

Self-Formation of Ti-rich Interfacial Layers in Cu(Ti) Alloy Films

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1. Introduction

Reduction of the device feature size to deep submicron scale, the large resistance-capacitance delay and poor device reliability became critical issues. Specifically, a significant increase in the resistivity of the Cu wires by reducing the line width less than 70 nm is one of our most serious concerns. In order to address this issue, an investigation of Cu alloy metallization with self-formed thin diffusion barriers is very important in addition to development of low dielectric interlayers and passivation materials. A fabrication technique to form the barrier layers in Cu alloy films by annealing at elevated temperatures was extensively studied. This technique is called "self-formation of the barrier layer" and is attractive to apply to the Cu wires. We reported self-formation of Ti-rich barrier layers in Cu(Ti) alloy films at the film/substrate interface¹. The purpose of the present study was to make the self-formation mechanism of the Ti-rich interfacial layer in the Cu(Ti) alloy films clear. We investigated effects of annealing atmosphere and elements contained in substrates on the self-formation mechanism.

2. Methods of approach

The 300 nm-thick Cu(Ti) alloy films were deposited on to SiO₂/Si, Si₃N₄/Si and NaCl substrates by a radio frequency magnetron sputter system. The base pressure of the deposition chamber was approximately 5×10^{-7} Pa. To prepare the Cu(Ti) films, small pieces of rectangular Ti plates were mounted on the Cu targets. The purities of the Cu targets and the Ti plates were 99.9999% and 99.9%, respectively. The compositions of the Cu(Ti) films prepared were approximately Cu-7.3 at.% Ti. The sputtering power and the working pressure were maintained at 400 W and 1 Pa or 300 W and 0.1 Pa, respectively, during depositions. The substrate holder was placed at 100 mm above the target. After the film depositions, the Cu(Ti) films were annealed isothermally at 400 and 500°C in high vacuum and Ar gas atmospheres for about two hours.

The electrical resistivities in the Cu(Ti) films were measured by a four-point probe method. Microstructures of the films were analyzed by x-ray diffraction (XRD), scanning ion microscopy (SIM) in a focused ion beam fabrication system and transmission electron microscopy (TEM). The elemental depth distribution in the films was analyzed by Rutherford backscattering spectroscopy (RBS) and energy-dispersive x-ray spectrometry (EDS) equipped in the

TEM instrument.

3. Results and Discussion

Self-formation of Ti-rich layers dependent on annealing atmosphere

As-deposited Cu(Ti) alloy films deposited on to SiO₂/Si substrates were annealed at 500°C in high vacuum and Ar gas atmospheres for about two hours. The electrical resistivities of the Cu(Ti) alloy films are dependent on the atmospheres. The electrical resistivities were significantly reduced to about 3.2 $\mu\Omega\text{cm}$ after annealing in the Ar gas atmosphere. However, those after annealing in the high vacuum atmosphere are still high and were about 16.3 $\mu\Omega\text{cm}$.

RBS analyses show that Ti atoms segregate only at the film/substrate interface regions after annealing in the high vacuum atmosphere. TEM cross-sectional images show that a thin layer formed uniformly on the SiO₂/Si substrate and Cu₄Ti grains formed on the uniform thin layer after annealing in the high vacuum atmosphere as shown in Fig. 1(a). No surface layer was formed. These indicate that the super-saturated Cu(Ti) alloy decompose into the Cu(Ti) solid solution phase and the Cu₄Ti phase based on the Cu-Ti binary phase diagram. The high resistivity of the Cu(Ti) alloy films after annealing in the high vacuum atmosphere could be explained by both high Ti content and Cu₄Ti second phases in the Cu(Ti) alloy films.

On the other hand, RBS analyses and TEM observations show that Ti atoms segregate both at the film surface and at the film/substrate interface after annealing in the Ar gas atmosphere. Cu atoms were not detected in the self-formed Ti-rich layers at the film surface and the film/substrate interface. Self-formation of the Ti-rich surface and interfacial layers suggests that Ti atoms would react with oxygen atoms in the atmosphere and in the SiO₂/Si substrate, respectively, forming Ti oxides in both Ti-rich layers. The reaction of the Ti atoms with oxygen atoms would reduce Ti content in the Cu(Ti) alloy significantly below to its upper limit, yielding the low resistivity observed in the Cu(Ti) alloy film after annealing in the Ar gas atmosphere.

The electrical resistivities of the Cu(Ti) alloy films with Cu₄Ti phases were reduced to about 3.3 $\mu\Omega\text{cm}$ after additional annealing in the Ar gas atmosphere for two hours. Ti-rich surface layer was newly formed and thickness of the Ti-rich interface layer increased. The Cu₄Ti phases were

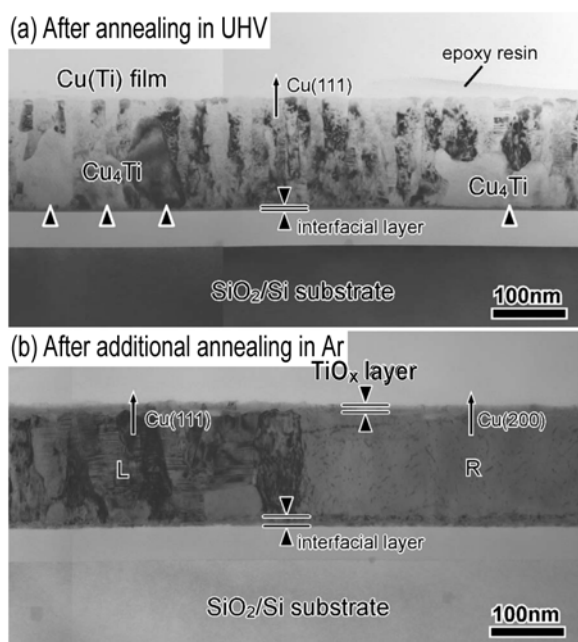


Fig. 1 TEM cross-sectional images of Cu(Ti) alloy films deposited on SiO₂/Si substrates after annealing at 500°C for two hours (a) in the high vacuum atmosphere and (b) after additional annealing in Ar gas atmosphere.

completely disappeared.

Self-formation of Ti-rich layers dependent on a substrate

The reaction of the Ti atoms in the Cu(Ti) alloy films with impurity oxygen atoms is indicated to be essential for reducing resistivity of the Cu(Ti) alloy film as well as the self-formation of Ti-rich interfacial layer on the SiO₂/Si substrate. In order to study an effect of elements contained in substrates on the self-formation of the Ti-rich interfacial layers, as-deposited Cu(Ti) alloy films deposited on SiO₂/Si, Si₃N₄/Si and NaCl substrates were annealed at 400°C in an Ar gas atmosphere for two hours.

The electrical resistivities of the three Cu(Ti) alloy films decrease significantly after the annealing and are achieved to be below 4 μΩcm. RBS analysis and TEM observation show that Ti atoms segregate only at the film surface for the Cu(Ti) alloy films on the NaCl substrate, in contrast both at the film surface and at the film/substrate interface for those on the SiO₂/Si and Si₃N₄/Si substrates (Fig. 2). The Cu atoms was not detected in the self-formed Ti-rich layers at the film surface and the film/substrate interface. Note that the interfacial layer on the Si₃N₄/Si substrates is found to consist of TiN (Fig. 3), indicating that Ti atoms react with nitrogen atoms in the Si₃N₄/Si substrates. No interfacial layer observed on the NaCl substrate indicates that Ti atoms would not react with Na and Cl atoms in the NaCl substrates. The Ti-rich interfacial layer in the Cu(Ti) alloy film on the Si₃N₄/Si substrate is thicker than that on the SiO₂/Si substrate, while the thickness of the surface layers has opposite tendency. This indicates that reaction of Ti atoms in the Cu(Ti) alloy films with nitrogen

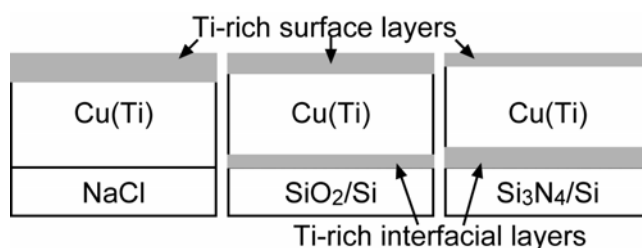


Fig. 2 Schematic illustrations of the self-formed Ti-rich surface and interfacial layers in the Cu(Ti) alloy films deposited on various substrates.

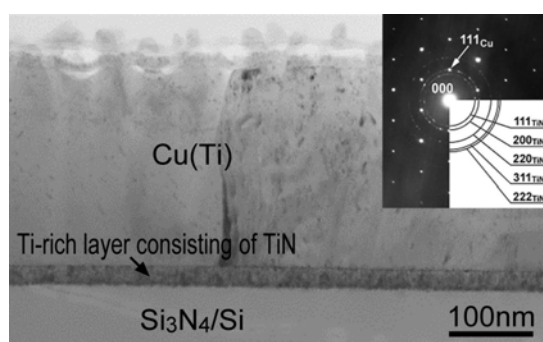


Fig. 3 A TEM cross-sectional image of a Cu(Ti) alloy film deposited on a Si₃N₄/Si substrate after annealing at 400°C for two hours in an Ar gas atmosphere. Inset figure shows a SAD image of the Ti-rich interfacial layer.

atoms is more favorable than that with oxygen atoms.

4. Conclusions

The electrical resistivities of the Cu(Ti) alloy films are dependent on the annealing atmospheres. Reaction of Ti atoms in the alloy films with impurity oxygen atoms in the atmosphere is essential to reduce resistivity of the films, forming the Ti-rich surface layer. Similarly, reaction of the Ti atoms in the alloy films with the oxygen and nitrogen atoms in the substrate is essential for self-formation of the Ti-rich interfacial layer. Thickness of the self-formed Ti-rich interfacial layer could be controlled by Ti content in the Cu(Ti) alloy films as well as elements contained in the substrates. The self-formed Ti-rich interfacial layer on the Si₃N₄/Si substrate is thicker than that on the SiO₂/Si substrate.

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