

Patterned Chemical Vapor Deposition of Tungsten Films on Silicon Dioxide

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Patterned chemical vapor deposition (CVD) is performed to deposit tungsten (W) films on silicon dioxide (SiO_2). First, titanium (Ti)-ion irradiation through a stencil metal mask is performed at 600 eV for a dose of 1.1×10^{16} atoms/cm². Second, Argon-fluoride (ArF) excimer laser-CVD with tungsten hexafluoride (WF_6) and hydrogen (H_2) is carried out for 40 seconds at 400 K. Finally, low-pressure (LP)-CVD is carried out at 600 K. Metallic feature W films appear only on the Ti-ion-irradiation pattern. Without the laser CVD step, no W film deposition occurs. Therefore, laser radiation has essential roles in our experiments.

INTRODUCTION

The maskless metallization process is one of the most attractive interconnection techniques for fabricating future LSIs^{1,2,3}). The aim of the present research is to achieve patterned CVD of W films on SiO_2 .

In conventional LP-CVD with WF_6 and H_2 , W films are selectively deposited on Si but not on SiO_2 . Such selectivity originates in the reduction reaction of WF_6 by Si, not by SiO_2 ⁴). To deposit metal films, two different types of ion irradiation have been adopted and they are performed before the CVD step^{5,6}). Hennessy et al. has demonstrated selective CVD tungsten on Si implanted SiO_2 in which Si acts as a reducing agent of WF_6 ⁶). In their process, however, etching of the SiO_2 surface has been necessitated to expose the Si layer to the reactant gases, because Si has been implanted into the SiO_2 layer at 25 KeV.

In the present research, in order to achieve patterned CVD of W films on SiO_2 ,

Ti-ion irradiation is performed through a stencil metal mask at 600 eV before consecutive processes of laser CVD and LP-CVD. A low-acceleration energy is applied to ensure that Ti is not implanted into the SiO_2 layer. Laser radiation is indispensable for initiating deposition reactions. Our results indicate that a few monolayers of Ti-ion irradiation and laser CVD enable the control of W deposition and the maskless W metallization on SiO_2 .

EXPERIMENTAL

The experimental apparatus consists of a stainless steel reaction chamber, an ion beam system, and an ArF excimer laser, as shown in Fig. 1. Si wafers were thermally oxidized in steam at 1173 K. The SiO_2 -covered wafers were etched with a solution of 5 % hydrofluoric acid to remove surface contamination just before they were introduced into the reaction chamber.

The first step of patterned CVD was Ti-ion irradiation through a stencil metal mask. The mask pattern was transferred on

the SiO₂ surface. The total dose of ion irradiation corresponded to a few monolayers of Ti. Background pressure during ion irradiation was 5×10^{-3} Pa. The second step was ArF excimer laser CVD with WF₆ and H₂ at 400 K. Total pressure was 53 Pa. A laser beam controlled by pulse mode was magnified about six times. The wafers in the reactant gases were irradiated perpendicular to the rectangular laser beam for 40 seconds. Arrangement of the substrate, stencil mask, ion beam, and laser beam has been illustrated in detail elsewhere⁷⁾. The final step was LP-CVD at 600 K. Total pressure was raised to 210 Pa by reducing the pumping speed of the reaction chamber. The experimental conditions are summarized in Table I.

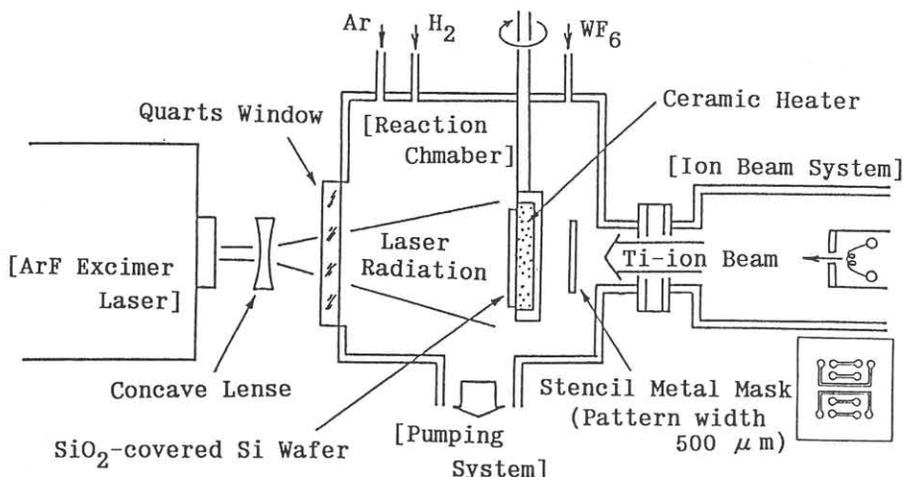


Fig. 1 Experimental apparatus.

Results of Patterned CVD

The results of the patterned deposition of the W films are presented in Fig. 2. The ion-irradiation pattern is not clear, as shown in Fig. 2(a). After the laser CVD, the pattern in Fig. 2(a) became a little more clear, but metallic features (gloss) still do not appear. At the beginning of the subsequent LP-CVD, the ion-irradiation pattern once faded but did not disappear completely. Then, as shown in Fig. 2(b), a metallic pattern appears, but only on the Ti-ion-irradiation pattern.

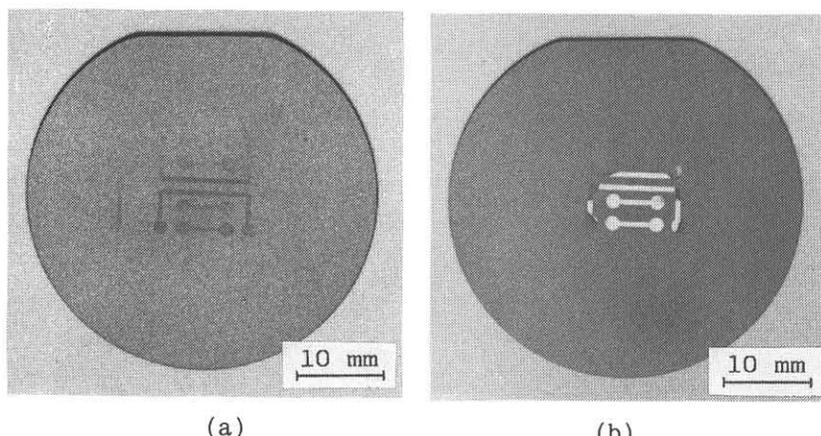
It must be noted that, without the laser CVD step, the ion-irradiation pattern disappears during LP-CVD and no W deposition occurs. This fact implies that the laser radiation initiates deposition reactions. However, longer laser CVD times cause non-selective W depositions on the entire laser-irradiated SiO₂ surface during LP-CVD. It is thought that these non-selective depositions were induced by the photon absorption of WF₆⁸⁾ in the gaseous phase or on the SiO₂ surface.

Fig. 3(a) shows an edge structure of the pattern. A machining burr of the stencil mask was also transferred as a fimbriation of the pattern. This result

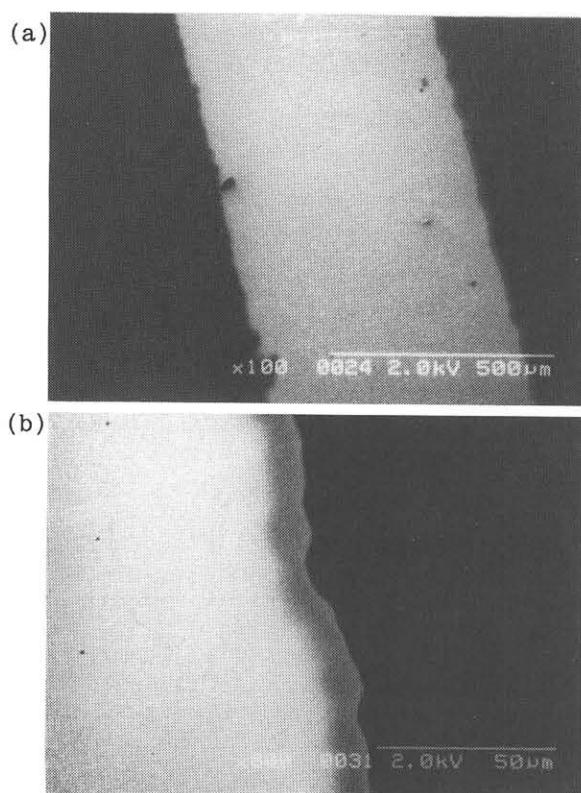
Table I. Experimental Conditions

| | |
|------------------------------|--------------------------------------|
| Ti ion irradiation | |
| Ion energy | 600 eV |
| Dose | $1.1 \times 10^{16} \text{ cm}^{-2}$ |
| Substrate temperature | R.T. |
| Laser CVD | |
| Flow rate of WF ₆ | 16 ccm |
| H ₂ | 200 ccm |
| Ar* | 200 ccm |
| Total pressure | 53 Pa |
| Substrate temperature | 400 K |
| Laser energy density | $330 \text{ mJ/m}^2\text{s}$ |
| CVD time | 40 s |
| LP-CVD | |
| Flow rate of WF ₆ | 16 ccm |
| H ₂ | 200 ccm |
| Ar* | 200 ccm |
| Total pressure | 210 Pa |
| Substrate temperature | 600 K |

*Ar is also fed into the reaction chamber near a laser introducing window to avoid undesired deposition of reaction products on the inside of the window.



(a) (b)
 Fig. 2 Patterned CVD of W film on Ti-ion-irradiated SiO_2 . (a)After ion irradiation, and (b)after LP-CVD.



(a) (b)
 Fig. 3 SEM micrographs. (a)500-micron W pattern, and (b)edge of the pattern.

indicates that the deposition of a 10-micron pattern is possible.

In Fig. 3(b), a gloomy field is observed at the pattern edge. The border between the gloomy and bright fields is examined in more detail as shown in Fig. 4. These two fields exhibit different stages in the film formation process⁹⁾. Coalescence of islands is progressing in the gloomy

field. On the other hand, secondary nucleation has already started on the continuous film in the bright field. Hence, initial nucleation density in the gloomy field was lower than that in the bright field.

The gloomy field corresponds to a penumbra (a partial shadow outside the complete shadow of the stencil mask at the ion-irradiation step). It is thought that the small amount of ion irradiation in the penumbra resulted in low nucleation density at the laser CVD step. Therefore, we strongly believe that the amount of Ti-ion irradiation can control the nucleation density at the initial stage of the film formation process.

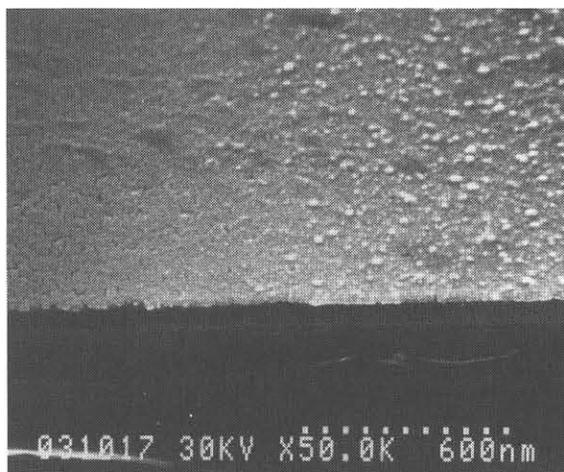


Fig. 4 Magnified SEM micrograph of the border between the gloomy field (left) and the bright field (right) in Fig. 3(b).

DISCUSSION

A mechanism of the patterned CVD of W films on SiO_2 is explained by consecutive reactions of a H_2 reduction of TiO_2 and a Ti reduction of WF_6 during laser CVD.

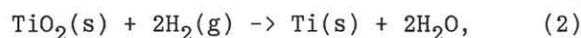
Auger electron spectroscopy (AES) showed that the material deposited by Ti-ion irradiation was fairly well oxidized Ti, i.e., TiO_2 . In the case of skipping the laser CVD step, TiO_2 reacts with WF_6 during

LP-CVD. This reaction is given by,



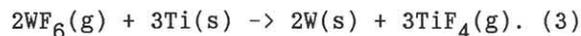
where WOF_4 has a boiling point of 459 K and vaporizes into gas. Consequently, the ion-irradiation pattern completely disappears.

On the other hand, in the case of the regular process, a H_2 reduction of TiO_2 given by,



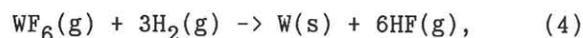
is induced by the photon absorption of TiO_2 at the early stage of the laser CVD. The positive sign of the free energy change (+93 Kcal/mol at 400 K) predicts that the reaction (2) does not proceed spontaneously. However, TiO_2 is an n-type semiconductor and can absorb ultraviolet photons which force the reaction (2). Therefore, the laser radiation is indispensable for the reaction (2).

The reaction product of the reaction (2), Ti, immediately reduces WF_6 , i.e.,



This reaction does not occur in pyrolysis. Broadbent et al. reported that reaction products of WF_6 and Ti are W and nonvolatile TiF_3 which remain on the substrate¹⁰⁾. In the present experiment, no TiF_x layer was detected by AES after the laser CVD. Therefore, laser radiation was able to change the reaction path. In addition, fluorine atoms could be vaporized as volatile TiF_4 molecules. As a result, W nuclei are selectively formed on the Ti-ion-irradiated SiO_2 surface.

Finally, during the LP-CVD, a H_2 reduction of WF_6 given by,



occurs on the surfaces of W nuclei and continuous W films appear only on the Ti-ion-irradiated SiO_2 . The TiO_2 not reduced in the laser CVD step is etched off at the

beginning of LP-CVD by the reaction (1). Therefore, the ion-irradiation pattern once faded at the beginning of the LP-CVD.

SUMMARY

Patterned CVD of W films on SiO_2 has been achieved using consecutive processes of Ti-ion irradiation, ArF excimer laser CVD, and LP-CVD. Ti acts as a reducing agent of WF_6 . Laser radiation is indispensable for initiating deposition reactions.

As described, a few monolayers of Ti-ion irradiation and laser CVD control the deposition of W films and enable the maskless W metallization on SiO_2 .

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REFERENCES

- 1) S. D. Allen and A. B. Tringubo, *J. Appl. Phys.* **54**, 1641(1983).
- 2) M. E. Gross, G. J. Fisanick, P. K. Gallagher, K. J. Schnoes, and M. D. Fennell, *Appl. Phys. Lett.* **47**, 923(1985).
- 3) J. S. Ro, A. D. Dubner, C. V. Thompson, and J. Melngailis, *J. Vac. Sci. Technol.* **B6**, 1043(1988).
- 4) E. K. Broadbent and C. L. Ramiller, *J. Electrochem. Soc.* **131**, 1427(1984).
- 5) R. L. Kubena, T. F. Stratton, and T. M. Mayer, *J. Vac. Sci. Technol.* **B6**, 1865(1988).
- 6) W. A. Hennessy, M. Ghezzi, and R. H. Wilson, *J. Electrochem. Soc.* **135**, 1730(1988).
- 7) H. Okuhira, S. Nishimatsu, and K. Ninomiya, *Materials Research Society Symposium Proceedings, "In Situ Patterning: Selective Area Deposition and Etching"*, edited by R. Rosenberg, J. G. Black, and A.F. Bernhardt.
- 8) K. N. Tanner and A. B. F. Duncan, *J. Am. Chem. Soc.* **73**, 1164(1951).
- 9) B. Lewis and J. C. Anderson, "Nucleation and Growth of Thin films", p.15. Academic Press.
- 10) E. K. Broadbent, A. E. Morgan, J. M. DeBlasi, P. van der Putte, B. J. Burrow, D. K. Sadana, and A. Reader, *J. Electrochem. Soc.* **133**, 1715(1986).