구리배선용 베리어메탈로 쓰이는 Ta-N/Ta/Si(001)박막에 관한 X-선 산란연구

X-ray Scattering Study of Reactive Sputtered Ta-N/Ta/Si(001)Film as a Barrier Metal for Cu Interconnection

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Abstract

In order to compare the barrier properties of Ta-N/Si(001) with those of Ta-N/Ta/Si(001), we studied structural properties of films grown by RF magnetron sputtering with various Ar/N_2 ratios. To evaluate the barrier properties, the samples were annealed in a vacuum chamber. Ex-situ x-ray scattering measurements were done using an in-house x-ray system. With increasing nitrogen ratio in Ta-N/Si(001), the barrier property of Ta-N/Si(001) was enhanced, finally failed at 750℃ due to the crystallization and silicide formation. Compared with Ta-N/Si(001), Ta-N/Ta/Si(001) forms silicides at 650℃. However it does not crystallize even at 750℃. With increasing nitrogen composition in Ta-N/Ta/Si(001), the formation of tantalum silicide was reduced and the surface roughness was improved. To observe the surface morphology of Ta-N/Ta/Si(001) during annealing, we performed an in-situ x-ray scattering experiment using synchrotron radiation of the 5C2 at Pohang Light Source(PLS). Addition of Ta layer between Ta-N and Si(001) improved the surface morphology and reduced the surface degradation at high temperatures. In addition, increasing N_2/Ar flow ratio reduced the formation of tantalum silicide and enhanced the barrier properties.

Key Wards : tantalum nitride, tantalum silicide, tantalum, barrier metal, XRD

1. Introduction

Since the advent of copper interconnections for ULSI, Ta and Ta-N films have been received considerable attention as barrier metals due to their high melting temperature and thermal stability. Ta and Ta-N films are considered to be one of the most promising diffusion barriers to prevent the highly diffusing copper from reacting with the underlying silicon. The feasibility of Ta and Ta-N thin films as a barrier metal has been extensively studied, particularly in terms of chemical inertness and electrical property. The effectiveness of barrier metal in terms of the chemical inertness for Cu interconnection is reported to be enhanced with increasing the amounts of nitrogen components. From the perspective of electrical property, however, Ta is preferred since the resistivity of Ta-N increases rapidly with an addition of nitrogen content. This means that the speed of the electrical signal in Ta-N is lower than in Ta. As a result, the improvement of the chemical inertness may cost reduction in electrical property and vice versa. To optimize both chemical inertness and electrical property, recent works are focused on thinning tantalum nitride films. As the very thin film requires high uniformity at elevated temperatures, thermal stability of surface morphology becomes more important. To enhance thermal stability and barrier property, we introduce Ta layer between Ta-N and Si(001). In this work,

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we demonstrate the thermal stability of Ta-N/Ta/Si(001) in comparison with Ta-N /Si(001). From this experiment, we found that the Ta-N/Ta/Si(001) is a potential diffusion barrier for Cu interconnection.

2. Experimental Details

RF magnetron reactive sputtering system was used to deposit Ta and Ta-N films on commercial n-type Si(001) over a wide range of Ar/N_2 flow ratios. Substrates were cleaned by standard RCA cleaning method. To remove the native oxides from the substrates, hydrofluoric acid(50%) was used. During depositing the film, the substrate was held at room temperature and the Ar pressure was fixed at 5×10^{-3} Torr. Two types of samples were prepared for this experiment. One is a series of 600ÅTa-N /Si(001). Three different $N_2/(Ar+N_2)$ gas flow ratios were chosen; Ta-N(10%)/Si(001) ,Ta-N(38%)/Si(001), Ta-N(58%)/Si(001). The other is a series of Ta-N /Ta/Si(001). A 200Å Ta film was grown on the substrates followed by a 400Å Ta-N film on it. Three different $N_2/(Ar+N_2)$ gas flow ratios were chosen;Ta-N(10%)[2]/Ta/Si(001),Ta-N(38%)/Ta/Si(001), Ta-N(58%) /Ta/Si(001).

3. Result and Discussion

3.1 Ex-situ x-ray scattering measurement

Figure 1 shows the ex-situ powder diffraction patterns of Ta-N/Si(001) at various annealing temperatures for 30 min. As-dep Ta shows a poly-crystalline β-Ta(002), while Ta-N films are amorphous. Ta forms tantalum silicides at 600℃. As-dep amorphous Ta-N films do not form tantalum silicides even at 700℃. As the annealing temperature is raised up to 750℃, amorphous tantalum nitrides crystallize abruptly. Phase formations of TaN(38%) and TaN(58%) are similar except for relative quantity of tantalum silicides. Formations of tantalum silicides are suppressed to a degree as nitrogen flow ratio in tantalum nitride increases. The surface morphology as well as phase transformation is sensitive to nitrogen flow ratio. Fig.2 shows transverse profiles of Ta-N/Si(001) at $2\theta=3^{\circ}$. As shown in Fig.2(b) and

2) In this paper, we will denote % as N_2 gas flow percentage, that is, $P_{N2}/(P_{N2}+P_{Ar}) \times 100$.

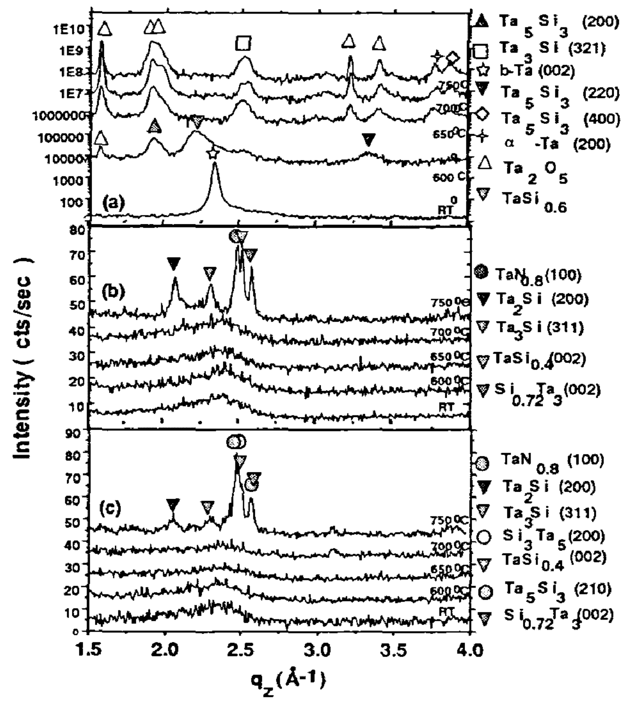

Fig.1. Powder scan of Ta-N/Si(001) after annealing for 30min (a) Ta/Si(001) (b) TaN(38%)/Si(001) (c) TaN(58%)/Si(001)

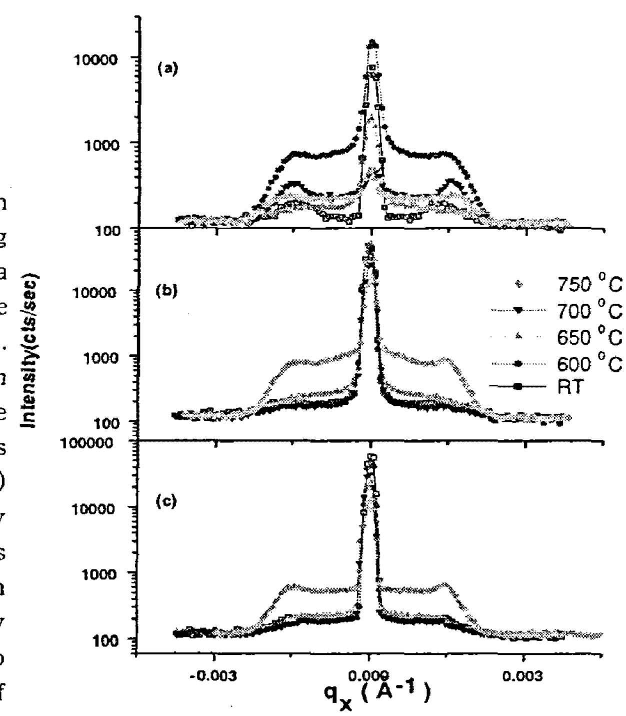

Fig.2. Transverse scan of Ta-N/Si(001) at $2\theta=3^{\circ}$ after annealing for 30min (a) Ta/Si(001) (b) TaN(38%)/Si(001) (c) TaN(58%)/Si(001)

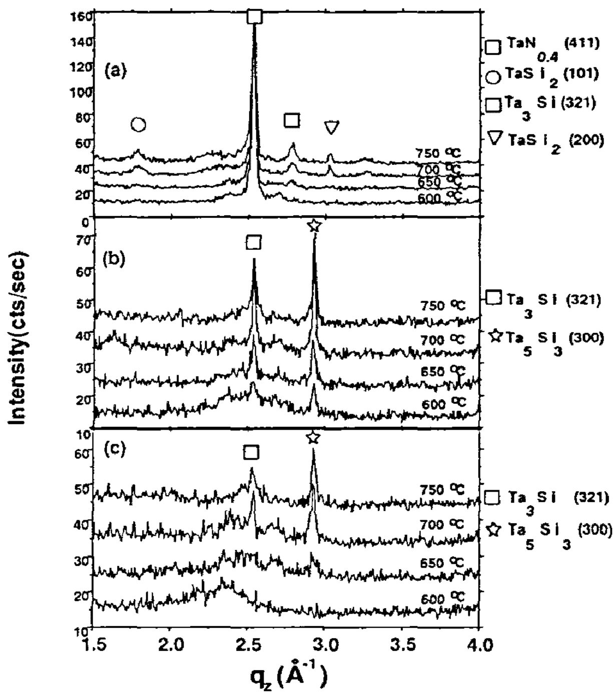

Fig.3. Powder scan of Ta-N/Ta/Si(001) after annealing for 30min (a)TaN(10%)/Ta/Si(001) (b)TaN(38%)/Ta/Si(001) (c)TaN(58%)/Ta/Si(001)

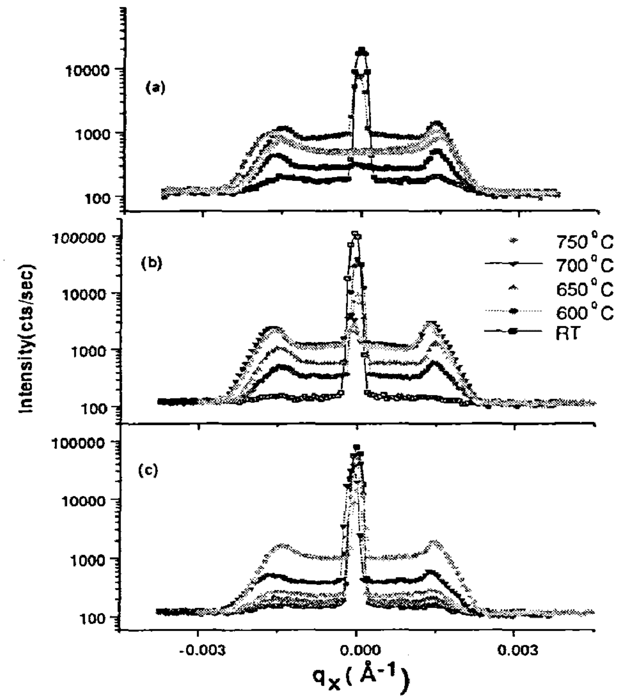

Fig.4. Transverse scan at $2\theta=3^{\circ}$ after annealing for 30min (a)TaN(10%)/Ta/Si(001) (b)TaN(38%) /Ta/Si(001) (c)TaN(58%) /Ta/Si(001)

Fig.2(c), the increase in the nitrogen flow ratio enhances the surface stability against annealing temperature. In case of TaN(58%), surface morphology does not change seriously below 700℃. As an amorphous tantalum nitride crystallizes, rearrangement of atoms causes surface morphology to be degraded abruptly. Compared with Ta-N/Si(001), Ta-N/Ta/Si(001) behaves in a different way. Existence of the polycrystalline Ta layer activates the formation of tantalum silicides at low annealing temperatures. As shown in Fig.3, TaN(38%)/Ta begins to form silicides at 600℃, while TaN(58%)/Ta forms silicide at 650℃. Even though Ta-N/Ta/Si(001) films form silicides at lower temperature, they do not crystallize even at 750℃ and not change abruptly as in Ta-N/Si(001) films. From these phenomena, we can argue that nucleation sites for crystallization of an amorphous Ta-N film should be the interface of Ta-N and Si(001). If surface or bulk is a nucleation site, Ta-N films will crystallize regardless of existence of Ta layer. High nitrogen flow ratio in Ta-N/Ta/Si(001) films reduces the formation of tantalum silicide. This implies that nitrogens in Ta-N layer diffuse into Ta layer and enhance the barrier properties of Ta layer. Surface morphology of Ta-N/Ta/Si(001) is also related to the nitrogen flow ratio in Ta-N layer. Fig.4 shows transverse scans at $2\theta=3^{0}$. Surface roughness increases at high annealing temperature and decreases at high nitrogen flow ratio. While the surface of Ta-N/Si(001) evolves at 750℃ due to the crystallization of Ta-N layer, surface morphology of Ta-N/Ta degrades gradually even at 750℃. According to Fig.5, existence of Ta layer in as-deposited samples does not make any difference for surface morphology. At 750℃, however, the addition of Ta layer will inhibit the crystallization of Ta-N and, thus, avoid an abrupt surface degradation.

3.2 In-situ x-ray scattering measurement

To investigate surface and interface behaviors of TaN(58%)/Ta/Si(001) in real time, we carried out in-situ x-ray scattering experiment at 5C2 beamline in Pohang Light Source. Fig.6 shows a specular reflectivity of TaN(58%)/Ta/Si(001). As-deposited film thickness of TaN(58%)/Ta are about 500Å, 200 Å respectively. The longer period of the intensity

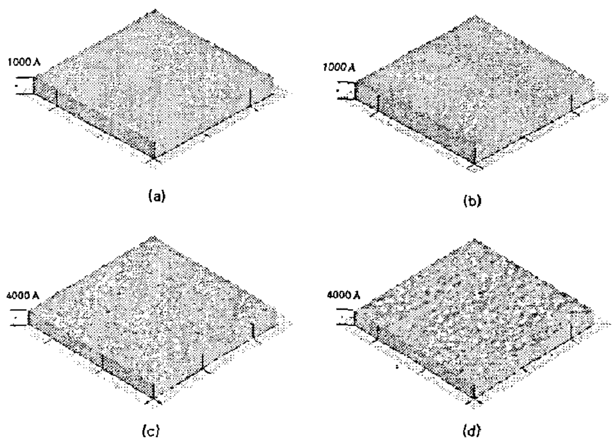

Fig.5. AFM images of surface morphology(10㎛ X 10㎛) (a)as-dep TaN(58%)/Ta/Si(001):RMS =2.44Å (b)as-dep TaN(58%)/Si(001):RMS=3.54Å (c) TaN(58%)/Ta/Si(001) annealed at 750℃ for 30min:RMS=8Å (d) TaN(58%)/Si(001) annealed at 750℃ for 30min:RMS=73Å

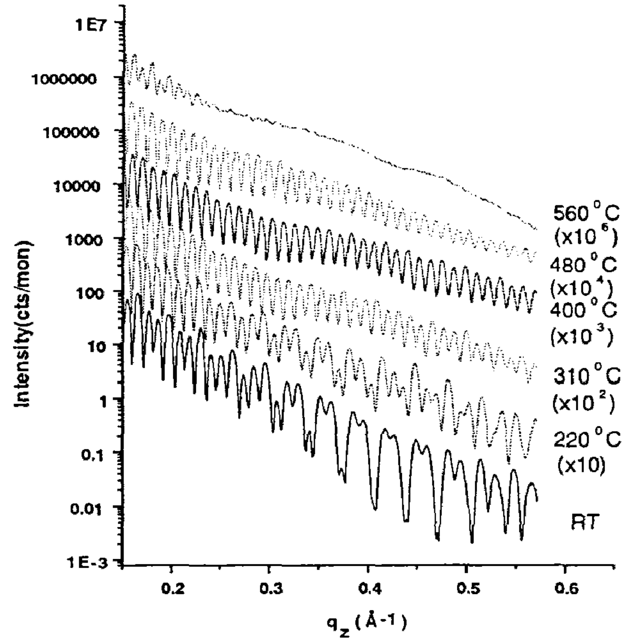

Fig.6. Reflectivity curves of TaN(58%)/Ta/Si (001) measured during annealing experiment

oscillation indicates Ta film, while the shorter period of the intensity oscillation describes TaN(58%) film. When we raise the annealing temperature up to 310℃, the longer period of the intensity oscillation disappears. This indicates that the density difference between TaN(58%) and Ta decreases. In other words, diffusion of nitrogen from TaN(58%) to Ta occurs. In addition, a longer period of the intensity oscillation occurs at 310℃. This implies that a new phase in about 50Å thickness formed uniformly. This new phase corresponds to tantalum silicide. With increasing annealing temperature, tantalum silicide tends to grow. However, incorporation of nitrogens into Ta layer also occurs and these nitrogens seem to suppress tantalum silicide. Thus, thickness of tantalum silicide does not change seriously. Finally, tantalum silicide layer reduces nucleation site for Ta-N crystallization.

4. Conclusion

We studied the phase formation behaviors of Ta-N/Ta/Si(001) and Ta-N/Si(001) during annealing using in-situ and ex-situ x-ray scattering experiments. In case of Ta-N/Si(001), it is difficult for Ta to react with Si to form tantalum silicide due to the Ta-N structural stability. Only after enough energy is provided, the rearrangements of atoms can occur. This explains an abrupt crystallization at 750℃. As Ta-N film crystallizes at 750℃, the rearrangements of atoms in Ta-N layer degrade the surface morphology. In contrast, the existence of the poly-crystalline Ta layer in Ta-N/Ta/Si(001) leads to a different behavior. Ta layer can react with Si to form tantalum silicide at 650℃ while the diffusion of nitrogen into the Ta layer occurs. The formation of tantalum silicide reduces the nucleation sites for Ta-N crystallization at Ta/Si interface and, thus, inhibits the rearrangements of Ta-N layer. This explains good thermal stability of Ta-N/Ta/Si(001) at 750℃ compared with Ta-N/Si(001). In addition, increasing N_2/Ar flow ratio reduced the formation of tantalum silicide and enhanced the barrier properties.

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