Deposition of TaN Films by RF Sputtering and Their Barrier Properties in Cu/TaN/Dielectrics/Si MIS Structures

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The electrical resistivity and the barrier property of Tantalum nitride (TaN) thin films were systematically investigated as a function of annealing temperature using two different types of MIS structures of TaN/SiO₂/Si and Cu/TaN/dielectric/Si(100), where either the thermally grown SiO₂ (th-SiO₂) or spin-on dielectric (SOD) hydrogen silsesquioxane (HSQ) films was used as a dielectric layer. We observed that the resistivity of TaN thin films before Cu deposition became lower with the growth of TaN(200) as compared with the growth of TaN(111) and TaN(220). Cu diffusion barrier properties of MIS diodes with TaN films were improved up to 500°C for both dielectric films due presumably to the decrease in sputter damage of dielectric films by annealing, while those without TaN thin films were degraded due to the diffusion of Cu into the dielectric films. The oxygen desorption from dielectric films and the oxidation of TaN films due to the reverse-sputtering of dielectric films during the sputtering of Ta in N₂ is possible model of sputter damage. [DOI: 10.1380/ejssnt.2012.107]

Keywords: Metal-oxide-semiconductor (MOS) structures; Tantalum; Nitrides; Copper; X-ray diffraction; spin-on dielectric (SOD); C-V characteristics; Hydrogen silsesquioxane (HSQ)

I. INTRODUCTION

Tantalum nitride (TaN) has many attractive characteristics such as good chemical stability, high hardness, high melting point (3090°C), low electrical resistivity and high thermal conductivity [1-7], which make it possible to use as a diffusion barrier between Copper (Cu) wiring and interlayer dielectric film in ultra large scale integrated circuits (ULSIs) [2-10]. TaN can also be used in wide variety of applications such as corrosion-resistant materials, write-head materials in high-density magnetic recording and high-speed thermal printing head as well as thin film resistors. Moreover, in recent years work function of TaN has received considerable attention for commonly used metal source/drain and metal gate electrodes of group IV/V/Ge CMOS technologies with heterogeneous integrations on Si platform [11]. So far, TaN thin films have been prepared typically by sputtering tantalum in the argon and nitrogen gas mixture [1-7]. TaN has a defective structure [12], and deviations from stoichiometry are common. Consequently, the properties of TaN thin films are extremely influenced by the film’s microstructure and growth morphology as well as deviation from stoichiometry. According to previous reports [2-4], the properties of TaN thin films, e.g., the chemical composition, microstructure and the electrical resistivity strongly depended on the deposition condition.

Diffusion barrier properties of TaN between Cu and dielectric materials during annealing have been investigated by many researchers. R. Hübner et al. suggested that the barrier property of Ta-based thin films was determined by the diffusion temperature of barrier material itself [8]. They showed that for Cu/TaN/SiO₂/Si structures, the nitrogen involved in the TaN thin films could play an important role of suppressing the diffusion of Ta itself, where TaN showed better diffusion barrier property compared with pure Ta at a temperature of 500°C. For Cu/Ta/SiO₂/Si structures, they observed Ta diffusion towards the Cu surfaces at 500°C. On the other hand, Takeyama et al. observed that the barrier property of TaN thin films between Cu and Si can be maintained even after annealing at 750°C for 1h [9]. After annealing at 800°C for 1h, however, barrier property of Cu/TaN/Si layered structures was broken and formation of TaSi₂ and Cu₃Si were observed [8,9].

Shrinking the widths in interconnect line causes a significant increase in RC delay time, which can be one of the bottlenecks for designing high-speed ULSIs. To improve the situation, combination of Cu wiring and low-k interlayer dielectrics whose dielectric constant is under 3 has been introduced instead of that of Al wiring and SiO₂ interlayer dielectrics with dielectric constant of around 4. Barrier metals are especially important for Cu wiring because the diffusion of Cu into the dielectrics forms Cu₃Si, which results in an increase in resistivity and poor adhesion with Cu and dielectrics and so on. Now, the barrier metals are requested to have thinner thickness and lower resistivity as the wiring width reduces. For practical use of interlayer low-k dielectrics in further shrinkage of device dimension, further reduction of dielectric constant of less than 2.5 is needed. Moreover, spin-on dielectric (SOD) materials have generated much interest as alternatives to currently used chemical vapor deposition (CVD) and high density plasma (HDP) deposited materials for applications of interlayer dielectric in ULSIs, because SOD is usually spin-coated, which is low process temperature, environment-friendly and low cost of fabrication. Progress in development of SOD materials and their fabrication processes has been made all over the world.

So far we have investigated the influence of the resistivity of TaN thin films deposited by RF magnetron sputtering on the N₂ gas flow ratio and sputtering power, and the results were compared with their structural properties and chemical compositions before Cu film deposition [7]. In this study we focus on the barrier properties of TaN

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films deposited on dielectrics such as thermally grown th-SiO$_2$ and SOD hydrogen silsesquioxane (HSQ) films in the Cu/TaN/Dielectrics/Si MIS structures. Comparison of post-sputtering annealing ambient either argon or nitrogen to obtain low resistivity TaN films is shown. The influence of post Cu deposition annealing on crystal structures and resistivities of Cu/TaN layered structures as well as current-voltage (I-V) and capacitance-voltage (C-V) characteristics of MIS devices is also demonstrated.

II. EXPERIMENTAL

In this study, TaN films were characterized with different layered structures. First, the electrical resistivity of TaN thin films was measured with TaN/th-SiO$_2$/Si structure. Next, the barrier property of TaN films was investigated with MIS diode structures of Cu/TaN/dielectric/Si, where either the thermally grown SiO$_2$ (th-SiO$_2$) or SOD hydrogen silsesquioxane (HSQ) films was used as a dielectric layer. The wafers used in this study are (100) and (111)-oriented Si substrates.

For the evaluation of TaN layers, TaN films were deposited on th-SiO$_2$ films (500 nm in thickness) grown on (111)Si substrates. Before depositions, the th-SiO$_2$/Si substrates were cleaned with wet chemical solutions in an ultrasonic cleaning system sequentially; trichloroethylene, acetone, ethanol and pure water. Then, TaN thin films were deposited on the th-SiO$_2$/Si substrates at room temperature by radio frequency (RF) sputtering at a power of 200 W under Ar-N$_2$ plasma using a tantalum target (99.99% pure, 4 inches, Kojyundo Chemical Laboratory Co., LTD). The thickness of deposited TaN films was around 1400 nm. During the sputtering of Ta, N$_2$ gas flow ratio defined as (N$_2$/Ar+N$_2$)×100 [%] was maintained at 20% and total gas flow was kept at 10 sccm. For TaN/th-SiO$_2$/Si structure samples, after the deposition of TaN, annealing was performed under either Ar or N$_2$ (both 99.9995% pure) ambience within a temperature range between 300 and 600°C for 1 hour. MIS diodes were prepared with three-step process. At first, either th-SiO$_2$ films or HSQ films with a thickness of 150 nm were formed onto (100)-oriented p-type Si substrates by different processes. Thermal oxidation was carried out at temperature of 1100°C for 20 min in H$_2$O vapor ambience. HSQ was used as a low-k dielectric material in this experiment. HSQ films were formed onto (100)-oriented p-type Si substrates by spin-coating method at rotational frequency of 6000 rpm. After spin-coating, the HSQ films were heated on conventional hot-plate in air at multiple-step temperatures of 80°C, 150°C and 200°C for 1 min at each temperature. After that, the HSQ films were annealed at 400°C for 30 minutes in nitrogen ambience to cure the HSQ films. Secondly, the TaN thin films were deposited onto the above two types of dielectrics by RF magnetron sputtering at a power of 200 W under Ar-N$_2$ plasma using a Ta target. During the sputtering of Ta, N$_2$ gas flow ratio defined as (N$_2$/Ar+N$_2$)×100 [%] was maintained at 20% and total gas flow was kept at 10 sccm. The nominal thickness of TaN thin films was 10 nm. Finally, the Cu thin films were sputtered at sputtering power of 200 W under Ar plasma using a Cu target (99.99% pure, 4 inches, Kojyundo Chemical Laboratory Co., LTD). During the sputtering of Cu, Ar gas flow was maintained at 4 sccm. The nominal thickness of Cu thin films was 250 nm. For fabrication of MIS diode, Cu/TaN electrodes with a diameter of either 1 mm or 0.7 mm were formed by sputtering using metal masks made of molybdenum (Mo). Then, annealing was performed under Ar ambience within a temperature range between 300 and 500°C for 1 hour. The distance between the target and the substrate in sputtering chamber was about 42 mm in all experiments. The base pressure of the sputtering system used in this study was below 6×10$^{-7}$ Torr, and the pressure during the sputtering was maintained at 1×10$^{-2}$ Torr. Prior to TaN or Cu deposition, the Ta or Cu target was cleaned by pre-sputtering in Ar plasma for 10 min or more.

The structural properties of TaN thin films were investigated through X-ray diffraction (XRD) using a $\theta - 2\theta$ diffraction (Rigaku Co.) with a Cu $\alpha$ radiation (1.5406 Å). The film thickness was measured by stylus surface profiler (Dektak 6M, ULVAC), and the electrical resistivity was measured at room temperature by four-point probe method with a hall effect system (HL5500PC, AC-CENT). The microstructure of thin films was observed using scanning electron microscopy (SEM, SU6600, Hitachi high technologies) and the chemical composition was analyzed using energy dispersive X-ray spectrometry (EDX). C-V and I-V characteristics of MIS diode were investigated at room temperature by using LCR meter (4284A, Agilent Technologies Ltd.) and DLTS system (DL8000, nano metrix Inc.), respectively. C-V characteristics were measured at 960 kHz by applying AC bias of 40 mV. Using the MIS diode, we evaluated the barrier properties electrically, which can be alternative to TEM or RBS so on.

III. RESULTS AND DISCUSSIONS

A. Characterization of sputtered TaN thin films

Figure 1 shows the dependence of annealing temperatures in Ar ambience on XRD spectra for TaN thin films...
FIG. 2. The electrical resistivity and normalized XRD intensities of TaN(110)/TaN(200) and TaN(220)/TaN(200) for TaN/th-SiO$_2$/Si(111) as a function of annealing temperature in Ar ambience.

FIG. 3. Annealing temperature dependence of XRD spectra for TaN/th-SiO$_2$/Si(111) substrates, where the annealing was performed in N$_2$ ambience.

FIG. 4. The electrical resistivity and normalized XRD intensities of TaN(110)/TaN(200) and TaN(220)/TaN(200) for TaN/th-SiO$_2$/Si(111) as a function of annealing temperature in N$_2$ ambience.

From Fig 3, TaN(220) peak started to observe from the annealing temperature at 400$^\circ$C, which is much lower than the case of Ar as shown in Fig. 1. In Figs.1 and 3, the diffraction angle of TaN(111) shifts to higher angle with increasing annealing temperature up to 550$^\circ$C. It has been reported that the diffraction angle of TaN(111) shifts to lower angle with increasing N$_2$ fractions in mixed N$_2$/Ar gases for sputter deposition of TaN, which causes an increase in electrical resistivity of TaN films [4]. They reported that N-rich phases, e.g., Ta$_3$N$_5$, Ta$_5$N$_6$ could be attributed to the steeply increased resistivity of the TaN films with increasing partial N$_2$ pressure in N$_2$/Ar gases. Based upon this reports, our results showing the higher shift of the diffraction angle of TaN(111) with increasing annealing temperature can be interpreted by a decrease in nitrogen in TaN films. We assume that N-rich TaN films were grown in as-deposited samples and then the TaN films were varied to stoichiometric composition with the annealing. Figure 4 shows an annealing temperature dependence of electrical resistivity and crystallographical orientation of TaN films shown in Fig. 3. In Fig. 4, the electrical resistivities of TaN thin films were increased with increasing annealing temperature above 400$^\circ$C. This observation by us is different from the reported results, which showed an increase in resistivity of TaN thin films when the diffraction angle of TaN(111) shifted to lower angles [4]. Next, we will discuss about the reason of this difference. From Fig. 4, one can see that the electrical resistivity of TaN thin films rapidly increases with increasing TaN(220) intensity. We assumed that in N$_2$ ambient annealing nitridation of TaN thin films was promoted, which results in the formation of TaN (220) at lower temperatures. From these results we can say that the electrical resistivity of TaN(220) crystals was higher than that of TaN(111) crystals and the preferential growth of TaN(220) had to be suppressed to obtain TaN films with lower resistivity. Thus, we determined to perform post deposition annealing in Ar ambience. It should be noted that after the N$_2$ annealing at 600$^\circ$C, the diffraction angle of TaN(111) returned to the original diffraction angle of TaN(111) for as-deposited samples as shown in Fig. 3. This reason is currently unclear.
FIG. 5. Comparison of XRD spectra between various types of Cu underlayered structures.

FIG. 6. Comparison of resistivity and FWHM of Cu(200) between various types of Cu underlayered structures.

B. MIS properties

Figure 5 shows comparison of XRD spectra between various types of Cu underlayered structures: Cu on Si (Cu/Si), Cu/th-SiO$_2$/Si, Cu/TaN/th-SiO$_2$/Si, and Cu/TaN/HSQ/Si. In Fig. 5, the three main peaks were observed at 43.3 degrees, 50.4 degrees and 74.1 degrees, which originate from the cubic structures with Cu(111), Cu(200) and Cu(220) orientations, respectively. Fig. 6 shows the comparison of resistivity and (FWHM) of Cu(200) peak for the samples used in Fig. 5. Although the FWHMs of Cu(200) for samples with Cu/Si, Cu/th-SiO$_2$/Si and Cu/TaN/th-SiO$_2$/Si structures were observed sharply, that for the sample with Cu/TaN/HSQ/Si structures was relatively broad, which makes the resistivity higher. Between two samples with Cu/Si and Cu/th-SiO$_2$/Si structures in Fig. 6, both the full width at half maximum electrical resistivity and FWHM of Cu(200) were almost the same. On the other hand, the resistivity of Cu/TaN/th-SiO$_2$/Si was slightly lower than that of Cu/Si and Cu/th-SiO$_2$/Si, although the FWHM of Cu(200) of Cu/TaN/th-SiO$_2$/Si were higher than that of Cu/Si and Cu/th-SiO$_2$/Si. One reason for this contradiction may be explained from our previous results that the Cu films with higher Cu(220) peak intensity get the resistivity of Cu thin films lowered (data not shown here).

Fig. 7 shows the electrical resistivity of the Cu/TaN/th-SiO$_2$/Si and Cu/TaN/HSQ/Si structures as a function of annealing temperature in Ar ambience. From Fig. 7, the electrical resistivity of Cu/TaN/th-SiO$_2$/Si system was almost the same in the annealing temperatures up to 500$^\circ$C. On the other hand, the electrical resistivity of Cu/TaN/HSQ/Si showed, however, a drastic decrease after annealing at 300$^\circ$C and it was almost steady between 300 and 500$^\circ$C. In order to clarify the behavior of electrical resistivity of Cu/TaN/HSQ/Si against annealing temperature, XRD spectra of samples with Cu/TaN/HSQ/Si structures were measured and the results are shown in Fig. 8 as a function of annealing temperature. It can be seen from Fig. 8 that for as-deposited samples, both peak intensities of Cu(111) and Cu(200) were clearly lower and FWHM of Cu(200) was broader in comparison with the annealed samples, which resulted in an increase in resistivity for as-deposited samples.

Annealing temperature dependences of C-V characteristics of two types of MIS diodes, Cu/TaN/th-SiO$_2$/Si(100) and Cu/TaN/HSQ/Si(100) were shown in Fig. 9 and Fig. 10, respectively. In Fig. 10, one can notice a gradual increase in capacitance value by applying negative applied voltages, which is anomalous for CV curve of MIS diodes. The anomalous C-V characteris-
FIG. 9. Annealing temperature dependence of C-V characteristics for Cu/TaN/th-SiO$_2$/p-Si(100).

FIG. 10. Annealing temperature dependence of C-V characteristics for Cu/TaN/HSQ/p-Si(100).

tics in Fig. 10 are due to larger dielectric loss values of $0.51 \pm 0.59$ for Cu/TaN/HSQ/p-Si(100) than those of $0.019 \pm 0.025$ for Cu/TaN/th-SiO$_2$/p-Si(100) in Fig. 9, where dielectric loss values were measured simultaneously by CV measurements at 960 kHz by applying AC bias of 40 mV and they are known to originate from AC leakage current. Tables I and II summarize the annealing temperature dependences of C-V and I-V characteristics of MIS diodes with different types of dielectric thin films, th-SiO$_2$ and HSQ, respectively. For Cu/TaN/th-SiO$_2$/Si(100) MIS diodes, negative flat band shift of $V_{fb}=\mp 6.0$ V with hysteresis width of $\Delta V_{fb}=1.5$ V were observed from as-sputtered samples. After the annealing, both values became smaller. The similar tendency was observed from Cu/TaN/HSQ/Si(100) MIS diodes.

Compared the C-V characteristics of two types of MIS diodes with as-sputtered state, the $V_{fb}$ and $\Delta V_{fb}$ values of th-SiO$_2$ showed better characteristics than those of HSQ films. The leakage current values measured at $-20$ V of both diodes are also shown in tables I and II. With increasing the annealing temperature, the leakage current values of both diodes became smaller. We consider that this tendency is probably interpreted by a decrease in damage induced in dielectrics by sputtering with increasing the annealing temperature, which was evidenced by an improvement of C-V and I-V characteristics by post-sputter annealing. There is a further evidence that for Al (deposited by resistive heated evaporation)/th-SiO$_2$/Si(100) MIS diodes, the $V_{fb}$ and $\Delta V_{fb}$ were $-3.9$ V and $0.1$ V, respectively, which were apparently lower than that of both MIS diodes in this study. Figure 11 shows the cross-sectional SEM image and the EDX mapping of O, N and Ta for TaN/th-SiO$_2$/Si, which was deposited at sputtering power of 200 W in N$_2$ gas flow ratio of 20%. From the mapping of Fig. 11, the diffusion of oxygen from SiO$_2$ layer into adjacent TaN thin films can be clearly identified. We considered that the negative flat band shift of $V_{fb}$ is caused by sputtering damage. The sputtered oxygen from SiO$_2$ surfaces was caught by tantalum layer because of higher oxidation degree of tantalum than that of silicon. After annealing, damaged and oxygen-poor SiO$_2$ films were recovered by supplying oxygen from TaN layers involving oxygen during annealing. The damage recovery of dielectrics film leads to the reduction of $\Delta V_{fb}$ and leakage current as well as a decrease in Cmax. In our understanding, amount of oxygen involved in TaN films deposited on HSQ/Si during TaN deposition could be higher than that deposited on th-SiO$_2$/Si. Thus, the higher oxygen content in TaN thin films can cause higher oxidation of Cu when Cu was deposited on TaN by sputtering. The high electrical resistivity and low peak intensities of Cu(111) and Cu(200), which was only observed from as-deposited Cu/TaN/HSQ/Si samples (as was shown in Figs. 7 and 8), could be explained by defective surface structures of TaN due to the weaker Si-O bonding of HSQ films than that of th-SiO$_2$. After annealing, oxygen involved in Cu films was moved toward TaN/HSQ films because the oxidation degree of Cu was higher than that of TaN.

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<th>$\Delta V_{fb}$ [V] $I@-20V$ [$\mu$A]</th>
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TABLE I. Summary for the annealing temperature dependences of C-V and I-V characteristics of MIS diodes with Cu/TaN/th-SiO$_2$/Si(100) structures.

TABLE II. Summary for the annealing temperature dependences of C-V and I-V characteristics of MIS diodes with Cu/TaN/HSQ/Si(100) structures.
is lower than that of Ta and Si. Figure 12 shows the leakage current values measured at $-20\, \text{V}$ of three types MIS diodes as a function of annealing temperature. One can notice that two types of MIS diodes including TaN thin films reduced the leakage current values with increasing annealing temperature, whereas the MIS diode without TaN thin films increased the leakage current value. Actually, it has been reported that Cu diffusion into SiO$_2$ starts at $250-300$ $\degree\text{C}$ [13]. From this result, we can say that TaN thin films had the barrier property for suppressing the diffusion of Cu into th-SiO$_2$ thin films.

It should be noticed that the leakage current for as-deposited Cu/th-SiO$_2$/Si was lower than that for as-deposited Cu/TaN/dielectrics/Si. We discuss the origins of this difference for as-deposited samples. We assumed that the amount of oxygen involved in films was dependent on the degree of oxidation of an atom involved in films. The degree of oxidation of Ta is higher than that of Si. When TaN films are deposited on th-SiO$_2$ films, oxygen atoms reverse-sputtered and/or diffused from th-SiO$_2$ surfaces were caught by Ta atoms in TaN layers shown in Fig. 11. We believe that the insufficient oxygen thus produced in th-SiO$_2$ films caused the high leakage current. However, when Cu is deposited directly on th-SiO$_2$ films, the reverse-sputtered and/or diffused oxygen from th-SiO$_2$ layer could stay in th-SiO$_2$ layer, because the degree of oxidation of Cu is lower than that of Si. In Fig. 12, the reason why the leakage current for as-deposited Cu/th-SiO$_2$/Si was lower than that for as-deposited Cu/TaN/dielectrics/Si is thought to be due to the effects mentioned above.

IV. CONCLUSIONS

We investigated the electrical resistivity of TaN thin films as a function of annealing temperature and ambience before the deposition of Cu films. It was found from the XRD and resistivity measurements that the growth of TaN(220) made the resistivity of TaN thin films higher and the (200)-oriented TaN films have lower resistivity than those of (111)- and (220)-oriented TaN films. As for the difference of annealing ambience, the appearance of TaN(220) was suppressed by annealing below $600\degree\text{C}$ in Ar ambience, while it was suppressed by annealing below $400\degree\text{C}$ in N$_2$ ambience. We believe that the increase in resistivity above $400\degree\text{C}$ in N$_2$ ambience is caused by the promotion of nitridation of TaN, which results in the formation of TaN (220) at lower temperatures.

After the deposition of Cu films on TaN/dielectric/Si, where either the thermally grown th-SiO$_2$ or spin-on dielectric (SOD) hydrogen silsesquioxane (HSQ) films was used as a dielectric layer, we observed an improvement of crystalline quality of Cu and a decrease in resistivity of Cu films as well as an improvement of MIS properties for both dielectrics with increasing annealing temperature up to $500$ $\degree\text{C}$. The improvement of MIS diode is presumably due to the recovery of sputter damage of dielectric films during the annealing in Ar ambience. On the other hand, Cu diffusion barrier properties of MIS diodes without TaN films were degraded above $300\degree\text{C}$ presumably due to the diffusion of Cu into the dielectric films. One possible model of sputter damage is an oxygen desorption from dielectric films due to the reverse-sputtering of dielectric films during the sputtering of Ta in Ar and N$_2$, which results in an increase in leakage current of MIS diodes.

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