Correlation of W-Si-N Film Microstructure with Barrier Performance against Cu Diffusion.

Yoshiaki SHIMOOKA, Tadashi IIJIMA, Shinichi NAKAMURA*, and Kyoichi SUGURO

Microelectronics Engineering Lab., Environmental Engineering Labs. *
TOSHIBA Corporation
1, Komukai Toshiba-cho, Saiwai-ku, Kawasaki 210, Japan
Phone: +81-44-549-2208, Fax: +81-44-549-2213

ABSTRACT
The relationship between microstructure of WSiN films and barrier capability against Cu diffusion is discussed in this paper. Microstructure of the WSi6N films was analyzed by XRD and TEM. The chemistry of the WSi6N films was analyzed by XPS. Cu in-depth profiles were analyzed by SIMS and an amount of Cu diffused to the interface was calculated by integrating the Cu profiles. The activation energy of Cu diffused through WSi6N layer was constant at 2.5 eV in the 800 - 900 °C temperature range, although W micro-crystals in amorphous WSi6N film grew at 850 °C. Hence, it was found that the excellent barrier capability was due to the absence of continuous grain boundaries throughout the film, where Cu atoms can easily migrate. That is, the W micro-crystal formation does not change the Cu diffusion mechanism up to 900 °C, and the Cu diffusion is controlled by diffusion in amorphous matrix.

1. Introduction
Low resistivity copper (Cu) will be indispensable in high speed ULSIs in the deep submicron generations. However, Cu metallization involves several issues. One of the most important issues is to develop a good barrier metal against Cu diffusion into SiO2 and Si substrate.1) Amorphous metal-Si-N alloys are reported as a barrier metal for Cu interconnections.2) Among them, W-Si-N3,4) was selected as a barrier metal against Cu diffusion, because of its thermal stability at high temperature and chemical stability in an acid such as HF solution, which is used in the cleaning process after chemical mechanical polishing (CMP). We reported an application of the WSiN barrier metal to double level Cu interconnects which were formed by laser melt reflow and CMP.5) It has previously been reported that the resistivity of WSiN is 0.45 mΩ-cm and the as-deposited film has 0.8 GPa compressive stresses and 0.2 GPa tensile stress after annealing at 450 °C.5) However, the mechanism of Cu diffused into amorphous WSiN layer has remained unclear, especially with regard to the furnace annealing process. In this paper, the relationship between microstructure of WSiN films and barrier capability against Cu diffusion is discussed and a dominant Cu diffusion scheme is presented for the first time.

2. Experimental
Amorphous WSiN barrier layers were deposited on a Si(100) substrate with or without thermally grown SiO2. The WSiN deposition was carried out by reactively sputtering a W3Si3 target in a gas mixture of 25 % N2 and Ar. The N2 and Ar were controlled by mass flow controllers and the total pressure was 0.3 Pa during sputtering. Cu films were sequentially sputtered without breaking the vacuum, following WSiN deposition. In order to study the thermal stability of a Cu (50 nm)/WSiN (25 and 100 nm)/Si and WSiN (100 nm)/SiO2/Si system, isochronal annealing was carried out at temperature ranged from 450 °C to 900 °C for 30min at 1atm pressure in 20 % H2/N2. Composition of the WSiN films was identified to be WSi6N by Rutherford backscattering spectroscopy (RBS) and atom absorption spectroscopy. Microstructure of the WSi6N films was analyzed by X-ray diffraction spectroscopy (XRD) and transmission electron microscopy (TEM). The chemistry of the WSi6N films was analyzed by X-ray photoelectron spectroscopy (XPS). Cu in-depth profiles were analyzed by secondary ion mass spectroscopy (SIMS).

3. Results and Discussion
SIMS results showed that the Cu diffusion was successfully blocked by the amorphous WSi6N layer up to 600 °C for 30 min. At 800 °C or higher temperature, Cu diffused to the Si substrate and piled up at the interface as shown in Fig. 1. By integrating Cu profiles, an amount of Cu diffused into the interface was calculated and the result is shown in Fig. 2. The activation energy was found to be 2.5 eV which was higher than the activation energy generally reported of grain boundary diffusion in metal films.6) There was no change in X-ray diffraction patterns for annealing at temperatures below 880 °C.
After annealing at 880 °C, W(200) and W(211) diffraction peaks appeared, and full width at half maximum of W(110) diffraction peak abruptly decreased and the diffraction peak became clear as shown in Fig. 3. Si2p peaks of X-ray photoelectron spectra for WSi_{0.6}N films are shown in Fig. 4 (a). While the intensities of Si - O bonds in WSi_{1.6}N films were increased, those of Si - W bonds were decreased after annealing at 880 °C compared with as-deposited WSi_{0.6}N films. The intensities of Si - N bonds were not changed by annealing at temperatures up to 880 °C. W4f peaks of photoelectron spectra for WSi_{1.6}N films are also shown in Fig. 4 (b). From these results, it was found that the intensities of W - W bonds increased after annealing at 880 °C, while the intensities of W - Si bonds decreased. That is, the total amount of W increased near the surface layer. The W atoms may come from the deeper region in WSi_{0.6}N films, and segregate at the surface.

In order to clarify the existence of the W micro-crystals, the annealed WSi_{0.6}N films were observed by high resolution TEM. As a result, as-deposited WSi_{0.6}N films showed an amorphous state which was found to be stable up to 800 °C. TEM results also showed that about 3 nm W micro-crystals were nucleated and the density was approximately 200 /μm² at 850 °C. Fig. 5 shows typical plan-view micrographs after annealing at 800 °C and 880 °C. Precisely analyzing TEM images, Fig. 6 shows that the W micro-crystals density abruptly increased from 200 /μm² to 7400 /μm² with temperature at around 850 - 880 °C and a saturation point was at around 900°C, above which W grain growth was dominant and the coalescence occurred. W micro-crystals were observed independently of WSIN thickness.

From these results, it was found that the activation energy of Cu diffused through WSi_{0.6}N layer was constant at 2.5 eV in the 800 - 900 °C temperature range, although W micro-crystals in WSi_{0.6}N film occurred at 850 °C. Hence, Cu diffusions in amorphous and crystalline WSi_{0.6}N are the same mechanism in the 800 - 900 °C temperature range.

4. Conclusion
The excellent barrier capability is due to the absence of continuous grain boundaries throughout the film, where Cu atoms can easily migrate. It was found that the W micro-crystal formation did not change the Cu diffusion mechanism up to 900 °C, and the Cu diffusion was controlled by diffusion in amorphous matrix. By using the WSi_{0.6}N barrier layer, inlaid Cu interconnections were successfully formed on shallow pn junction without degradation in electrical characteristics.

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References

Fig.1. SIMS in-depth profiles of Cu for a Cu(50nm)/WSIN(100nm)/Si system before and after annealing. Isochronal annealing length is 30min.

Fig.2. Annealing temperature dependence of the amount of Cu diffused in Si for a Cu/WSIN/Si system.
Fig. 3. X-ray diffraction spectra for a WSiN/SiO₂/Si system before and after annealing.

Temperature (°C)
1000 900

Density (μm⁻²)

Temperature (°C) versus density of WSiN films.

Fig. 4. XPS spectra for a WSiN film before and after annealing at 880 °C. (a) Si2p peaks. (b) W4f peaks.

Fig. 5. Plan-view TEM micrographs of WSiN films.

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<tr>
<th>Temperature Structure</th>
<th>800 °C</th>
<th>880 °C</th>
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<tr>
<td>WSiN 25nm /SiO₂/Si-sub.</td>
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<tr>
<td>WSiN 100nm /SiO₂/Si-sub.</td>
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Fig. 6. W micro-crystal density as a function of reciprocal annealing temperature for WSiN films.