Vacancy Trapping by Solute Atoms during Quenching in Cu-Based Dilute Alloys Studied by Positron Annihilation Spectroscopy

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Abstract. Frozen-in vacancies and the recovery have been investigated in some Cu-based dilute alloys by using positron annihilation lifetime spectroscopy. Cu-0.5at%Sb, Cu-0.5at%Sn and Cu-0.5at%In dilute bulk alloys were quenched to ice water from 1223 K. A pure-Cu specimen was also quenched from the same temperature. As a result, no frozen-in vacancies have been detected in as-quenched pure-Cu specimen. On the other hand, as-quenched Cu-0.5at%Sb alloy contained frozen-in thermal equilibrium vacancies with concentration of $3 \times 10^5$. Furthermore, these frozen-in vacancies in Cu-0.5at%Sb alloy were stable until 473 K, and began to migrate at 523 K. Finally, the Cu-Sb alloy were recovered to the fully annealed state at 823 K. This thermal stability clearly implies some interaction exists between a vacancy and Sb atom and due to the interaction, thermal equilibrium vacancies are trapped by Sb atoms during quenching.

1. Introduction
Currently, large-scale integration (LSI) Cu interconnects are fabricated by using electroplating techniques. However, accelerated reduction of feature size in Si devices makes it difficult to fill trenches or via holes with copper by using the present techniques. Therefore, a new process has been proposed for fabricating Cu interconnects; filling trenches or via holes with physical vapor deposited copper (PVD-Cu) using high-pressure annealing treatment [1]. What is more, it has already been recognized that the addition of Sb to the PVD-Cu film improves the reflowability.

In the proposed high-pressure reflow process, atomic diffusion is an important factor, and the atomic diffusion rate is proportional to the vacancy concentration. Therefore, it is expected that vacancies are concerned in the improvement of the reflowability. Thus, in this study, we investigated vacancy behaviors in the quenched bulk Cu-Sb dilute alloy and other Cu-based dilute alloys compared with a quenched bulk pure-Cu specimen by using positron annihilation lifetime spectroscopy.
2. Experimental

Cu-0.5at%Sb, Cu-0.5at%Sn and Cu-0.5at%In dilute bulk alloys were prepared by melting 4N Cu and 5N Sb (4N Sn, 6N In) in sealed quartz tubes under an argon atmosphere in a furnace at 1373 K and cooled to room temperature. After cooling, these ingots sealed in quartz tubes were heated at 1223 K for 24 h to homogenize the solute distribution. From these ingots, two sheet-like specimens with thickness of about 1 mm were cut out in each alloy. Then, each two sheets of specimen were encapsulated in argon atmosphere quartz tubes again and were annealed at 1073 K for 2 h after that each alloy was maintained at 1223 K for 2h and quenched to ice water. Two sheets of pure-Cu (4N) specimen were also water-quenched from the same temperature.

The positron annihilation lifetime was measured for each as-quenched specimen at room temperature. A polyimide film sealed positron source (~1 MBq 22NaCl) was sandwiched by two sheets of specimen and positron annihilation lifetime spectra were acquired using a fast-fast coincidence positron annihilation lifetime spectrometer. Furthermore, to observe the annealing behavior of frozen-in vacancies, isochronal annealing in steps of 15 min/50 K was performed. Positron annihilation lifetime spectra were acquired for each annealing temperature and all of the measurements were carried out at room temperature. The time resolution of full width at half maximum (FWHM) was 192 ps, and approximately $1 \times 10^6$ total counts were accumulated for each lifetime spectrum.

3. Results

Mean positron lifetimes for all specimens before quenching were in a range of 108-111 ps, which are not corresponding to positrons trapped at vacancy-type defects but to positrons delocalized and annihilated in interstitial sites [2-6]. Figure 1 shows the change in mean positron lifetime $\tau_M$ for quenched Cu alloys before and during isochronal annealing, the result of as-quenched pure-Cu specimen is also shown. The as-quenched alloys measurement results show that the addition of Sb led to increase the mean positron lifetime. Cu-Sb alloy indicates the highest value of 154 ps and then the value of Cu-Sn alloy is 135 ps. The lifetime of as-quenched Cu-In alloy 112 ps is slightly above the value of Cu perfect crystal 110 ps. Furthermore, mean positron lifetimes of these Cu-Sb, Cu-Sn and Cu-In alloys were fully recovered at 823 K, 573 K and 423 K, respectively. On the other hand, no vacancies were detected in as-quenched pure-Cu specimen with a mean positron lifetime of 110 ps.

To clarify the recovery process, the positron annihilation lifetime spectra of Cu-Sb and Cu-Sn alloys were decomposed into two components. The longer positron lifetime $\tau_D$ and the relative intensity $I_D$ of the longer lifetime component are shown in Fig. 2. The dotted horizontal line in the figure shows the calculated positron lifetime which corresponding to positrons trapped at mono-vacancies in a copper crystal. In the case of Cu-Sb alloy, the longer positron lifetime $\tau_D$ was stable around 156 ps below 473 K and the relative intensity $I_D$ was also maintained around 90%. Above 523 K, $\tau_D$ began to increase and $I_D$ began to decrease drastically. Further, in the case of Cu-Sn alloy, $\tau_D$ was stable around 151 ps below 373 K and the relative intensity

![Figure 1. The change in mean positron lifetime $\tau_M$ for quenched Cu alloys before and during isochronal annealing. The result of as-quenched pure-Cu specimen is also shown.](image-url)
was maintained around 74%, and besides, $\tau_D$ began to increase and $I_D$ began to decrease above 423 K. In the matter of the Cu-In alloy, we could not resolve a longer positron lifetime $\tau_D$ because of the intensity of the longer component was too low.

4. Discussion

In Fig. 1 the value of the $\chi^2 q$ is also shown as a measure of the fitting accuracy of the analysis; in case where the quantity of $\chi^2 q$ is significantly larger than unity, the measured spectrum is not adequately fitted by the analysis [7,8]. Below 473 K, the $\chi^2 q$ value of the Cu-Sb alloy was approximately unity and the mean positron lifetime $\tau_M$ was maintained around 154 ps. It indicates that almost all positrons were trapped at mono-vacancy sites and annihilated there. This is also supported by the resolved analysis of the positron annihilation lifetime spectra in Fig. 2. When the Cu-Sb alloy was annealed at 523 K, the $\chi^2 q$ value showed over 4 and the mean positron lifetime $\tau_M$ decreased significantly which means that the existence of the matrix component besides the defect component because of the decrease of the vacancy concentration. This is also indicated in Fig. 2. In the case of the Cu-Sb alloy, above 523 K, the longer positron lifetime $\tau_D$ increased and the intensity of the longer component $I_D$ decreased with increasing the annealing temperature, which indicates that frozen-in mono-vacancies began migrating and clustering, and ultimately annihilated at sinks. On the other hand, frozen-in mono-vacancies in the Cu-Sn alloy started clustering at 423 K. It is known that mono-vacancies in pure-Cu can migrate below room temperature [2-6,9,10]. However, the present results show that the addition of 0.5at%Sb led to increase the thermal stability of mono-vacancies in a copper crystal. These results clearly imply vacancies are strongly binding with Sb atoms. A similar phenomenon was observed in Cu-Sn and Cu-In alloys, but the vacancy mobile temperatures were lower compared to the Cu-Sb alloy. From the results, it is reasonable to suppose that the values of the interaction are high in order of Sb-V, Sn-V and In-V, and that interaction causes thermal equilibrium vacancy trapping during quenching.

Then, in order to estimate the binding energy between a solute atom and a vacancy, we calculated the energy difference between the supercell including a solute atom-V pair and that including an isolated solute atom and mono-vacancy using first-principles pseudopotential method as implemented in the Vienna ab initio simulation package (VASP) [11,12]. We employed the $2\times2\times2$ supercell containing 32 lattice sites. The calculation results of the binding energies of Sb-V, Sn-V and In-V were 0.46 eV, 0.38 eV and 0.30 eV, respectively. The present experimental results show good agreement with the calculation results. Therefore, the binding energy contributes to trapping thermal equilibrium vacancies during quenching and the difference of frozen-in vacancy concentrations in as-quenched alloys are caused by the value of the binding energy between a vacancy and a solute atom. We estimated vacancy concentrations in as-quenched alloys from the resolved analysis of the positron annihilation lifetime spectra, the value of $1 \times 10^{15}$ s$^{-1}$ was used as the specific positron trapping rate [13]. As a result, as-quenched Cu-Sb and Cu-Sn alloys contained frozen-in thermal equilibrium vacancies with the
concentration of $3 \times 10^{-5}$ and $7 \times 10^{-6}$, respectively. We consider that vacancies are also introduced during deposition in PVD-Cu alloy films fabricated for LSI interconnects by the same mechanism as mentioned above and such vacancies lead to improving the refloowability in the high-pressure annealing process.

5. Conclusions
Frozen-in vacancies in quenched Cu-0.5at%Sb, Cu-0.5at%Sn and Cu-0.5at%In alloys were investigated using positron annihilation lifetime spectroscopy. The results showed that the addition of 0.5at%Sb led to increase the frozen-in vacancy concentration in a copper crystal. In the case of Cu-0.5at%Sn or Cu-0.5at%In alloy, a similar phenomenon was observed but the frozen-in vacancy concentration was lower than that of the Cu-0.5at%Sb alloy. Furthermore, vacancy dissociation temperatures were high in order of Sb-$V$, Sn-$V$ and In-$V$ pair. These experimental results showed good agreement with the calculation results of the binding energy between a vacancy and a solute atom. In conclusion, the addition of solute atoms which have high binding energy with vacancies lead to promoting thermal equilibrium vacancy trapping during quenching and such frozen-in vacancies promote atomic diffusion. We consider a similar vacancy trapping mechanism occurred during deposition in PVD-Cu films and such frozen-in vacancies might improve the refloowability in the high-pressure annealing process.

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