 shows the XPS spectra of Cu_{2p} , O_{1s} , and Mg_{2p} photoelectrons of sample B. Fig. 5c reveals that elemental Mg atoms were also present near the copper surface in addition to the MgO surface layer. As assumed herein, these Mg atoms occupied the surface vacancy sites, which are necessary for copper oxidation to proceed via Cu^+ ions hopping between the vacancies [12,19,20]. Consequently, sample B has a degradation temperature of 375°C , which is the highest among the samples studied in this work. Thermally treating sample B in air at 375°C dramatically changed the Mg profile as the Mg atoms were widely distributed throughout the Cu film, resulting in a decrease of Mg atoms occupying the vacancy sites in the surface region. Fig. 6 shows the XPS spectra of Cu_{2p} , O_{1s} and Mg_{2p} photoelectrons for sample B thermally treated in air at 375°C . This figure indicates that a Cu_2O layer was present at the outermost surface, and that both Mg and MgO were buried under the outermost Cu_2O layer while the presence of Cu_2O continued inward. On the

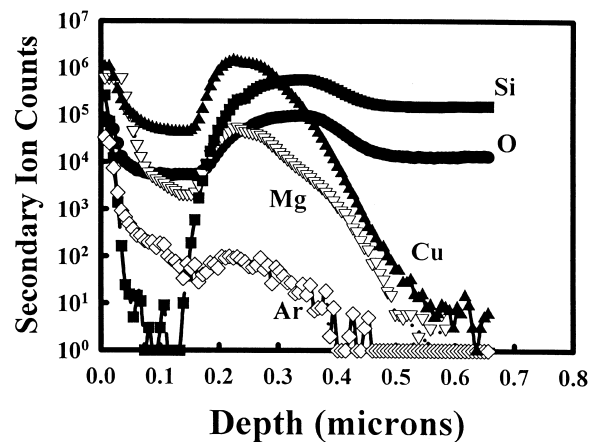


Fig. 4. SIMS depth profiles of sample B ($\text{Cu}(\text{Mg})/\text{SiO}_2/\text{Si}$) with Ar^+ implantation at 130 keV to a dose of $5 \times 10^{15} \text{ cm}^{-2}$.

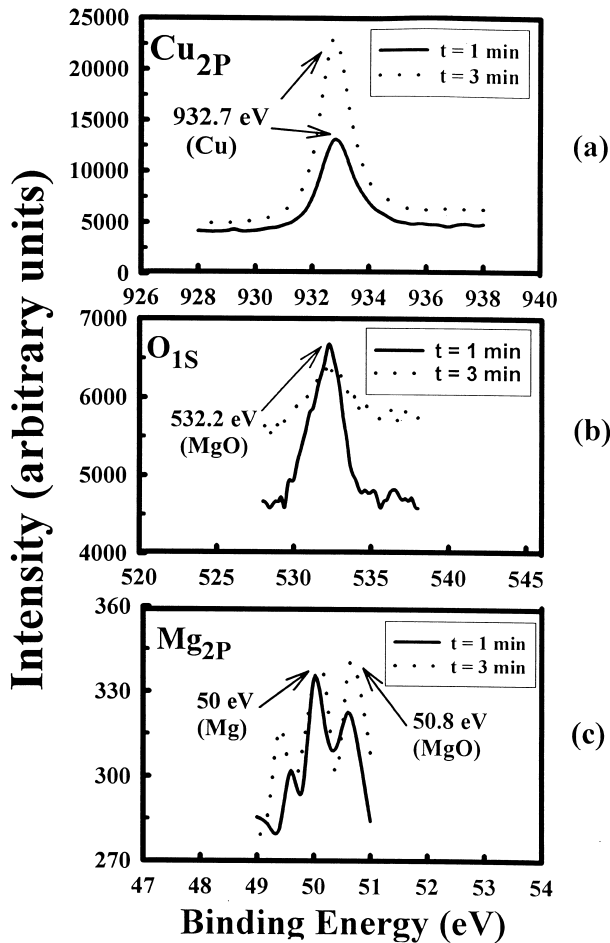


Fig. 5. XPS spectra showing the chemical states of (a) Cu_{2p} , (b) O_{1s} , and (c) Mg_{2p} photoelectrons for sample B ($\text{Cu}(\text{Mg})/\text{SiO}_2/\text{Si}$) with Ar^+ implantation at 130 keV to a dose of $5 \times 10^{15} \text{ cm}^{-2}$.

other hand, for the control sample (sample D), the degradation temperature (T_d) was 175°C, which is the same as the as-deposited pure copper films. Thus, deterioration of oxidation resistance due to the possible implantation induced structural defects can be ruled out. We conclude that only partial passivation was achieved in sample B, and that a complete impervious passivation layer was not formed and the cuprous oxide layer continued to grow, although at a much slower rate. This observation might imply that the MgO layer formed was not a continuous and pin-hole free layer, still capable of inducing the oxidation of Cu films. Although the recoil implantation appears to successfully dope Mg into the copper film to strengthen its oxidation resistance, complete formation of a pin hole free MgO passivation layer may require careful inert annealing after implantation.

For samples implanted with Ar^+ ions at 140 keV, instead of 130 keV, to a dose of $5 \times 10^{15} \text{ cm}^{-2}$ (sample C), the degradation temperature (T_d) reduced drastically from 375 to 200°C (Fig. 3). Since the SIMS depth profile of Mg atoms and the XPS analyses results for sample C resemble those of sample B (as shown in Figs. 4 and 5, respectively),

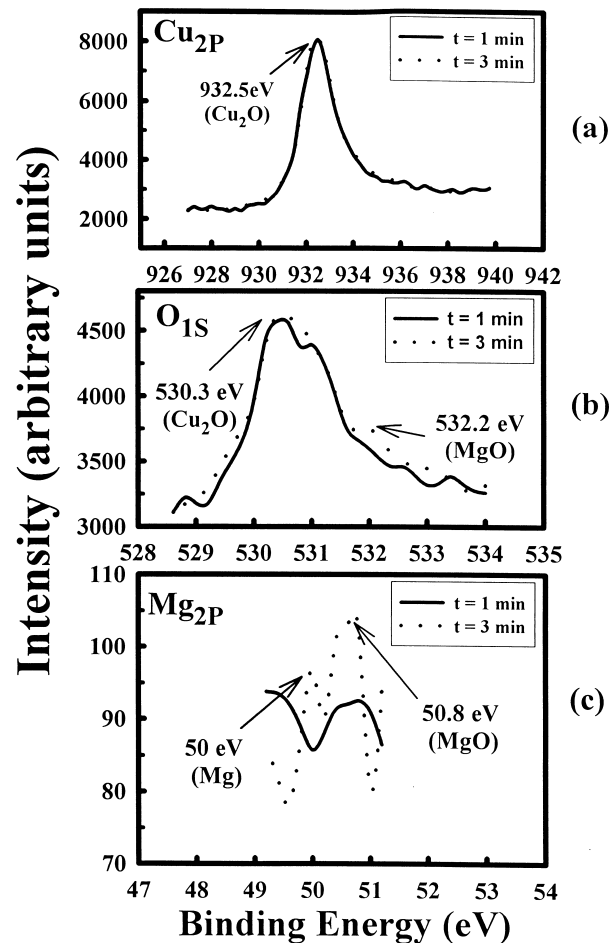


Fig. 6. XPS spectra showing the chemical states of (a) Cu_{2p} , (b) O_{1s} , and (c) Mg_{2p} photoelectrons for sample B thermally treated in air at 375°C.

sample B and sample C would not be expected to differ in terms of oxidation behavior. However, higher implantation energies generally lead to more implantation defects [8]. Moreover, the diffusion of oxidizing species via these

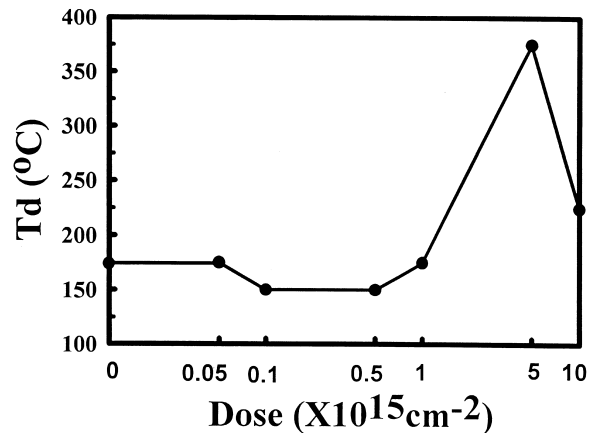


Fig. 7. Degradation temperature (T_d) of Mg-doped Cu films vs. implantation dose of Ar^+ ions; the implanted energy is 130 keV.

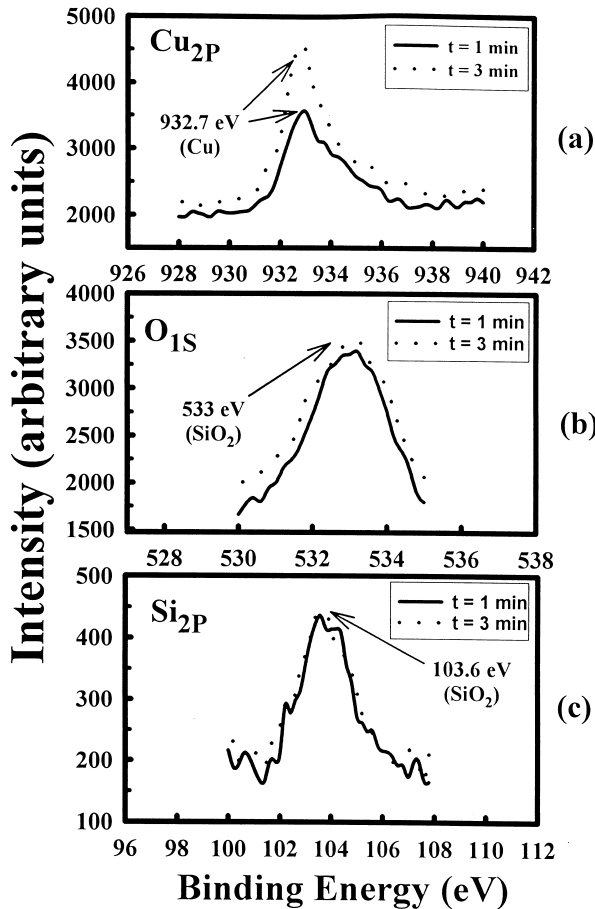


Fig. 8. XPS spectra showing the chemical states of (a) Cu_{2p} , (b) O_{1s} , and (c) Si_{2p} photoelectrons for sample A thermally treated in air at 200°C .

defects might play an important role in the oxidation behavior of Cu films. According to our results, the degradation temperature of the corresponding control sample (sample E) was 150°C , which is 25°C lower than that of sample D as well as the as-deposited pure copper films. Compared with the T_d improvement from 175°C (sample D) to 375°C (sample B) by Mg doping associated with Ar^+ implantation at 130 keV, the Mg doping associated with Ar^+ implantation at 140 keV increased the T_d from 150°C (sample E) to merely 200°C (sample C). This observation implies that the implantation induced defects at an implantation energy of 140 keV might play an important role in the failure of the oxidation resistance.

Fig. 7 shows the degradation temperature (T_d) versus implantation dose for the Mg-doped Cu films associated with Ar^+ implantation at 130 keV. According to this figure, the implantation dose of $5 \times 10^{15} \text{ cm}^{-2}$ was the optimal dosage for the best oxidation resistance. Fig. 8 shows the XPS spectra of Cu_{2p} , O_{1s} , and Si_{2p} photoelectrons for sample A after thermal treatment at 200°C , which is below the degradation temperature of 225°C . According to this figure, the sample did not appear to be oxidized, which is consistent with the XRD analysis results (Fig. 1b).

However, SiO_2 was present on the surfaces of Cu films, where both Mg and MgO were deficient according to the XPS analysis results. We presume that the high dosage Ar^+ ion implantation into the $\text{SiO}_2/\text{Mg}/\text{Cu}/\text{SiO}_2/\text{Si}$ structure knocked out a large number of Si atoms to accumulate near the copper surface and a thin layer of porous silicon oxide was formed on the copper surface. Fig. 9 shows the XPS spectra of Cu_{2p} , O_{1s} , and Mg_{2p} photoelectrons for sample A after thermal treatment at 225°C . This figure indicates that the outermost surface layer consisted of both Cu_2O and SiO_2 while elemental Mg and MgO oxide were present underneath the outermost surface layer. Therefore, the deficiency of both Mg and MgO near the Cu surface after 200°C treatment suggests that the oxidation of copper might proceed with via the thin layer of porous silicon oxide at 225°C .

The cross-sectional interfacial structures resulting from Ar^+ implantation into a multilayer structure of $\text{SiO}_2/\text{Mg}/\text{Cu}/\text{SiO}_2/\text{Si}$ with and without post-implant thermal treatments, as deduced from the XPS analysis results, are summarized with schematic illustrations in Fig. 10. Each sample was thermally treated separately at two different temperatures: the degradation temperature (T_d) and a temperature 25°C below the corresponding degradation temperature.

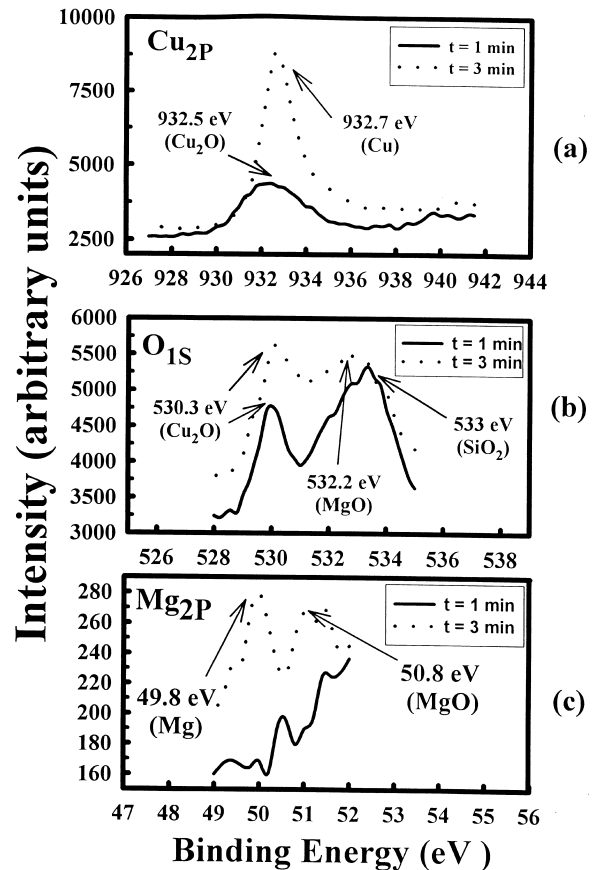


Fig. 9. XPS spectra showing the chemical states of (a) Cu_{2p} , (b) O_{1s} , and (c) Mg_{2p} photoelectrons for sample A thermally treated in air at 225°C .

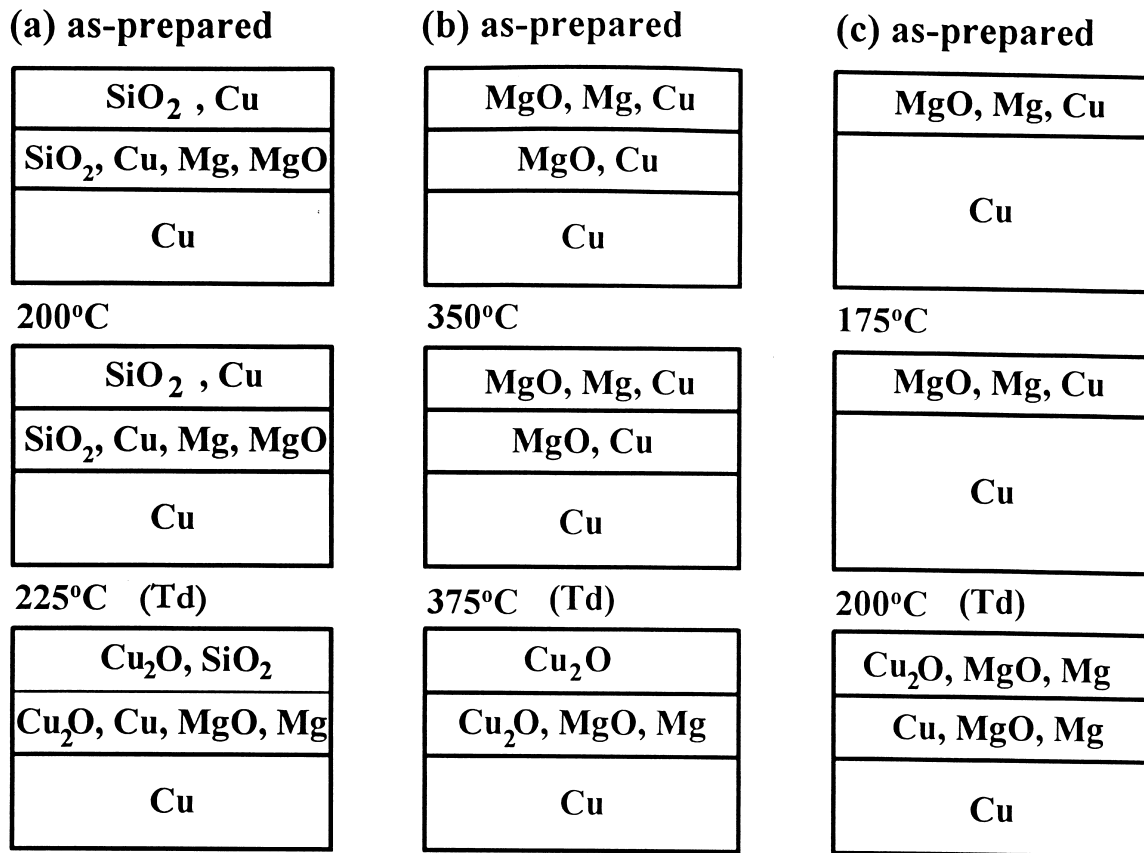


Fig. 10. Schematic illustrations of cross-sectional interfacial structures resulting from Ar⁺ implantation into a multilayer structure of SiO₂/Mg/Cu/SiO₂/Si (a) sample A, (b) sample B, and (c) sample C before and after thermal treatments at two different temperatures, one of which is the degradation temperature (*T_d*) and the other is a temperature 25°C below the corresponding degradation temperature.

4. Conclusions

Copper films are readily oxidized into Cu₂O at temperatures as low as 175°C in air. The oxidation resistance of the Cu film can be improved with appropriate Ar⁺ implantation into a multilayer structure of SiO₂/Mg/Cu/SiO₂/Si in order to place a small number of Mg atoms in the surface region of the Cu layer. The Mg atoms at the Cu surface tend to form a barrier layer of magnesium oxide (MgO) on the copper surface. This MgO layer effectively suppresses the diffusion of oxidizing species, thus preventing or retarding the oxidation of Cu films. Implantation at too high of an energy increases implantation induced surface defects that serve as diffusion paths for the oxidizing species. On the other hand, too high of a dosage implantation adversely affects the oxidation resistance of Cu films because a large number of Si atoms are knocked out and accumulated at the Cu surface, forming a porous silicon oxide (SiO₂) thin layer near the Cu surface. Rapid oxidation of copper might proceed with via the porous silicon oxide. Our results further demonstrate that the best oxidation resistance of Cu films can be obtained by Ar⁺ implantation at 130 keV to a dose of $5 \times 10^{15} \text{ cm}^{-2}$ through a multilayer structure of SiO₂(100 nm)/Mg(20 nm)/Cu/SiO₂/Si. With this scheme,

the resulting Cu films can resist oxidation at temperatures up to 375°C.

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References

- [1] T. Nitta, T. Ohmi, T. Hoshi, S. Sakai, K. Sakaibara, S. Imai, T. Shibata, *J. Electrochem. Soc.* 140 (1993) 1131.
- [2] M.T. Bohr, *Solid State Technol.* 39 (1996) 105.
- [3] J. Tao, N.W. Cheung, C. Hu, *Electron Device Lett.* 14 (1993) 249.
- [4] H.M. Naguib, R.J. Krieger, J.A. Davies, J.B. Mitchell, *J. Vac. Sci. Technol.* 13 (1976) 396.
- [5] D.C. Kothari, L. Guzman, S. Girardi, A. Tomasi, S. Gialanella, P.M. Raole, P.D. Prabhawalkar, *Mater. Sci. Eng. A* 116 (1989) 135.
- [6] L.G. Svendsen, S.S. Eskildsen, P. Borgesen, *Thin Solid Films* 110 (1983) 237.
- [7] L.G. Svendsen, *Corros. Sci.* 20 (1980) 63.
- [8] P.J. Ratcliffe, R.A. Collins, *Phys. Stat. Sol. (a)* 78 (1983) 547.
- [9] P.J. Ratcliffe, R.A. Collins, *Phys. Stat. Sol. (a)* 108 (1988) 537.

- [10] P.J. Ding, W.A. Lanford, S. Hymes, S.P. Murarka, Proc. MRS Symp. 260 (1992) 757.
- [11] P.J. Ding, W.A. Lanford, S. Hymes, S.P. Murarka, J. Appl. Phys. 74 (1993) 1331.
- [12] P.J. Ding, W. Wang, W.A. Lanford, S. Hymes, S.P. Murarka, Nucl. Instrum. Methods B 85 (1994) 260.
- [13] P.J. Ding, W.A. Lanford, S. Hymes, S.P. Murarka, J. Appl. Phys. 75 (1994) 3627.
- [14] D. Adams, T.L. Alford, N.D. Theodore, S.W. Russell, R.L. Spreitzer, J.W. Mayer, Thin Solid Films 262 (1995) 199.
- [15] S. Hymes, K.S. Kumar, S.P. Murarka, W. Wang, W.A. Lanford, Proc. MRS Symp. 428 (1996) 17.
- [16] P. Atanasova, V. Bhaskaran, T. Kostas, M. Hampden-Smith, Proc. MRS Symp. 428 (1996) 25.
- [17] W.A. Lanford, P.J. Ding, W. Wang, S. Hymes, S.P. Murarka, Mater. Chem. Phys. 41 (1995) 192.
- [18] J. Li, J.W. Mayer, J. Appl. Phys. 70 (1991) 2820.
- [19] W.A. Lanford, P.J. Ding, W. Wang, S. Hymes, S.P. Murarka, Thin Solid Films 262 (1995) 234.
- [20] P.J. Ding, W. Wang, W.A. Lanford, S. Hymes, S.P. Murarka, Appl. Phys. Lett. 64 (1994) 2897.
- [21] T. Takewaki, R. Kaihara, T. Ohmi, T. Nitta, Tech. Dig. (1995) 253.
- [22] J.F. Ziegler, J.P. Biersack, U. Littmark, The Stopping and Range of Ions in Solids, Pergamon Press, New York, 1985.