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Laser Initiated Chemical Vapor Deposition of Tungsten Films on Silicon Dioxide

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Photo-chemical vapor deposition technique using ArF excimer laser has been employed to deposit W films on SiO_2 from the gas phase reaction of WF_6 and H_2. Well-adhesive films to SiO_2 have been obtained for substrate temperatures higher than 300°C or H_2/WF_6 gas flow ratios above 2. For these films, excellent conformal coverage has been observed without W encroachment. Film resistivities as low as two times the value of bulk W have been obtained at temperatures raging 250°- 500°C. The activation energy of film formation, 8.2 Kcal/mol, is half that for thermal CVD

1.INTRODUCTION

In order to be able to take full advantage of the benefits emerging from technologies leading to faster and smaller Si LSI devices, it has become necessary to develop new materials to take the place of polycrystalline silicon (polysilicon) in gates and interconnections. The formation, characterization, and properties of refractory metals have, therefore, once again become subjects of study due to their applicability to the fabrication of low-resistance gates, interconnections and contacts for VLSIs.

Refractory metals are most commonly prepared by some forms of physical vapor deposition (PVD) process (sputtering[1], electron beam evaporation[2], etc.) or chemical vapor deposition (CVD) process (thermal CVD[3], RF-enhanced CVD[4], etc.). Chemical vapor deposition techniques have several advantages over PVD techniques. These CVD techniques allow achievement of uniform step coverage over patterned substrates. Moreover, highly pure depositions and excellent uniformity of thickness can be assured without the need for ultra-high-vacuum techniques.

In the context of film formation on SiO_2 at temperatures around 400°C, however, W CVD using WF_6 as the W source is very difficult. Adhesive W film deposition on SiO_2 from WF_6 requires substrate temperatures higher than 700°C. Accordingly, selectively deposited W on polisilicon and single crystalline silicon surfaces has been demonstrated as possible interconnections shunt material and contact diffusion barrier by Gargini and Beinglass[5,6].

As a potential solution to the above mentioned problems, photo-assisted process technologies, including laser-initiated CVD (LCVD), have received much attention because of reductions in process temperature and process-induced damage, as well as other advantages (direct pattern writing, etc.). Deutsch and Rathman[7] recently showed that ArF excimer laser radiation can be useful to deposit W film on SiO_2 at temperatures lower than 500°C by initiating a reaction between WF_6 and H_2.

In the present work, we have also investigated LCVD with the aim of obtaining high quality W film on SiO_2 at low temperatures ($\leq$500°C). We have studied in detail the correlation between characteristics regarding W film adhesion to SiO_2 as well as film resistivity, and film formation conditions. This paper reports on the results of these studies, and also provides of discussion of the activation energy of W LCVD.

2.EXPERIMENTAL

The experimental apparatus consists of a stainless-steel chamber, vacuum system, WF_6

and H_2 gas flow control system, and ArF laser as shown in Fig. 1. The 193 nm ArF laser (Lambda Physik EMG201) was operated at 5 Hz and an 0.2 J/pulse. A beam having a cross section 30 mm wide and 8 mm high was passed about 10 mm above the substrate through a fused quartz window of the chamber. The WF_6 and H_2 were introduced through mass flow controllers to the chamber evacuated to a background pressure of 10^{-6} Torr. Typical total pressure for the reactant gases was about 1 Torr. The Si substrates, coated by thermal SiO_2, were mounted on a stainless-steel pedestal heated at temperatures between 200° and 500°C.

3.RESULTS AND DISCUSSION

Using ArF excimer laser light irradiation, shiny metallic W films were easily obtained on SiO_2 over a temperature range of 250°-500°C. However, it was difficult to obtain W films that adhered well 3 inch-diameter substrates at temperatures lower than 300°C. In this low temperature region, the films sometimes cracked, or were partly removed. With a substrate temperature decrease down to 200°C, no film formation was found, though W particles were deposited. Good adhesion of the film to SiO_2 was found to occur with an increase in substrate temperature or H_2/WF_6 gas flow ratio.

These results are qualitatively summarized in Fig. 2. The figure indicates that substarte temperature higher than 350°C and an H_2/WF_6 ratio above 2 are necessary to obtain well-adhering films. Deutsch and Rathman[7] predicted that the good adhesion of films deposited on SiO_2 at high temperatures may be due to reduced stress for α(stable phase)-W films. They found the existence of β (metastable phase)- W in films deposited at 330°C, but not in films done at 440°C. In contrast, we found no β-W in all our films grown even at temperatures lower than 330°C, as will be described later. Our results imply that the adhesion of CVD W film to SiO_2 correlates not only to the crystal phase of W film, but also to a chemical reaction among WF_6, $H_2$and SiO_2. At present, however, a more detailed investigation is necessary to facilitate clarification of quantitative details regarding film adhesion to SiO_2.

With these films, excellent conformal step coverage over PSG steps was observed (see Fig. 3). However, figure 3 (a) shows great encroachment, that is, lateral W (or tungsten silicide) penetration underneath PSG steps. The encroachment in this figure runs parallel to the interface between the PSG step and substrate. Encroachment of other shapes was also sometimes observed.

These encroachment phenomena were already observed in conventional CVD W deposition[8], and they are considered to be caused by the reaction of WF_6 with Si substrates. The encroachment observed in conventional CVD was found to increase with an increase of substrate temperature or of WF_6 partial pressure[9]. Similar results were also observed in LCVD W deposition. That is, with an increase of the H_2/WF_6 ratio, no W penetration was found underneath PSG steps, as indicated in Fig. 3 (b). No encroachment was found with a decrease in substrate temperature, either.

Metastable phase β -W is considered to be formed at temperatures lower than 650°C in an enviroment where there is a small amount of impurity oxygen. This β -W sometimes exists in W films grown by other deposition techniques (e.g. electron beam sputtering[10]). Deutsch and Rathman, as mentioned above, found β -W in their films deposited at temperatures lower than 365°C. In our work, however, the results of x-ray diffraction measurements on W films grown even at 250°C indicated no β-W, but only stable phase α -W (Fig. 4). This is likely due to low background pressure of the reaction chamber.

Metastable β -W shows strong electric resistivity (100 - 300 $\mu\Omega\cdot$cm)[11], to which the resistivities of W films grown from $W(CO)_6$ by LCVD are comparable.[12] The existence of β-W in the film accordingly raises film resistivity. As a result, films grown by Deutsch and Rathman show a great temperature dependence of resistivity.[7] And, to obtain resistivities lower than 20 $\mu\Omega\cdot$cm, their films

had to be deposited at temperatures higher than 400°C.

Non-existence of β-W in the films grown in our work could lead to temperature independence for film resistivity. X-ray diffraction measurements imply that our W films features stable, low resistivity. In fact, the resistivities of films thicker than 100 nm exist over the range of 7 - 11 $\mu\Omega \cdot$ cm (Fig. 5). These resistivities are comparable to those for films grown by conventional CVD W, and are lower than those for films formed by other deposition techniques. Figure 5 indicates no thickness dependence of film resistivity in the thickness range 100 - 900 nm. This is in contrast to the great film thickness dependence of resistivity as observed in films grown by conventional CVD.[13] These results imply that LCVD can be used to supply stable W films of low resistivity.

The film formation mechanism of conventional CVD W has been investigated by many researchers. The activation energy of thermal CVD W has been found to be around 16 Kcal/mol, and its energy to be due to the rate determining step of H_2 decomposition on W.[14] Temperature dependence of W deposition rate on SiO_2 and Si substrates using ArF excimer laser irradiation is shown in Fig. 6, together with the thermal CVD rate on Si. Deposition rates in the figure are estimated on the basis of a linear proportion of film thickness to deposition time. The activation energy obtained from the figure for our W-CVD, 8.2 Kcal/mol, was half that for thermal CVD. No difference was found in activation energy between SiO_2 and Si substrates; no difference in activation energy between Si and Al substrates was already observed for thermal CVD[14].

These results indicate that the substrate material does not contribute to the film deposition rate. The activation energy of 8.2 Kcal/mol in LCVD W formation is in agreement with the activation energy of H atom surface diffusion on a W surface. Although H_2 molecules in thermal CVD are thermally decomposed on such a W surface, H atoms are generated by the effect of ArF laser irradiation. ArF laser energy (620 KJ/mol) can release approximately two F atoms from WF_6, because the formation enthalpy of WF_6 is 1750 KJ/mol. Generated F atoms can react easily with H_2 molecules, and the reaction releases H atoms.

4. SUMMARY

Photo-chemical vapor deposition technique using ArF excimer laser has been employed to deposit W films on SiO_2 from WF_6 and H_2 system. Adhesion characteristics of LCVD W film to SiO_2 was found to depend on substrate temperature or H_2/WF_6 gas flow ratio: good adhesion was obtained with the increase of these film growth parameters. Excellent conformal coverage of the films was observed without W encroachment. Film electric resistivities as low as two times the value of bulk W were obtained for substrate temperatures in the range from 250° to 500°C. The laser deposited films include no β phase W, but only α phase W. For formation of these films, the activation energy of 8.2 Kcal/mol was estimated from temperature dependence of deposition rates.

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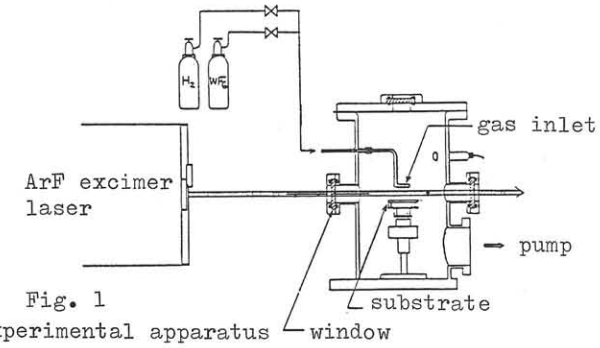

Fig. 1
Experimental apparatus

H_2/WF_6 / Temp.	200	300	400	500 (°C)
2-5	C C A	C C A	A A A A	A A A
0.5	P P C P C	A C C C		
0-0.12	P P P P	R R P	R C P	

Fig.2 Correlation between film adhesion to SiO_2 and growth conditions. A=adhesive, C=cracked, R=partly removed, P=non film (particle).

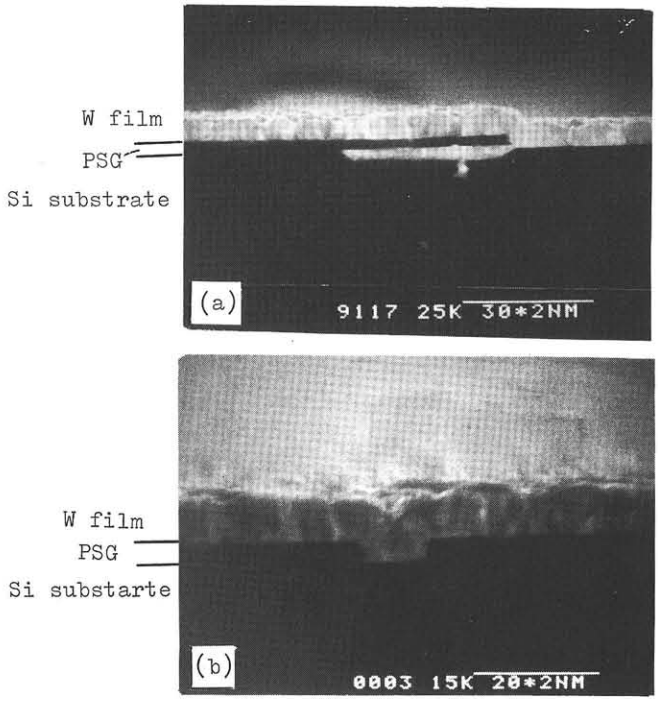

Fig. 3 SEM micrographs showing side views of W films over PSG steps. (a)=a great encroachment (b)=non encroachment

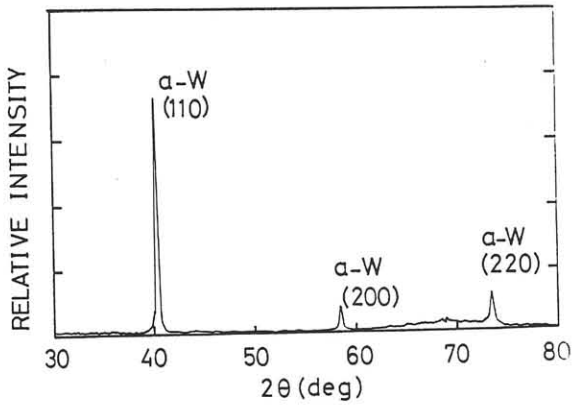

Fig. 4 X-ray diffraction spectra for laser deposited W film on SiO_2 at 250°C.

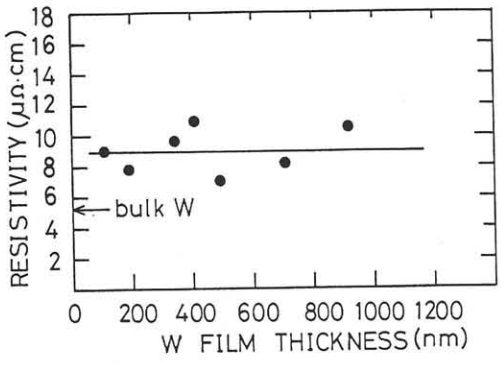

Fig. 5 W film resistivity as a function of film thickness.

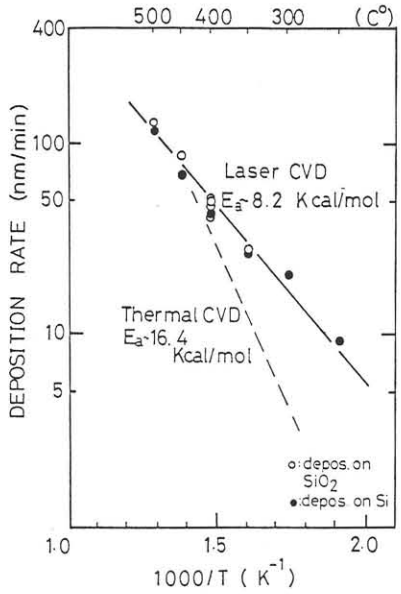

Fig. 6 Temeprature dependence of the depeosition rate for LCVD and thermal CVD.