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New method to improve thermal stability in the interface of silicon and tungsten by the interposition of plasma deposited tungsten nitride thin film

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Thermally stable tungsten nitride/tungsten bilayer has been proposed for the application of metallization. This bilayer is sequentially formed by plasma enhanced chemical vapor deposition without breaking vacuum. The Rutherford backscattering spectrometry and cross-sectional transmission electron microscopy reveal that the interaction between the W and Si substrate can be prevented by interposing a 800-Å-thick $W_{67}N_{33}$ layer. The $W_{67}N_{33}$/W bilayer maintains the integrity of the interface during annealing at 850 °C for 30 min without the formation of Si_2W and interdiffusion phenomena. Sheet resistivity of the $W_{67}N_{33}$/W bilayer is gradually decreased from 17 to 12 $\mu\Omega$ cm at annealing temperatures up to 850 °C.

Tungsten (W) has been studied as a low resistive refractory metallization material in very large scale integrated (VLSI) circuit metallization schemes.[1] However, the submicrometer process causes particularly serious problems in the W metallization, such as increases in contact resistance due to the silicidation and degradation of shallow junction by the interdiffusion of W and Si during heat treatment.[2] Therefore, various diffusion barrier materials such as physical vapor deposited (PVD) TiN, ZrN, W-N, and HfN have been used to establish a thermally stable W contact system.[3] Then, several disadvantages of PVD barrier layers, such as poor step coverage, residual tensile stress, and poor control of stoichiometry of metal nitride composition are undesirable for chemical vapor deposited W metallization. Consequently, chemical vapor deposited metal nitride films such as TiN and $W_{100-x}N_x$ have been intensively studied.[4] However, low pressure chemical vapor deposition (LPCVD) of $W_{100-x}N_x$ film has been deposited at temperatures as high as 450–700 °C[5] and the detailed properties of LPCVD-$W_{100-x}N_x$ film as a barrier layer have not been reported yet. In this work, we have proposed a new method to prepare the plasma enhanced chemical vapor deposition (PECVD)-$W_{67}N_{33}$/W bilayer without interrupting the deposition process since $W_{67}N_{33}$ and W films are sequentially deposited by the same PECVD system without breaking vacuum. Particularly, $W_{67}N_{33}$ film can be deposited at a relatively lower temperature (about 350 °C) than LPCVD (about 450–700 °C) due to the plasma assisted fragmentation process of WF_6-NH_3-H_2 gas system. After deposition of $W_{67}N_{33}$ film, W film is in sequence deposited with the WF_6-H_2 gas system. The PECVD-$W_{67}N_{33}$/W bilayer has several benefits, i.e., the resistivity of PECVD-W film is as low as that of LPCVD-W,[6,7] $W_{67}N_{33}$ film suppresses encroachment and SiO_2 etching during CVD-W deposition,[8] and the adhesion strength of W is effectively improved.[9] Therefore, we have investigated the thermal stability of a plasma deposited $W_{67}N_{33}$/W bilayer at annealing temperatures up to 850 °C for 30 min.

Starting materials are phosphorus-doped (100)-oriented Si wafers with resistivities of 5–6 Ω cm. Si wafers are cleaned by the RCA method and spin dried.[10] The deposition of W and $W_{67}N_{33}$ film is carried out with a homemade parallel-type cold wall PECVD reactor.[7] In order to remove the native oxide layer on Si wafers, H_2 and Ar sputtering are carried out in the PECVD reactor by controlling the rf power density. The partial pressures of WF_6 and NH_3 are fixed at 2×10^{-2} and 1×10^{-2} Torr, respectively (WF_6, NH_3 flow rates are 4 and 2 sccm), and the H_2 flow rate is fixed at 100 sccm. 800-Å-thick $W_{67}N_{33}$ thin film is deposited with a $H_2/NH_3/WF_6$ flow ratio of 25/0.5/1 and then 1500-Å-thick W thin film is *in situ* deposited on this $W_{67}N_{33}$ layer with a H_2/WF_6 flow ratio of 25/1. The total pressure of the CVD reactor is maintained at 0.5 Torr by controlling the throttle valve from the initial base pressure of 10^{-6} Torr. The deposition temperature is 350 °C and rf power density is 0.7 W/cm^2. Resistivity and thickness are determined by a four-point probe and the β-ray backscattering method, respectively, and the atomic concentration of N in $W_{67}N_{33}$ film is measured by Rutherford backscattering spectrometry (RBS). Furnace annealing is carried out at 850 °C for 30 min in Ar ambient after evacuating the initial pressure of furnace down to 10^{-4} Torr. Annealing effects on thermal stability of the $W_{67}N_{33}$/W bilayer are studied with x-ray diffraction (XRD), RBS and cross-sectional transmission electron microscopy (XTEM).

In order to study the stoichiometry of $W_{100-x}N_x$ thin film deposited with a $H_2/NH_3/WF_6$ flow ratio of 25/0.5/1, RBS measurement is carried out for the Si/$W_{67}N_{33}$/W structure as shown by the solid line of Fig. 1. The RBS spectrum is obtained through the following conditions; He acceleration energy is 2.42 MeV and its scattering angle is 170°. The tungsten signal can be seen in backscattering at high energy of 2.3 MeV, and the Si signal is around 1.2 MeV. N signal can be obviously seen around 0.78 MeV although the back-

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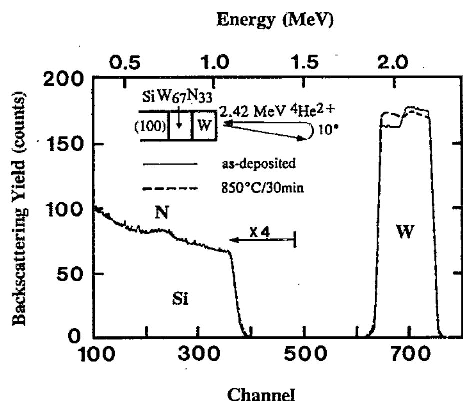

FIG. 1. RBS spectra for $Si/W_{67}N_{33}/W$ as-deposition after furnace annealing at 850 °C for 30 min.

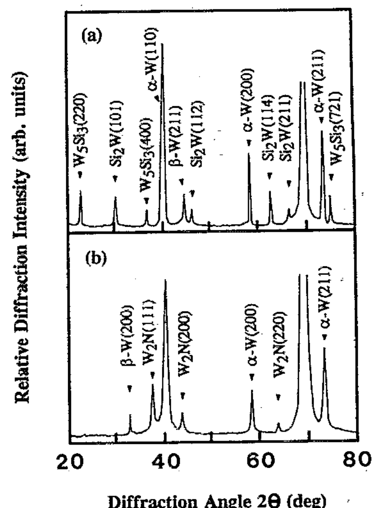

FIG. 3. XRD patterns for (a) Si/W and (b) $Si/W_{67}N_{33}/W$ samples after furnace annealing at 850 °C for 30 min.

scattering yield signal of N, whose atomic number is smaller than Si, overlaps with the Si signal. From the calculation of the RBS spectrum of $W_{100-x}N_x$, it is determined that the atomic ratio of W to N is $W_{67}N_{33}$.[11]. The yield height of W atoms in the $W_{67}N_{33}$ film (1.8–2.0 MeV) is lower than that in the W film (2.0–2.3 MeV), which is represented on the right side of the solid line in Fig. 1, because backscattering yield from the W atoms in the $W_{67}N_{33}$ film is reduced due to the N atoms. A comparison of the solid and dashed lines of Fig. 1 also shows the annealing effect on thermal stability of $Si/W_{67}N_{33}/W$. After annealing at 850 °C for 30 min the W yield of $W_{67}N_{33}$ film (1.85–2.05 MeV) is higher than that of as-deposited $W_{67}N_{33}$ film and the W yield of W film (2.05–2.3 MeV) is rather lower than that of as-deposited W film, which is ascribed to the intermixing of nitrogen atoms from $W_{67}N_{33}$ to W film during annealing process. Although the stoichiometry of $W_{67}N_{33}$ is changed to $W_{83}N_{17}$ (dashed line in Fig. 1) after annealing, RBS spectra of $Si/W_{67}N_{33}/W$ before and after annealing indicate that the W (1.85 MeV), Si (1.2 MeV), and N (0.78 MeV) signals do not shift and remain unchanged at the annealing temperature up to 850 °C for 30 min. In contrast, RBS spectra of Si/W before and after annealing at 850 °C 30 min (solid and dashed lined in Fig. 2 show that the low energy part of the W signal extends from 2.1 to 1.86 MeV and high energy part of Si signal also extends to 1.28 MeV, which implies the interdiffusion between W and Si during annealing process. Corresponding to such interdiffusion, the reduced yield of the top and left side of W signal also reveal the silicidation between W and Si. Therefore, from the RBS results of $Si/W_{67}N_{33}/W$ and Si/W, it can be concluded that 800 Å $W_{67}N_{33}$ layer maintains the role of diffusion barrier inhibiting the interface reaction with Si surface during high temperature annealing process even though intermixing of N atoms occurs between W and $W_{67}N_{33}$. XRD patterns corresponding to the equivalently annealed samples of Si/W [Fig. 3(a)] and $Si/W_{67}N_{33}/W$ [Fig. 3(b)] show additional evidence for the performance of the $W_{67}N_{33}$ diffusion barrier to prevent the silicidation between W and Si. Figure 3(a) shows that Si_2W and W_5Si_3 phases are formed after annealing at 850 °C for 30 min. However, in the as-deposited $W_{67}N_{33}$ film, (110)-oriented α-W and (200)-oriented W_2N peaks are dominantly observed. After annealing at 850 °C for 30 min, (110)-oriented α-phase W remains unchanged although (200)-oriented β-phase W appears because N atoms are mixed into the W film as an impurity. (111)- (220)-oriented W_2N peaks are observed together with (200) oriented W_2N peak as shown in Fig. 3(b). Atomic force microscope attached to scanning tunneling microscopy shows that average surface roughness of the annealed W film on $W_{67}N_{33}$ is about 150 Å, which is smoother than that (200 Å) of W film deposited on Si before annealing. XTEMs of Si/W [Fig. 4(a)] and $Si/W_{67}N_{33}/W$ [Fig. 4(b)] interfaces are performed to investigate the reaction in these interfaces during annealing process at 850 °C for 30 min. Figure 4(a) shows the severe interfacial reaction between W and Si. Hence, the W-Si interface is destructed by deep penetration of W after heat treatment. Figure 4(b) indicates that W-Si interface keeps a crystalline perfection because $W_{67}N_{33}$ layer prevents the interdiffusion between W and Si. The results of XTEM are well consistent with the results of RBS, which show that

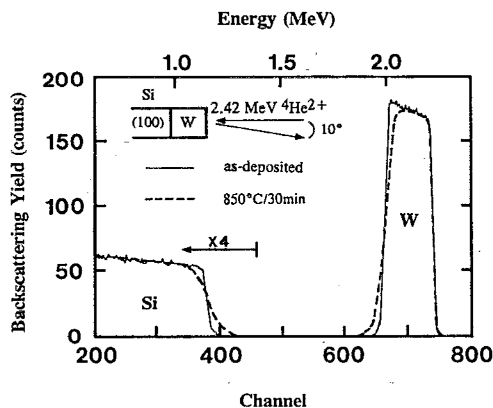

FIG. 2. RBS spectra for Si/W as-deposition after furnace annealing at 850 °C for 30 min.

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FIG. 4. Cross-sectional transmission electron micrographs of (a) Si/W and (b) Si/$W_{67}N_{33}$/W annealed at 850 °C for 30 min.

the interposed $W_{67}N_{33}$ film prevents the interaction between W and Si.

In general, sheet resistivities of metal thin films indirectly reveal the metallurgical interactions between W or $W_{67}N_{33}$/W bilayer and Si substrate because resistivities of these films are increased by the formation of silicide. Figure 5 shows the resistivities of W, $W_{67}N_{33}$/W films a function of annealing temperatures. The resistivity of 2000-Å-thick W film (closed circular shape in Fig. 5) is changed from 10 to 29 $\mu\Omega$ cm at the annealing temperature of 850 °C and it reaches up to 59 $\mu\Omega$ cm after 1000 °C (not shown here). From the results of RBS, XRD, and XTEM, the high resistivity of Si/W should be ascribed to the silicidations such as Si_2W and W_5Si_3 formed at the W-Si interface. It is known that, in general, the resistivity of W is affected by impurity scattering, lattice scattering, and crystal structure.[12] In contrast, the resistivity of 1500-Å-thick W on 800-Å-thick $W_{67}N_{33}$ film is slightly decreased from 17 to 12 $\mu\Omega$ cm with increasing the annealing temperature. The reason that the resistivity of $W_{67}N_{33}$/W bilayer decreases with further annealing is explained by the prevention of silicidation, grain growth of $W_{67}N_{33}$ film, and reduction of nitrogen atoms.

In summary, it is concluded that PECVD-$W_{67}N_{33}$/W metallization scheme, which is sequentially deposited with

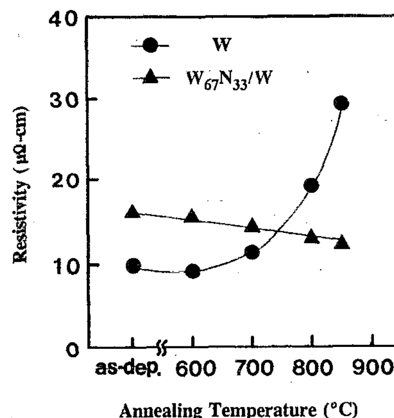

FIG. 5. Variation of resistivity of Si/S and Si/$W_{67}N_{33}$/W samples as a function of furnace annealing temperature.

the same PECVD system, has an unique thermally stable process to eliminate LPCVD and PVD processes for refractory metal and nitrides such as W, TiN and W-N. In addition, the lower resistivity of the PECVD-W/$W_{67}N_{33}$ bilayer can be achieved after the high temperature annealing processes. After annealing process at 850 °C for 30 min, even though $W_{67}N_{33}$ is changed to $W_{83}N_{17}$, W_2N phases remain. Therefore, the role of the $W_{67}N_{33}$ diffusion barrier can be explained by the impermeable structure of the W_2N layer: $W_{67}N_{33}$ film has face-centered-cubic (fcc) structure of W_2N. Since the packing density of fcc W_2N is higher than that of bcc W, the lattice diffusion through fcc W_2N should occur slower than that in body-centered-cubic W. Also, nitrogen impurities may be spread between W_2N grain boundaries and these N impurities block the grain boundary diffusion path.

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