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New insights on the effect of hydrogen to tungsten hexafluoride partial pressure ratio on plasma deposited tungsten thin films

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Resistivities of tungsten thin films deposited by plasma enhanced chemical vapor deposition are very sensitive to the H_2/WF_6 partial pressure ratio, while the resistivities of tungsten films deposited by low pressure chemical vapor deposition are insensitive to the H_2/WF_6 ratio. The reason is investigated with x-ray diffraction, transmission electron microscopy, Auger electron spectroscopy and optical emission spectroscopy. As a result, when the H_2/WF_6 partial pressure ratio is higher than 15, plasma deposited tungsten has a low resistive (11 $\mu\Omega$ cm) bcc structure without F impurities. However, if the H_2/WF_6 ratios are decreased, porous and β -phase W films are formed due to the incomplete reduction of F concentrations.

It has been known that plasma enhanced chemical vapor deposition of tungsten (PECVD-W) thin films have high resistivity of about 48–100 $\mu\Omega$ cm.¹⁻³ Recently, Greene and Hess,⁴ after using the reactant system of WF₆ and H₂, reported that PECVD-W films have the possibility of a relatively lower resistivity. Especially, they suggested the interesting fact that the plasma environment created a nonequilibrium surface condition, which, in effect, was similar to an increase in the effective surface temperature. We reported that low resistive PECVD-W thin films of about 11 $\mu\Omega$ cm were obtained with WF₆-H₂ by controlling the real surface deposition temperatures⁵ since the crystal structure and removal of fluorine were very sensitive to deposition temperature. In order to obtain low resistive PECVD-W, it may be also important to investigate the effect of the H₂/WF₆ partial pressure ratio on electrical resistivity and crystal structure of PECVD-W thin films. However, there is still no intensive work that pays attention to the detail plasma reaction process when the H_2/WF_6 partial pressure ratios are varied. In this work, in order to monitor the plasma deposition process dependence on the various H_2/WF_6 partial pressure ratios, the optical emission actinometric technique was performed using Ar gas as the actinometric reference gas for F atom estimation. After the deposition process, W film thickness is measured by the β -ray backscattering method. The resistivity, the compositional analysis and the crystal structure of deposited films are examined with a four-point resistivity probe, Auger electron spectroscopy (AES) and electron spectroscopy for chemical analysis (ESCA), transmission electron microscopy (TEM), and x-ray diffraction (XRD). As a result, it is found that the resistivity and the microstructure of PECVD-W are strongly dependent on the H_2/WF_6 partial pressure ratios.

The substrates are boron-doped (100) oriented Si wafers with a resistivity of 5–6 Ω cm. In order to study blanket tungsten deposition on SiO₂ layers, some wafers are oxidized and 5000 Å SiO₂ layers are obtained. Tungsten thin-film deposition on both Si and SiO₂ layers is carried out in home-built PECVD reactor and the reactant gases are WF₆, H₂, and Ar. Deposition temperatures of 350 °C are measured by a thermocouple in contact with the Si surface.⁵ The rf power density is 0.7–1 W/cm². The H₂/WF₆ partial pressure ratios were varied from 4 to 25 while WF₆ partial pressure was fixed at 2×10^{-2} Torr. The total pressure was maintained at 5×10^{-1} Torr by controlling a throttle valve.

The effects of H₂/WF₆ partial pressure ratio on the resistivities of both low pressure chemical vapor deposition (LPCVD) and PECVD-W thin films of comparable thicknesses (8000 Å) grown on Si were examined as shown in Fig. 1. The resistivity of LPCVD-W did not change with the H_2/WF_6 partial pressure ratio, but the resistivity of PECVD-W decreased with the higher H_2/WF_6 partial pressure ratio and the resistivity of PECVD-W films were as low as the values of LPCVD-W films (10–11 $\mu\Omega$ cm) when the H_2/WF_6 partial pressure ratio was higher than 15. Therefore, we try to explain the reasons for the dependence of the resistivities of PECVD-W on the H_2/WF_6 partial pressure ratios. At first, x-ray diffraction patterns were studied for LPCVD and PECVD-W films grown at $Ar/WF_6 = 5$, $H_2/WF_6 = 3$ and 25. Figure 2(a) reveals that PECVD-W grown with the H_2/WF_6 ratio of 3 has β -phase W, although the PECVD-W has α -phase W structure at a H_2/WF_6 ratio of 25 as shown in Fig. 2(b). However, Fig. 2(c) shows that LPCVD-W has an α -phase W structure at Ar/WF_6 gas mixture. This means that in LPCVD-W thin-film growth, the reduction process of WF_6 is possible due to Si consumption without H₂ reduction. It was confirmed with ESCA that the LPCVD-W on the bar Si surface grown are Ar/WF_6 is a pure W thin film and the thickness is about 1000 Å, which is within the limit thickness of the silicon reduction process. Therefore, if there is no native oxide layer on the Si surface, it is plausible that the purity of LPCVD-W is insensitive to H_2/WF_6 partial pressure because the silicon reduction process is possible as well as hydrogen reduction. However, Figs. 2(a) and 2(b) indicate that whether the PECVD-W has β -phase or not strongly depends on H₂/WF₆ partial pressure ratios. According to our previous work,⁵ the activation energy of

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FIG. 1. The variation of resistivities of LPCVD and PECVD-W thin films grown on Si as a function of H_2/WF_6 partial pressure ratio.

PECVD-W (0.34 eV) was about 1/2 the value (0.72 eV) of LPCVD-W and the deposition rate of PECVD-W was faster than that of LPCVD-W, which is only controlled by the heterogeneous surface region of WF₆, H₂, and Si at the equivalent deposition conditions. However, PECVD-W deposition process dependence of H_2/WF_6 partial pressure ratio can be explained as follows: the PECVD-W thin-film growth is controlled by the gas phase reaction of the glow discharge of H_2 and WF_6 so that abundant F atoms can be involved into the fast growth of the W film when H_2 partial pressure is severely deficient to remove the F atoms. Hess⁶ also noted that resistivity of PECVD-W films increased presumably due to the limited scavenging of F atoms as the H₂/WF₆ partial pressure ratio decreased. Therefore, in order to confirm the relative concentration of F atoms with decreasing H₂/WF₆ partial pressure ratio, optical emission actinometry (OEA) was carried out to monitor in situ the plasma deposition process as the H_2/WF_6 partial pressure



FIG. 2. X-ray diffraction patterns for (a) PECVD-W grown with H_2/WF_6 ratio of 3, (b) PECVD-W grown with H_2/WF_6 ratio of 25, (c) LPCVD-W grown with $Ar/WF_6 = 5$, (d) LPCVD-W grown with H_2/WF_6 ratio of 25.



FIG. 3. The relative concentration of fluorine atoms vs H_2/WF_6 partial pressure ratio.

ratios was varied from 10 to 50 with Ar as a reference actinometric gas. The Ar partial pressure was maintained at 2% of the total pressure, which is within the limit of actinometric gas. The deposition temperature was fixed at 350 °C and rf power was kept at a constant value of 1 W/cm² during the OEA measurement. From the OEA spectrum, several emission lines can be identified⁷ from W (4074 Å), H (6562 Å), F (7037 Å), and Ar (7504 Å). Therefore, it is plausible that these W, H, F, and Ar radicals are produced from the glow discharge of WF₆, H₂, and Ar. The emission intensity of F (7037 Å), $I_{\rm F}$ is known to satisfy the actinometric relation with the intensity of Ar (7504 Å), I_{Ar} since the two excited states responsible for the optical emission are very close in energy (Ar = 13.7eV, F = 14.75 eV).⁸ With this assumption, the relative changes of F concentration with the variation of H_2/WF_6 partial pressure ratio can easily be determined by the emission intensity measurement, $I_{\rm F}/I_{\rm Ar}$ and the partial pressure of Ar, [Ar] as shown in Eq. (1).

$$[\mathbf{F}] \propto [\mathbf{Ar}] I_{\mathbf{F}} / I_{\mathbf{Ar}}, \tag{1}$$

where [F] is the relative concentration of F atoms. Figure 3 shows that as the H_2/WF_6 partial pressure ratio is increased, the relative concentration of F exponentially decreases. Although the fragmentation pathway for WF₆ is still not solved completely, it is possible that WF₆ gas gives off F and converts to WF_x (x = 4, 5). According to Creighton's work on the LPCVD-W process,⁹ it is known that WF₄ and WF₅ are observed during thermal pyrolysis of WF₆, and those WF_x react with atomic hydrogen and produce W radicals. Similarly in the PECVD-W process, the atomic hydrogen will react with F and WF_x and be removed as HF in the gas phase. Therefore, it is plausible to assume that F atoms remain in abundance due to the deficiency of H₂ at the fixed pressure of WF₆.

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FIG. 4. Transmission electron micrographs for PECVD-W thin films. (a) DF image of 1000 Å W films grown with H_2/WF_6 ratio of 10 (inset: SAD pattern) (b) BF image of 1000 Å W films grown with H_2/WF_6 ratio of 10 (c) DF image of 1000 Å W films grown with H_2/WF_6 ratio of 25 (inset: SAD pattern) (d) BF image of 1000 Å W films grown with H_2/WF_6 ratio of 25 (e) DF image of 2000 Å W films grown with $WF_6/SiH_4/H_2$ ratio of 1/0.5/10 (inset: SAD pattern) (f) BF image of 2000 Å W films grown with $WF_6/SiH_4/H_2$ ratio of 1/0.5/10.

In order to determine the initial stage of W film growth according to H_2/WF_6 ratios, TEM studies were carried out for 1000 Å thicknesses of PECVD-W films grown at the H_2/WF_6 partial pressure ratios of 10 and 25, respectively. The selected area diffraction (SAD) pattern of inset of Fig. 4(a) shows that the W film grown with the H_2/WF_6 partial pressure ratio of 10 has bcc (α -W) and A-15 structures (β -W), and the dark field (DF) image of Fig. 4(a) shows that grain sizes are about 300–900 Å. The bright field (BF) image of Fig. 4(b) shows that W grains are porous. However, if the H_2/WF_6 partial pressure ratio is increased to 25, it is found from Figs. 4(c) and 4(d) that the microstructure of W film is a bcc structure and the grains are not porous. The sizes are about 700–1000 Å. Therefore, it is

plausible that as the H₂ partial pressure decreases, the microstructure is changed by containing β -W along with α -W. The reason for containing β -W and the formation of porous films can be attributed to the incomplete reduction of F. In order to enhance the reduction of F on plasma deposited W films, SiH₄ gas adds to the H₂/WF₆ ratio of 10. The ratio of SiH_4/WF_6 is maintained at 0.5. As a result, the resistivity of the W film is reduced to 10 $\mu\Omega$ cm and a TEM of the 2000 Å W film [Figs. 4(e) and 4(f)] shows that β -phase and porous W films are not observed. AES measurements were carried out for W films grown at H_2/WF_6 input ratios of 10 and 25, respectively. At the H_2/WF_6 partial pressure ratio of 10, a F peak was observed at 647 eV. However, at the H_2/WF_6 input ratio of 25, the F peak was not observed, and the AES depth profile also confirms that F is below the detection limit of AES.

In summary, by decreasing H_2/WF_6 partial pressure ratios to values less than 10, F atoms may not be successfully removed due to the relatively low H_2 partial pressure. Consequently, porous β -phase W grains are observed and grain sizes are smaller than those of a PECVD-W film grown at H_2/WF_6 partial pressure ratio of 25. In addition, at the WF_6SiH_4/H_2 flow ratios of 4/2/40 sccm, large grain sizes and dense films are grown even if the H_2/WF_6 partial pressure ratio is fixed at 10. Therefore, it is concluded that the H_2/WF_6 partial pressure ratios is closely related with microstructures and crystal structures of PECVD-W, and the resistivity also depends on the microstructure and crystal structure since electron mobility is limited by grain boundary and impurity scattering.¹⁰

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