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Mechanism of adhesion improvement in ion-beam mixed Cu/SiO_2

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A thin copper layer (35 nm) deposited on SiO_2 has been subjected to ion-beam mixing with 80 keV Ar^+ at room temperature, 550 and 650 K. Interfacial properties of irradiated samples were investigated using Rutherford backscattering spectroscopy, grazing-angle X-ray diffraction, X-ray photo-electron spectroscopy and scratch testing. The adhesion of the copper film was improved by a factor of three at a dose of 1.5×10^{16} Ar^+ cm^{-2} by the ion-beam mixing at room temperature, while the high-temperature ion-beam mixing enhanced the adhesion by a factor of five. Ballistic mixing plays a role in the improvement of adhesion for the room-temperature ion mixing, and the creation of Cu_2O phase induced by ion-beam mixing contributes to the enhancement of adhesion at high temperature.

1. Introduction

Adhesion enhancement in metal/ceramic combinations is very important in practical applications such as micro-electronics. Many techniques are employed to enhance the adhesion between metals and ceramics. In most of these, adhesion enhancement can be achieved by the creation of an intermediate layer induced by solid-state reaction. However, this solid-state reaction cannot be applied to non-reactive combinations, because it is strongly dependent on thermodynamic factors such as the heat of reaction [1].

Recently, ion-beam mixing [2] has proved to be an effective technique to improve adhesion in metal/ceramic combination at relatively low temperature. This technique can be used to alter many factors critical to the adhesion, such as interfacial roughness, structural barriers, or interfacial stress without modifying the bulk substrate properties, and it can lead to a strong bonding in non-thermodynamic equilibrium conditions. Thus this technique has been used to improve the adhesion significantly even in non-reactive immiscible metal/ceramic systems [3].

The Cu/SiO_2 system is known to be a typical non-reactive combination because this system has a relatively high positive heat of reaction more than $+20$ kcal g at^{-1} [1]. Thus, in this system, the interfacial reactions may not occur during thermal processing and the copper may coalesce to form an island structure [4], which leads to the weak adhesion. In this case, the ion-beam mixing may be the most appropriate technique to improve the adhesion.

We employed the ion-beam mixing technique to enhance the adhesion in a Cu/SiO_2 system. Combined Rutherford backscattering spectroscopy (RBS), grazing-angle X-ray diffraction (GXRD), X-ray photoelectron spectroscopy (XPS) and scratch test results are reported to describe the mixing phenomena, the formation of the intermediate layer, and the origin of adhesion enhancement, in an ion-beam mixed Cu/SiO_2 system.

2. Experimental procedure

The commercially available fused quartz (SiO_2) substrates were first lightly etched in dilute HF and thoroughly rinsed in deionized water before electron-bean evaporation of copper in an oil-free vacuum of 2×10^{-7} torr. The thickness of the copper layer was chosen to match the mean projected range of 80 keV Ar^+ in the copper layer (35 nm). Ion-beam mixing was carried out at room temperature, 550 and 650 K. The ion dose ranged from 1×10^{15}–2×10^{16} Ar^+ cm^{-2} at a typical ion flux of 1.5 $\mu A\ cm^{-2}$. The working pressure in the target chamber during ion-beam mixing was 2×10^{-6} torr. The amounts of intermixing induced by ion mixing were evaluated using RBS. For RBS observation, the target was tilted to an angle of 60° from the incident direction of 2.4 MeV He^+, and the energy of the backscattered He^+ was analysed at a laboratory scattering angle of 170° with a detector of 14 keV energy resolution.

The adhesion of the copper films was measured using a standard scratch test [5]. A scratch tester equipped with a 120° Rockwell C diamond indentor with a tip radius of 200 μm was used, equipped with an acoustic emission detector. The critical load was measured from the acoustic signal resulting from the coating fracture event which was confirmed by the optical microscope observation. The scratching rate and load rate were 10 mm min^{-1} and 10 N mm^{-1}, respectively.

The formation of an intermediate layer at the interface was investigated with GXRD and XPS. GXRD

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analyses were performed with incident angles ranging from 0.1°–0.4° to obtain structural information in the ion-mixed layer. The XPS data were obtained with MgK_α radiation and depth profiles were obtained by rastering a 5 keV Ar^+ beam over a 5 mm diameter surface. We have taken the XPS core level lines of Cu $2p_{3/2}$ (932.4 eV), and Cu $L_3M_{4,5}M_{4,5}$ AES line (334.5 eV) to obtain chemical information in the mixed layer. The pass energy of the hemispherical analyser was 17.5 eV for the high-resolution studies of the core level, and 44.75 eV for the low-resolution survey analysis.

3. Results and discussion

Fig. 1 shows typical RBS spectra for an as-deposited specimen and for those mixed with a dose of 1.5×10^{16} Ar^+ cm^{-2} at room temperature (RT) and 650 K. The signals for various elements are indicated by arrows in the figure. In the case of ion-beam mixing at RT, the RBS spectrum of the mixed sample does not reveal significant modification of the atomic concentration profiles at the interface, compared with that for the as-deposited sample, except for the reduced area of the copper signal due to sputtering during ion irradiation. The interface remains more or less abrupt before and after ion mixing at RT. While the ion mixing at 650 K produces a broadening of the RBS signal for both copper and silicon signals, it reveals a fine step on the oxygen signal corresponding to the formation of a uniform intermediate layer having an atomic composition of Cu_2O, which is determined by using the RUMP program [6].

Quantitative analysis of the intermixing was performed using the RUMP program. The RBS spectra were analysed assuming a complementary error function distribution, $\mathrm{erfc}(x/\sigma 2^{1/2})$, for the inter-diffusion profiles. The variance (σ^2) was adjusted to fit the low-energy edge of the copper signal. The mixing variance is described [7] by $\Delta\sigma^2 = \sigma^2(\phi) - \sigma^2(0)$, where $\sigma^2(\phi)$ and $\sigma(0)$ are the measured variances at the dose ϕ and before mixing, respectively. The experimental mixing variances at RT for various ion doses are shown in Fig. 2. Below the ion dose of 5×10^{15} Ar^+ cm^2, the value of $\Delta\sigma^2$ is negligible, and above this ion dose, the mixing variance increases with increasing ion dose. The mixing efficiency, η, is usually defined [7] as twice the slope of $d(\Delta\sigma^2)/d\phi$. From Fig. 2 and using the above relation, the mixing efficiency is found to be 0.21 nm^4.

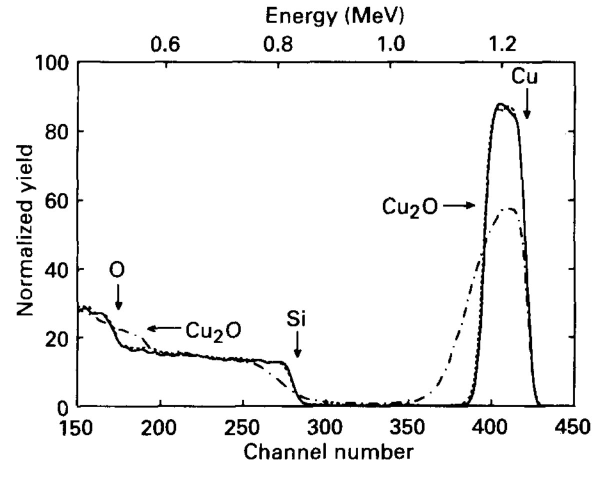

Figure 1 The RBS spectra for (——) the as-deposited sample, and ion-beam mixed samples with a dose of 1.5×10^{16} ions cm^{-2} at (– – –) room temperature and (—·—) 650 K. The incident energy of Ar^+ was 80 keV.

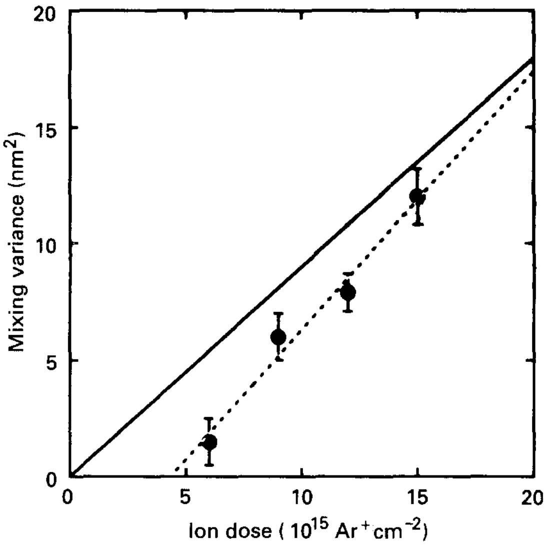

Figure 2 (——) Dynamic Monte-Carlo simulation results and (· · ·) experimental results for the mixing variances in the sample mixed with 80 keV Ar^+ at room temperature.

The ion-induced mixing process is commonly divided into three phases according to the time evolution occurring in a given system [8], that is, cascade phase, thermal spike phase, and radiation-enhanced diffusion (RED) phase. A dynamic Monte-Carlo simulation program [9] for the cascade mixing process is used in this study to elucidate the interfacial mixing process in the Cu/SiO_2 system at RT. The simulation result is also shown in Fig. 2. The simulated value of η is found to be 0.18 nm^4, which is in fairly good agreement with the experimental result. Thus the interfacial mixing in Cu/SiO_2 at RT might be induced by the cascade mixing.

In the case of the specimens mixed at 650 K, the intermixed layer shows a gradual change in the concentration profile even at a low dose of 3×10^{15} Ar^+ cm^{-2}. Above a dose of 5×10^{15} Ar^+ cm^{-2}, a fine step is seen on the oxygen signal, indicating the formation of a uniform layer of Cu_2O phase. When this fine step (plateau in the oxygen signal) appears, the low-energy edge of the copper signal does not fit $\mathrm{erfc}(x/\sigma 2^{1/2})$ well. Thus we estimated the approximate value of η for the sample mixed at 650 K with an ion dose of 1.5×10^{16} Ar^+ cm^{-2}. The value of η was found to be 8.87 nm^4, which is larger than that of the sample mixed at RT by a factor of 40. This value is too large to be explained by the cascade process, and the thermal spike process is available only for those systems which have negative heat of reaction. Thus this mechanism cannot be adapted for the Cu/SiO_2 system because of its high positive heat of reaction. The cascade and the thermal spike process occur [8] at a low temperature below RT, while the RED process is attributable to the relatively high-temperature ion-beam mixing. Moreover, the mixing efficiency for the RED process is generally larger [8] than that for the cascade process by an order of magnitude. Therefore, we suggest that the interfacial mixing in the Cu/SiO_2 system caused by ion-beam mixing at 650 K would be due to the RED process.

Ion-beam mixing can lead to an increase in the microscopic roughness in the interface region, intermixing of the interface species, disorder and mobilization of the atoms near the interface, and to the creation of an intermediate layer which can result in the enhancement of adhesion. The adhesion of ion-beam mixed Cu/SiO_2 specimens was evaluated using a scratch test in this study. The minimum force (critical force) required to remove the copper films from the quartz substrates was used as a measure of adhesion. Film removal was verified using an acoustic emission signal and optical microscope observation. The results of the scratch test are shown in Fig. 3. The adhesion for the sample mixed at RT (sample A) does not improve below an ion dose of 5×10^{15} Ar^+ cm^{-2}. Above an ion dose of 9×10^{15} Ar^+ cm^{-2}, the critical force increases significantly. At a dose of 1.5×10^{16} Ar^+ cm^{-2}, the critical force is larger than that for the as-deposited sample by a factor of three. For the sample mixed at 650 K (sample B), the critical force increases by a factor of two, even at a low dose of 3×10^{15} Ar^+ cm^{-2}, and then increases significantly up to the dose of 9×10^{15} Ar^+ cm^{-2}, and follows a saturated value, which is larger than that for the as-deposited sample by a factor of five. The thermally annealed sample at 650 K without ion-beam mixing, reveals very poor adhesion, that is, the critical force for this sample was less than 1 N, which is the minimum force that can be applied in our scratch tester.

The trend of the adhesion improvement for sample A is very similar to that of the mixing variance, as shown in Fig. 2. Thus we suggest that the disordered region of a few monolayers induced by the cascade mixing or the microscopic interfacial roughness induced by ion-beam mixing would result in the enhancement of adhesion during the RT ion-beam mixing. However, the enhancement of adhesion for sample B cannot be explained by the ballistic (cascade) mixing effect, because the thickness of the mixed layer in sample B is too thick. The thickness of the mixed layer of sample B ($x \approx 2^{1/2}\ \Delta\sigma$) was found to be ~ 13 nm at a dose of 1.5×10^{15} Ar^+ cm^{-2}, which is larger by a factor of four to five than the typical range for the cascade process (2–3 nm) at the same ion dose [10]. Moreover, the RBS spectrum from the sample mixed with 1.5×10^{16} Ar^+ cm^{-2} at 650 K (Fig. 1) shows a fine step in the oxygen signal, indicating the formation of a Cu_2O layer. Thus we suggest that the intermediate layer created by ion-beam mixing at 650 K would enhance the adhesion in sample B.

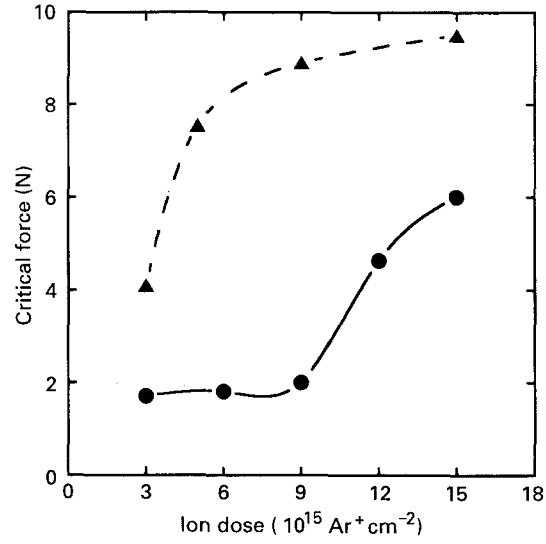

Figure 3 Critical load as a function of Ar^+ dose for the samples mixed at (——) room temperature and (– – –) 650 K.

XPS is preferred as a powerful diagnostic technique to yield information on the chemical characteristics at the surface and the interface. Thus we used XPS as a tool to investigate stable-phase formation at the surface and the interface during ion-beam mixing. The most stable oxides in the Cu–O system are CuO and Cu_2O phase [11]. The Cu $2p_{3/2}$ XPS core level of the CuO phase is known [12] to have two satellites associated with the $2p_{3/2}$ line; one is 8 eV and the other is 10 eV away from the primary line, which is a clearly different shape to that of the pure metallic copper. However, there are no chemical shifts and core line width changes of the copper core level lines ($2p_{3/2}$, $2p_{1/2}$ and $3s_{1/2}$) in Cu_2O phase, compared to those of pure copper. Gaarenstroom and Winograd [13] have shown that the distinction between CuO, Cu_2O and pure metallic copper is only possible by observing the Cu $L_3M_{4,5}M_{4,5}$ Auger peak shifts. Thus we observed the Cu LMM AES spectra to investigate the phase induced by ion-beam mixing at 650 K.

Fig. 4 shows the Cu LMM AES spectra for the sample mixed with an ion dose of 1.5×10^{16} Ar^+ cm^{-2} at 650 K by sputter etching the ion-mixed copper layer. The sputtering rate was around 0.2 nm min^{-1}. The appropriate peak positions [13] corresponding to the pure copper, CuO and Cu_2O phases are indicated in Fig. 4. The mutual concentration ratios for the CuO, copper and Cu_2O phases at various sputter etching times were determined using the measured Cu LMM AES peak areas after Gaussian curve fitting. The results are shown in Table I. The surface of the copper layer mixed with an ion beam at 650 K has already formed CuO phase, even though the thickness

TABLE I The mutual concentration ratios of copper, CuO and Cu_2O at various sputter etching times

Sputter time[a]	Concentration ratio (%)		
(min)	CuO	Cu	Cu_2O
0	100	0	0
20	7.4	88.5	4.1
60	0	82.8	17.2
120	0	14.7	85.3
150	0	< 5	> 95

[a] The sputtering rate is about 0.2 nm min^{-1}.

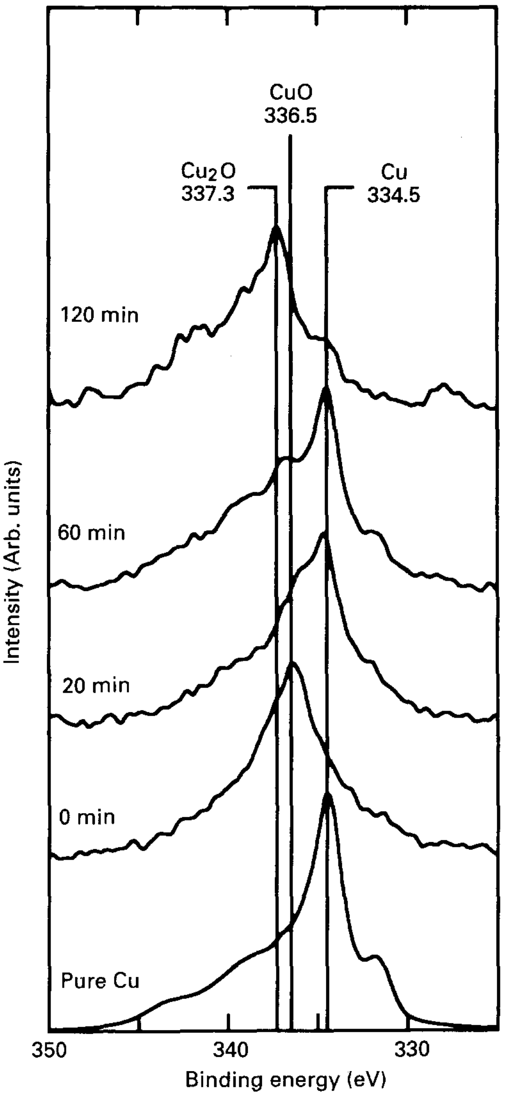

Figure 4 Cu $L_3M_{4,5}M_{4,5}$ Auger depth profile spectra from a Cu/SiO_2 sample mixed with an ion dose of 1.5×10^{16} ions cm^{-2} at 650 K. The sputter etching time is indicated in the figure.

of the CuO layer is around 2–4 nm. This result is as expected, because the CuO phase can be easily formed [12] by heating the pure copper at 523 K in an oxygen atmosphere. The very thin layer of CuO might be formed at 650 K due to residual oxygen gas in the target chamber during ion-beam mixing, even at a pressure of 10^{-7} torr. After sputter etching for 20 min, the copper layer is revealed to be a mixed state with pure metallic copper (88.5%), CuO (7.4%), and Cu_2O (4.1%) phase, and after 60 min sputter etching, the intensity of the peak corresponding to the CuO phase disappears, and a shoulder corresponding to Cu_2O (17.2%) phase appears. The dominant composition is pure copper (82.8%) in this region. After sputter etching for 120 min, which is near the Cu/SiO_2 interface region, the Cu *LMM* AES spectra clearly show the peak indicating Cu_2O phase (85.3%) formation along with a weak shoulder corresponding to pure copper (14.7%). On increasing the sputter etching time to longer than 120 min, the peak due to the Cu_2O phase increases, while the peak arising from the pure copper becomes progressively negligible (not shown in Fig. 4). In sample A, CuO and Cu_2O phases can hardly be seen, and in a sample annealed at 650 K in vacuum without ion-beam mixing, only a very thin layer of CuO is evident. Thus the results in Fig. 4 indicate that the stable Cu_2O phase is formed in the interface region by ion-beam mixing at 650 K.

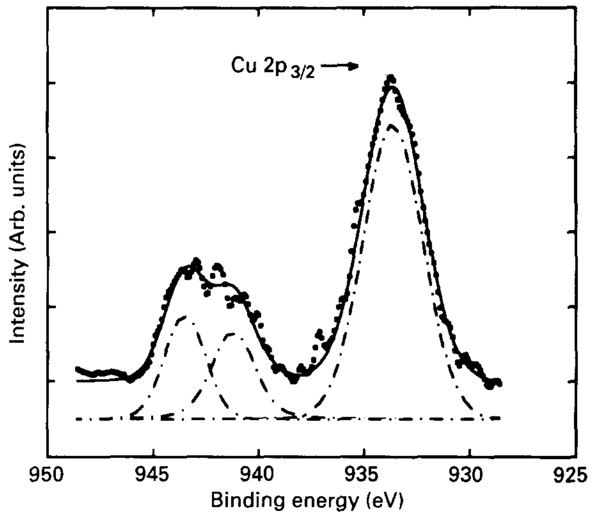

Figure 5 The Cu $2p_{3/2}$ XPS spectrum obtained at surface of the sample mixed with a dose of 1.5×10^{16} ions cm^{-2} at 650 K.

The Cu $2p_{3/2}$ XPS core level is known [12] to have a different shape from that of the pure metallic copper. Fig. 5 shows the Cu $2p_{3/2}$ XPS spectrum obtained from the surface (without sputtering) of the sample mixed with 1.5×10^{16} Ar^+ cm^{-2} at 650 K. It shows two satellites associated with the main Cu $2p_{3/2}$ line; one is 8.2 eV and the other is 10.2 eV away from the main line, which indicate [12] clearly the formation of the CuO phase at the surface. After sputter etching for more than 20 min, the satellites disappeared, and chemical shifts or shape changes in the main Cu $2p_{3/2}$ XPS spectrum could be found except for a small change in core line width (FWHM).

We performed GXRD observations to reconfirm the creation of a stable compound intermediate layer of Cu_2O. Fig. 6 shows the GXRD results for sample B mixed with an ion dose of 1.5×10^{16} Ar^+ cm^{-2} along with the as-deposited sample for comparison. In the as-deposited sample, only peaks corresponding to the metallic copper appear, while the mixed sample shows a peak corresponding to the Cu_2O phase, which is consistent with the above XPS results. The samples mixed at RT reveal almost the same results as the as-deposited sample, except for the broadening of the Cu(1 1 1) peak, and samples mixed at 550 K or those mixed with 1×10^{16} Ar^+ cm^{-2} at 650 K, also show the formation of Cu_2O phase, but the FWHM of the Cu_2O(1 1 1) peak is broader than that for the sample mixed with 1.5×10^{16} Ar^+ cm^{-2} at 650 K.

We suggest that the ion-beam mixing at high temperature causes breaking of the atomic bonding in a given system, and mobilizes the atoms near the interface to form a complex chemical bonding structure linking film and substrate. In the case of the Cu/Al_2O_3 system [14], a thermally stable ternary Cu–Al–O structure is formed by ion-beam mixing. However, no such complex exists for Cu–Si–O, thus, the Cu_2O phase might be created by ion-beam mixing at high temperature. The CuO and Cu_2O phases are the most

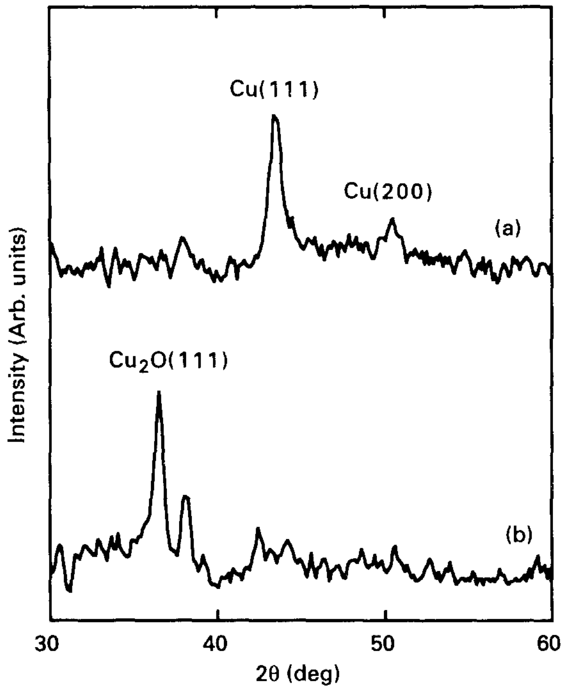

Figure 6 GXRD results for (a), the as-deposited sample and (b) 80 keV Ar^+ irradiated sample with a dose of 1.5×10^{16} ions cm^{-2} at 650 K.

thermally stable phases in the Cu–O system. The heat of formation for the CuO and Cu_2O phases are -24.0 and -29.9 kcal mol^{-1} at 600 K [15], respectively. These phases would compete to form thermodynamically during thermal annealing, because they have similar values of heat of formation.

The phases induced by ion-beam mixing are different from those formed by the conventional thermal annealing. The stable phase formation by ion-beam mixing is very sensitive to the crystalline structure of the phase [16], that is, a relatively simple structure is insensitive to the ion bombardment, and the phases with a complicated structure transform to phases having a simple structure or to the amorphous phase during ion bombardment. The crystalline structure [17] of CuO is monoclinic having eight atoms in a unit cell (mC8), and that of Cu_2O is cubic primitive, having six atoms in a unit cell (cP6). Thus the Cu_2O phase with a relatively simple structure might survive under subsequent ion bombardment, and might be more favourable than the CuO phase to creation by the ion-beam mixing. The formation of an intermediate layer of the stable Cu_2O phase would result in the enhancement of adhesion in Cu/SiO_2 mixed with an ion beam at high temperature.

4. Conclusion

The ballistic mixing phenomenon results in the improvement of adhesion in the Cu/SiO_2 system during ion mixing at RT, and the formation of Cu_2O phase, which is thermodynamically stable and insensitive to the ion bombardment, contributes to the enhancement of adhesion induced by ion-beam mixing at high temperature.

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