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Effects of BF_2^+ implantation on the oxidation resistance of copper films

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Abstract

This work investigates the effects of BF_2^+ implantation on the oxidation resistance of copper films. The BF_2^+ ions were implanted into Cu films through a 1000 Å thick screen SiO_2 layer. We found that the oxidation resistance of Cu films can be significantly improved by BF_2^+ implantation at appropriate conditions. In particular, BF_2^+ implantation at 35 to 40 keV to a dose of $1-8\times10^{14}$ cm^{-2} made the Cu films capable of resisting oxidation at temperatures up to 250°C. At these BF_2^+ implantation energies, boron atoms of peak concentration were projected near the Cu surface; thus the diffusion paths of oxidizing species were efficiently blocked. Implantation at too high energy would result in greater depth of projection, thus a lower concentration of boron at the Cu surface; moreover, it generally leads to increased implantation defects that might serve as diffusion paths for the oxidation species. On the other hand, too high dosage implantation would also have an adverse effect on the capability of oxidation resistance for Cu films owing to the higher density of implantation damage as well as the formation of reactive fluorine compound (CuF_2) near the Cu surface.

Keywords: Copper; Oxidation; Boron; Fluorine

1. Introduction

Copper has been extensively studied as an alternative to the Al-based alloys for the next generation ultra large scale integration (ULSI) applications because of its low resistivity (1.72 μΩ cm) and superior electro/stress-migration characteristics [1]. However, copper oxidizes easily on its exposed surfaces at low temperatures in the ambient normally used in the ULSI back-end process and this characteristic becomes a serious concern for integration with high temperature (>400°C) metallization process. To improve the oxidation resistance of copper films, a number of methods have been investigated, one of which is to implant a small amount of impurities in copper so as to modify its surface properties while retain its inherent bulk benefits. The impurity species that have been studied include B, N, Ti, Mg, Al, and Cr [2–7]. Naguib et al. implanted B ions into polycrystalline Cu and concluded that the implantation of B ions reduced the oxidation of Cu at 200°C irrespective of the ion energy [7]. Moreover, Ding et al. reported that corrosion resistant Cu films were obtained by B ion implantation at 50 keV to a dose of $(1–5)\times10^{15}$ cm^{-2} [8,9]. Similar results were found for corrosion resistance of materials other than copper. Rubio et al. reported that the corrosion resistance of steam generator material (Inconel 600) could be enhanced by implanting the near-surface region with high energy BF_2^+ ions [10].

In this work, we investigated the effect of BF_2^+ ion implantation on the oxidation resistance of copper films. Effort was made to determine the optimal implantation condition with respect to its effectiveness in improving the oxidation-resistant capability 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 SiO_2 was thermally grown at 1050°C in dry oxygen atmosphere. Copper films of 2000 Å thickness were sputter deposited on the SiO_2 covered substrate. The base pressure for the Cu deposition was 1.5×10^{-6} Torr, and the Cu films were sputter deposited using a pure Cu target in Ar ambient at a pressure of 7.6×10^{-3} Torr. A capping oxide layer of 1000 Å thickness was then deposited; the oxide was RF sputter deposited using an SiO_2 target in Ar ambient at a pressure of 7.6×10^{-3} Torr. This capping oxide was deliberately used to prevent the ion beam in the subsequent BF_2^+ implantation from directly impinging upon the underlayer copper film so as to retain its integrity and avoid unwanted contamination, such as hydrocarbon, which might adhere to the surface from the environment before the oxidation proceeded. The samples were implanted with BF_2^+ ions at

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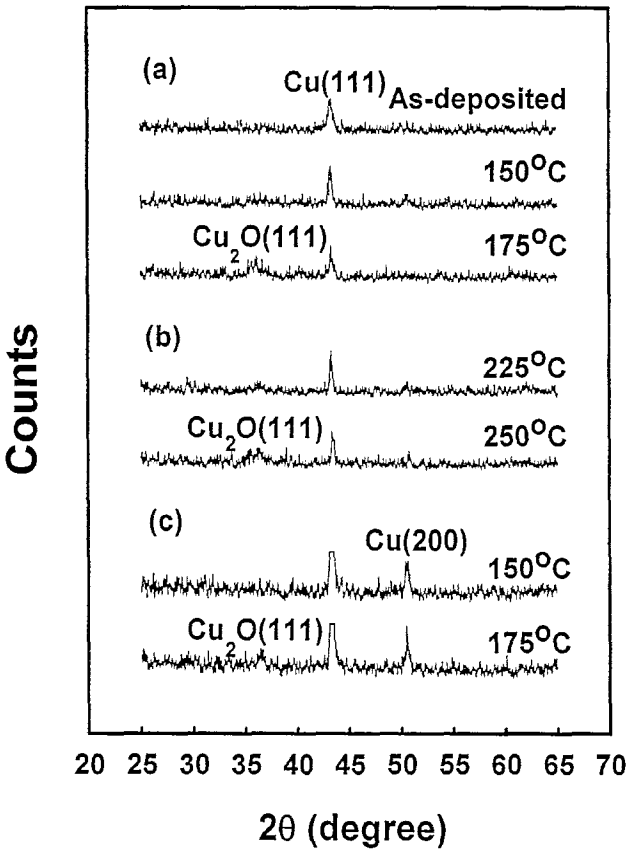

Fig. 1. XRD spectra for as-deposited and thermally treated Cu films (2000 Å thickness) on SiO_2/Si substrates: (a) unimplanted samples, (b) samples implanted with BF_2^+ at 35 keV to a dose of 5×10^{14} cm^{-2}, and (c) samples implanted with BF_2^+ at 50 keV to a dose of 5×10^{14} cm^{-2}.

an energy ranging from 25 to 50 keV to a dose of 5×10^{13} to 5×10^{15} cm^{-2}. After the ion implantation, the capping oxide was removed by reactive ion etching (RIE). The wafers were cut into pieces with a sample size of 1.5×1.5 cm^2 each for oxidation study. The samples were baked on a hot plate in open air at a temperature ranging from 150 to 300°C for 30 min.

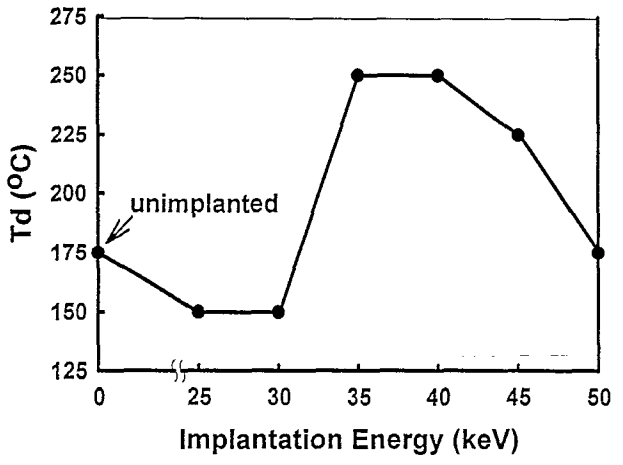

Fig. 2. Degradation temperature (T_d) of Cu films versus BF_2^+ implantation energy; the implanted dose is 5×10^{14} cm^{-2}.

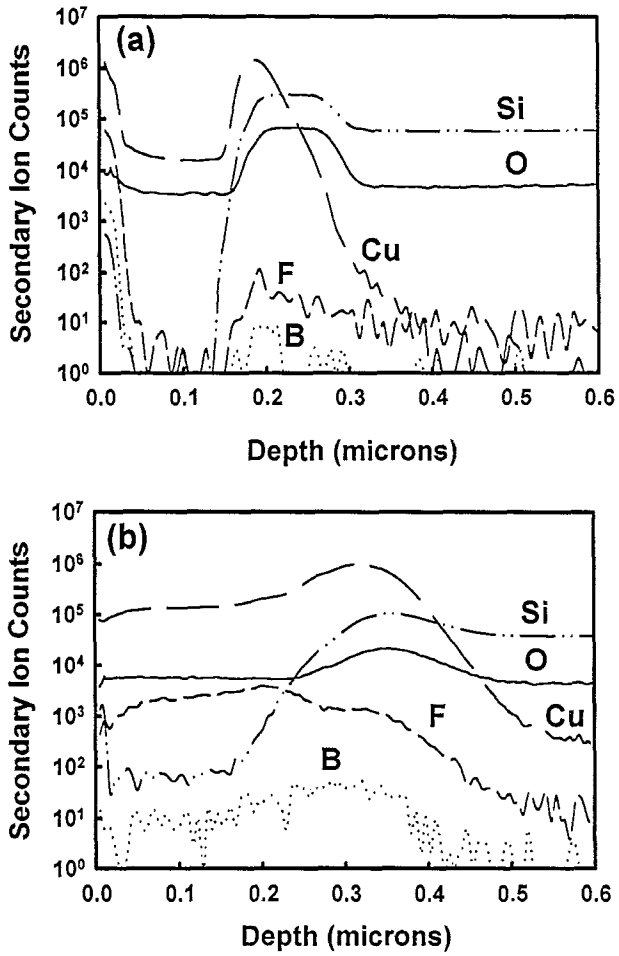

Fig. 3. SIMS depth profiles for Cu/SiO_2/Si samples implanted with BF_2^+ ions to a dose of 5×10^{14} cm^{-2} at an energy of 35 keV (a) before and (b) after thermal treatment in air at 250°C.

The oxidation behavior of the ion implanted Cu films was characterized by various techniques and measurements. The sheet resistance (R_s) of the samples was measured by a four point probe. The crystallinity of films was studied using X-ray diffraction (XRD) analysis. Surface morphology was observed using scanning electron microscope (SEM). 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 discussion

Fig. 1 shows the typical examples of XRD spectra for the as-deposited and thermally treated Cu films of 2000 Å thickness with and without BF_2^+ ion implantation. The distinct Cu(111) diffraction peak indicates that the film is highly [111]-oriented, a characteristic of the copper films. The diffraction peak of cuprous oxide Cu_2O started to appear after the samples were thermally treated at a certain temperature, which is designated as the degradation temperature (T_d)

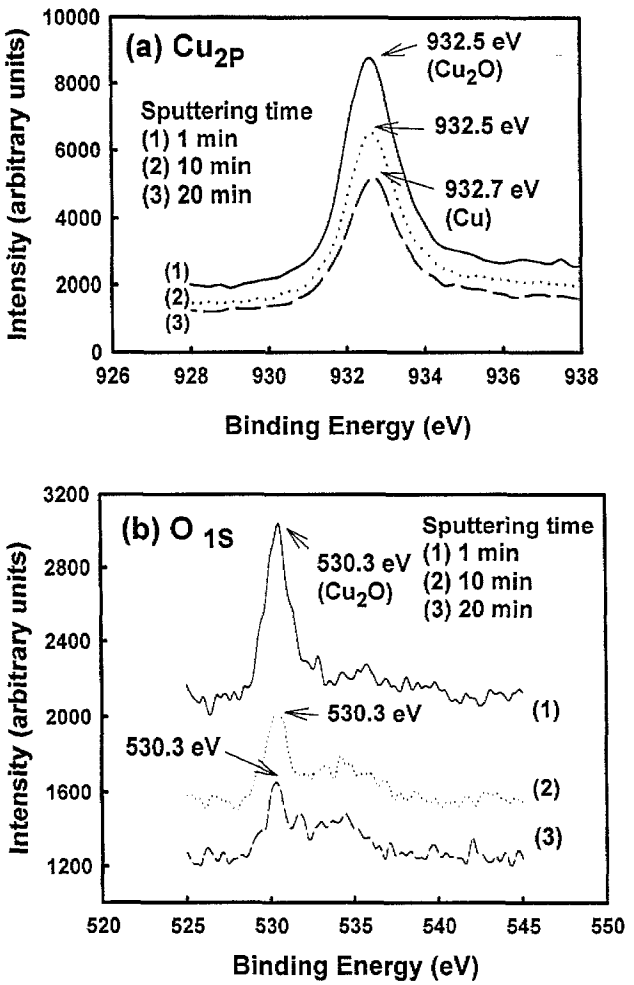

Fig. 4. XPS spectra showing the chemical states of (a) Cu_{2P} and (b) O_{1S} photoelectrons for $Cu/SiO_2/Si$ samples implanted with BF_2^+ ions at 35 keV to a dose of 5×10^{14} cm^{-2} and thermally treated in air at 250°C.

hereafter. The degradation temperatures (T_d) were found to be 175°C for the unimplanted as-deposited Cu films, 250°C for Cu films implanted with BF_2^+ at 35 keV to a dose of 5×10^{14} cm^{-2}, and 175°C for Cu films implanted with BF_2^+ at 50 keV to the same dose. It is worth noting that the sheet resistance of $Cu/SiO_2/Si$ samples made a drastic increase when the samples were thermally treated at their respective degradation temperatures (T_d). Fig. 2 shows the degradation temperatures (T_d) for Cu films implanted with BF_2^+ ions to a dose of 5×10^{14} cm^{-2} at various energies. We found that the implantation at energies of 35 and 40 keV was the most effective in retarding the oxidation of Cu film. Fig. 3 shows the SIMS depth profiles for $Cu/SiO_2/Si$ samples implanted with BF_2^+ ions to a dose of 5×10^{14} cm^{-2} at an energy of 35 keV. The implanted boron atoms were located basically at the Cu surface in a very shallow region (Fig. 3a); this boron-rich layer is expected to retard the penetration of oxygen, and thus improve the oxidation resistance of Cu films [7–9,11]. Implantation at higher energies would result in greater depth of maximum boron concentration, and less oxidation resistance would be anticipated because of a lower concentration of implanted boron atoms near the surface. This presumption was confirmed in view of the dose dependence to be reported later. Moreover, higher implantation energies generally lead to increased implantation defects [6]. These defects might serve as diffusion paths for the diffusion of oxidizing species. For the BF_2^+ implanted $Cu/SiO_2/Si$ samples thermally treated in air at 250°C, the boron distribution profile had a dramatic change (Fig. 3b); the as-implanted maximum boron concentration near the Cu surface disappeared, and the boron atoms were distributed throughout the Cu film resulting in rapid oxidation at this temperature. Similar phenomena were observed for the samples implanted at other energies. Fig. 4 shows the XPS spectra of Cu_{2P} and O_{1S} photoelectrons for the BF_2^+ implanted and 250°C thermally treated $Cu/SiO_2/Si$ sample. The spectra clearly show that a cuprous oxide (Cu_2O) layer was formed on the Cu film, and the intensity of the Cu_2O peak decreased gradually with Ar-sputtering time. From the experimental data, it was observed that the peak of pure copper at 932.7 eV evolved after further Ar sputtering, and no reactive fluorine compounds were detected. Fig. 5 shows the surface morphology for the as-deposited and thermally treated Cu films with and without BF_2^+ ion implantation. The as-deposited Cu films had smooth surfaces and dense structures which is a characteristic of sputtered Cu films (Fig. 5a), while implantation induced surface defects are clearly observed on the BF_2^+ implanted samples (Fig. 5b). Diffusion via these surface defects might play an important role in the oxidation behavior of Cu films. After thermal treatment of the as-deposited Cu films and the BF_2^+ implanted Cu films at their respective degradation temperature, which is 175°C for the former and 250°C for the latter, cuprous oxide (Cu_2O) was present on the surfaces of unimplanted samples (Fig. 5c) as well as BF_2^+ implanted samples (Fig. 5d), as confirmed by the XPS analysis (Fig. 4). The Cu_2O oxide was discontinuous as well as porous in nature [12], thus allowing diffusion to proceed through the pores. Moreover, thermal treatment at higher temperatures resulted in easier grain growth and thus larger grain size, as can be seen by comparing Fig. 5c with Fig. 5d.

Fig. 6 shows the degradation temperatures (T_d) for Cu films implanted with BF_2^+ ions at 35 keV to various doses. We found that the optimum dose was in the order of 10^{14} cm^{-2} for the purpose of oxidation resistance. For the samples with implanted dose of 5×10^{15} cm^{-2}, T_d was lowered to 175°C. The results of TEM analysis (not shown) indicated that the high dose (5×10^{15} cm^{-2} at 35 keV) implanted samples remained in a polycrystalline structure, similar to the medium dose (of the order of 10^{14} cm^{-2}) implanted samples. However, high dosage implantation is expected to result in higher damage density near the surface of implanted samples [13,14]. These high density defects could enhance diffusion of oxygen into Cu films, thus promoting the formation of copper oxide. Hence, implantation dose greater than 5×10^{15} cm^{-2} would deteriorate the capability of oxidation resistance relating to the damage density instead of the post-implant microstructure.

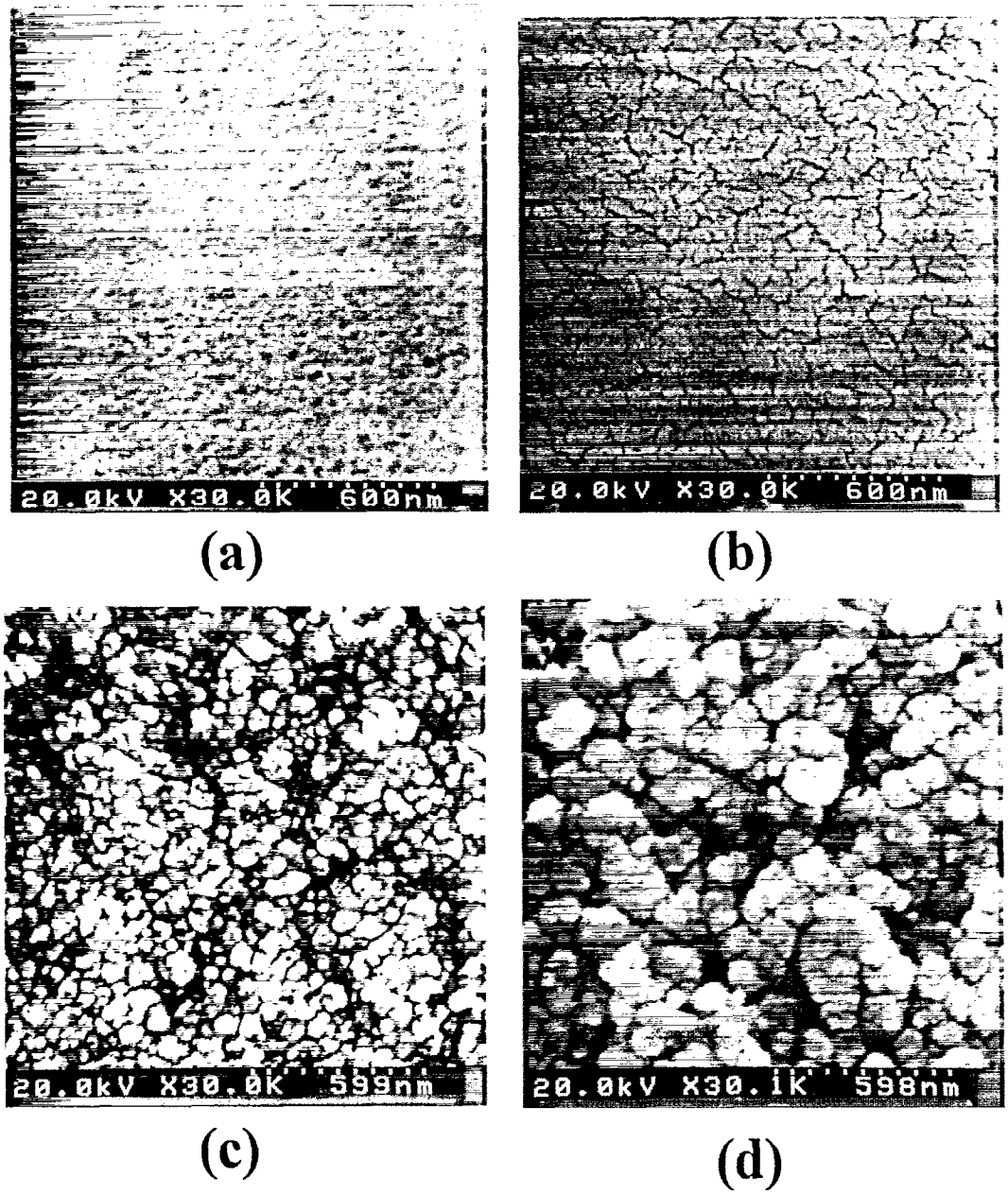

Fig. 5. SEM micrographs showing surface morphology for Cu films (a) as-deposited, (b) implanted with BF_2^+ at 35 keV to a dose of 5×10^{14} cm^{-2}; (c) sample of (a) after thermal treatment at 175°C, and (d) sample of (b) after thermal treatment at 250°C.

Moreover, high dose BF_2^+ implantation (5×10^{15} cm^{-2}) resulted in high concentration of fluorine as well as boron near the Cu surface, as shown in SIMS depth profiles illustrated in Fig. 7. It has been reported that high concentration of boron near the surface region would block the diffusion path for oxidizing species including Cu^+ ions [7–9,11]; however, enhanced oxidation might also occur as a result of the formation of reactive fluorine compounds [10]. The XPS spectra shown in Fig. 8 indicates the formation of cupric fluoride (CuF_2) phase [15] near the Cu surfaces for Cu films implanted with BF_2^+ ions to a dose of 5×10^{15} cm^{-2}; the fluorine compound was not detected in Cu films implanted with BF_2^+ ions to a dose less than 1×10^{15} cm^{-2}. The formation of CuF_2 compound was presumably associated with agglomeration of implanted fluorine ions above a certain dose [16]. This might have an adverse impact on degrading the capability of oxidation resistance for Cu films. The competing effect between boron and fluorine in the high dosage BF_2^+ implanted samples (5×10^{15} cm^{-2}) resulted in lowered degradation temperature. For the sample structure employed in this work, the BF_2^+ implantation at an energy of 35 keV must be limited to a dose no more than 1×10^{15} cm^{-2}.

4. Conclusions

Copper films are readily oxidized into Cu_2O at tempera-

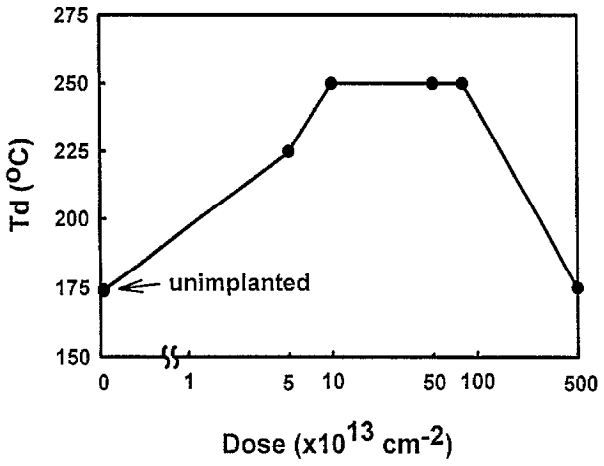

Fig. 6. Degradation temperature (T_d) of Cu films versus implanted dose of BF_2^+ ions; the implantation energy is 35 keV.

tures below 175°C in air. With appropriate BF_2^+ implantation into Cu films, the oxidation resistance of Cu films can be improved. The optimum condition of BF_2^+ implantation is to place boron atoms of proper concentration near the Cu surface so as to block the diffusion path for oxidizing species, i.e. oxygen and Cu atoms. Implantation at too high energy would result in greater depth of projection, thus a lower concentration of boron at the Cu surface, and generally lead to increased implantation defects that might serve as diffusion paths for the oxidizing species. On the other hand, too high dosage implantation would also have an adverse effect on the capability of oxidation resistance for Cu films due to the higher density of implantation damage as well as the formation of reactive fluorine compound (CuF_2) near the Cu surface. We found that the best results can be obtained by BF_2^+ implantation at 35 to 40 keV to a dose of $(1–8) \times 10^{14}$ cm^{-2}. With BF_2^+ implantation at these conditions, Cu films were able to resist oxidation at temperatures up to 250°C.

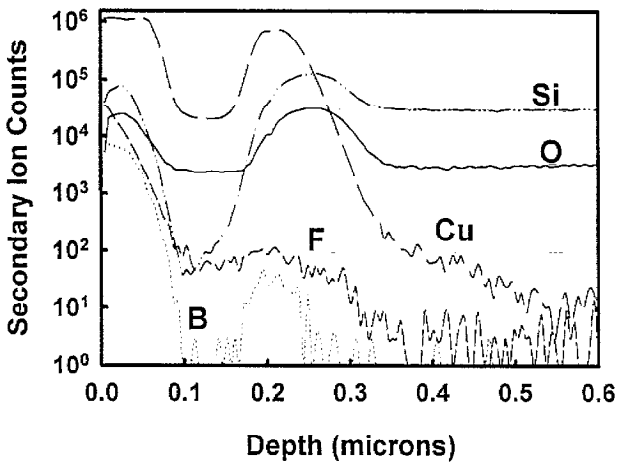

Fig. 7. SIMS depth profiles for $Cu/SiO_2/Si$ samples implanted with BF_2^+ ions to a dose of 5×10^{15} cm^{-2} at an energy of 35 keV followed by thermal treatment at 175°C.

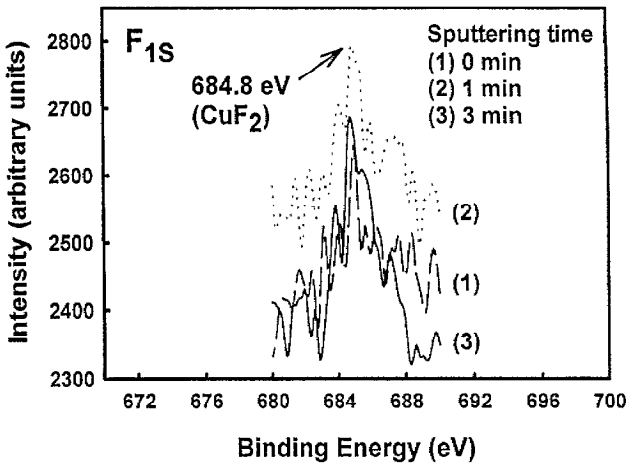

Fig. 8. XPS spectra showing the chemical state of F_{1S} photoelectrons for $Cu/SiO_2/Si$ samples implanted with BF_2^+ ions at 35 keV to a dose of 5×10^{15} cm^{-2} followed by thermal treatment in air at 175°C.

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