Frozen-in vacancies in PVD-Cu films with improved high-pressure reflowability studied using a slow positron beam

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Abstract. Recently, a new process has been proposed for fabricating a LSI interconnection; filling trenches and via holes with Cu using high-pressure annealing treatment. It is already known that a Cu film produced by physical vapor deposition (PVD) has a lower reflowability compared to a Cu film produced by electrochemical deposition (ECD). Additionally, it has also been recognized that the addition of Sb to the PVD-Cu film improves the reflowability. However, the factors responsible for the reflowability of Cu films have not yet been studied. In this work, we evaluated a PVD pure-Cu film and a PVD Cu-0.5at%Sb film by using a slow positron beam. Addition of Sb led to the introduction of lattice defects in the as-deposited film. These defects that were observed in the PVD-CuSb dilute alloy film were identified as frozen-in vacancies that were produced during deposition.

1. Introduction

Copper is currently used extensively as large-scale integration (LSI) interconnections because of its lower electrical resistivity and high resistance to electromigration damage. Cu interconnects are fabricated by embedding Cu into trenches and via holes by electrochemical deposition (ECD) and this is known as the Dual-Damascene process. However, the accelerated reduction of the feature size in LSI devices is making it difficult to completely fill high aspect-ratio structures with Cu. The international technology roadmap for semiconductors (ITRS) 2007 requires that a Metal 1 interconnect layer with a 64 nm wiring pitch will be in manufacturable by 2013. Therefore, a post-deposition high-pressure annealing process is proposed for the fabrication of Cu interconnections. It has been recognized that a physical vapor deposition (PVD) Cu film has low reflow performance compared to an ECD Cu film [1] despite Cu reflowability being an important characteristic for this process. It has been also found that the addition of Sb to the PVD-Cu film improves its reflowability.
A positron beam may be used as a unique probe to study lattice defects, in particular vacancy-type defects. When positrons are implanted into solids, they are annihilated by electrons and emit two 511 keV $\gamma$-rays. In perfect crystals, positrons delocalize in interstitial sites and annihilate with electrons there since positrons are strongly repelled by ion cores because of a Coulomb repulsion. In vacancies, vacancy clusters or dislocations, which have a lower density of ion cores than their surroundings, positrons are trapped in the defects and annihilate with electrons in the defects. These defects are detected by a decrease in the Doppler broadening of the annihilation radiation because of the absence of core electrons which have a higher momentum distribution than valence electrons. Generally, the resultant changes in Doppler broadening spectra are characterized by the $S$ parameter which reflects the ratio change of annihilation with low momentum valence electrons. The value of $S$ for the annihilation of positrons trapped by vacancies is larger than that for positrons annihilated from the interstitial sites. Recent positron annihilation spectroscopy studies have suggested that ECD-Cu films have a larger amount of vacancy clusters than PVD-Cu films [2-4]. In this paper, we investigate lattice defects in a PVD-CuSb dilute alloy film compared to a PVD-pure-Cu film by measuring the Doppler broadening of the annihilation radiation using a slow positron beam.

2. Experimental

Samples used in our experiments consisted of Cu (1 $\mu$m)/TaN (50 nm)/Si or Cu-0.5at%Sb (1 $\mu$m)/TaN (50 nm)/Si. TaN films were deposited on Si substrates by the DC magnetron sputtering technique. After deposition a 1-$\mu$m pure-Cu film or a 1-$\mu$m Cu-0.5at%Sb dilute alloy film was sputtered onto TaN/Si at room temperature. Sputtering conditions were as follows: the distance between the Cu target and the substrate was 55 mm, the Ar pressure was 0.25 Pa and the discharge power was 260 W. For comparison, a bulk-Cu (purity: 4N) sample was also characterized. This sample was annealed at 1073 K for 2 h under an Ar atmosphere.

These as-deposited PVD-Cu films and the annealed bulk-Cu sample were irradiated with a slow positron beam to measure the Doppler broadening spectra of the annihilation radiation as a function of the incident positron energy $E$. For each value of $E$, a spectrum of $5 \times 10^5$ total counts was measured. The $S$ parameter was defined as the number of annihilation events over an energy range of 511 $\pm$ 0.76 keV, which reflects the low momentum part of the spectrum. Positrons were implanted into samples at energies in the range of 0.025 – 30 keV. The positron lifetime in the bulk-Cu sample was also measured at room temperature using a conventional positron annihilation lifetime spectrometer with a time resolution of 182 ps (FWHM). Approximately $1 \times 10^6$ total counts were accumulated for each lifetime spectrum.

Furthermore, to observe the annealing behavior of lattice defects formed during deposition, isochronal annealing in steps of 15 min/50 K was performed. A monoenergetic positron beam with an energy of 15 keV was then used to irradiate each sample and Doppler broadening spectra of the annihilation radiation with $2 \times 10^6$ total counts were acquired for each annealing temperature. All of the measurements were carried out under ultra-high vacuum (UHV) conditions at room temperature.

3. Results and discussion

3.1. The $S$ parameter as a function of the incident positron energy $E$

$S$ parameters of as-deposited pure-Cu and Cu-Sb dilute alloy films are shown in Figure 1 as a function of incident positron energy $E$. The result for the annealed bulk-Cu sample is also shown. At low $E$ ($\approx$ 0 keV), higher $S$ values were observed for all samples. This is caused by positronium formation at the surface of Cu [5-6]. Pure-Cu and Cu-Sb dilute alloy films had $S$ values at $E > 20$ keV that tended to increase with increasing $E$. This was due to partial implantation of positrons into Si substrates in this energy range. For the annealed bulk-Cu sample, the $S$ value saturated in the range of $E = 25 – 30$ keV. The positron lifetime for this sample was 111 ps. This value agreed with the reported lifetime of positrons that are delocalized and annihilated in interstitial sites [3]. This indicates that the $S$ value of the
annealed bulk-Cu sample, observed at $E = 25 – 30$ keV, was the characteristic value of $S$ for a Cu perfect crystal.

For the pure-Cu film, values of $S$ were almost constant in the range of $E = 9 – 17$ keV. This means that the $S$ value in this energy range corresponds to the annihilation of positrons in the 1 µm pure-Cu film. A previous study on conventional positron annihilation lifetime spectroscopy indicated that almost all positrons which were implanted into a PVD-pure-Cu film were trapped at grain boundaries and annihilated there because of submicron grain sizes [3]. This was the reason for the higher value of $S$ for a pure-Cu film compared to the value of a Cu perfect crystal. Moreover, the value of $S$ for a Cu-Sb dilute alloy film was higher than the value for a pure-Cu film in the same range of $E = 9 – 17$ keV. This indicates that the Cu-Sb alloy film contains large amounts of defects compared to a pure-Cu film.

3.2. Change in the $S$ value during isochronal annealing

Figure 2 shows positron implantation profiles $P(z, E)$ in copper calculated for two incident positron energies, $E = 15$ or 30 keV. The calculation formula is described elsewhere [7-8]. This calculation result showed that almost all positrons were annihilated in the Cu film when positrons were implanted with energy of 15 keV. To put it another way, we do not need to consider the effects of interfaces or substrates. For this reason, we measured the $S$ value at $E = 15$ keV for each annealing temperature.

Figure 3 shows the change in $S$ value for pure-Cu and Cu-Sb dilute alloy films before and during isochronal annealing. The most prominent feature of these results is
that the S value of the Cu-Sb alloy film increases significantly at around 573 K and then decreases. In
general, lattice defects monotonically decrease as annealing temperature increases. Nevertheless, a
significant increase of the S value for the Cu-Sb alloy film was observed. This can be explained by the
migration and clustering of excess vacancies. The Cu-Sb film thus contains a large amount of vacan-
cies compared to a pure-Cu film. It is well known that the binding energy between a Sb atom and a Cu
mon-o-vacancy has a relatively high value (0.32 eV experimental value [9], 0.39 eV calculated value
[3]). Therefore, we can interpret this drastic change in the S value for the Cu-Sb dilute alloy film in the
following way: vacancies were introduced during deposition by the high binding energy between a Sb
and Cu mon-o-vacancy. In isochronal annealing experiments, the introduced excess vacancies started to
dissociate from Sb atoms at around 573 K and aggregated into vacancy clusters which led to an in-
crease the S value. Further annealing at 623 K or at higher temperature resulted in a decrease of
vacancy clusters.

4. Summary

Doppler broadening spectra of annihilation radiation have been measured for PVD-pure-Cu and PVD-
Cu-0.5at%Sb dilute alloy films to determine the behavior of lattice defects. Defects observed in the
Cu-Sb film were identified as frozen-in vacancies that were formed during deposition and which were
introduced by the high binding energy between a Sb atom and a Cu mon-o-vacancy. We conclude that
these excess frozen-in vacancies in the PVD-CuSb dilute alloy film causes good reflowability in the
post-deposition high-pressure annealing process.

Acknowledgement
This study was supported by Priority Assistance for the Formation of Worldwide Renowned Centers
of Research – The Global COE Program (Project: Center of Excellence for Advanced Structural and
Functional Materials Design) from the Ministry of Education, Culture, Sports, Science and Technol-
ogy (MEXT), Japan.

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