Preparation of Silicon Oxide Films by CVD Using Fluorotriethoxysilane

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フルオロトリエトキシシランを用いたCVDによる酸化ケイ素薄膜の合成

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Preparation of silicon oxide films was tried by chemical vapor deposition (CVD) at substrate temperatures (T_{sub}) from 298 to 308 K and pressures in CVD chamber (P_{chm}) from 4 to 13 kPa. Fluorotriethoxysilane (FTES) and water which were vaporized in thermostatic oil baths were used as source materials. Dense films were obtained at T_{sub} below 303 K and P_{chm} above 6.7 kPa, and the deposition rate was seriously affected by the bath temperature to evaporate water. Deposited films were examined by infrared reflection spectroscopy and X-ray photoelectron spectroscopy, and it was found that the deposits contained fluorine. The relation between current density and electric field of dense films was also examined.

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1. Introduction

Recent development in advanced very large scale integration (VLSI) require the preparation technique of multilayer wiring and/or coating in order to increase the packing density of the devices. Silicon oxide (SiO_2) is one of the most important materials for VLSI as an insulator for surface passivation and protection.^{1,2)} There have been a vast of studies for preparation of SiO_2 using chemical vapor deposition (CVD) because of its superior step coverage and high aspect ratio.^{3,4)} Oxidation of silicon hydride,^{4,5)} thermal decomposition of tetraethoxysilane (TEOS)^{6,7)} and oxidation of TEOS^{1-3,7-11)} were investigated for decreasing the process temperatures of CVD, however, substrate temperatures above 500 K were still required to obtain dense films even if plasma enhanced reactions were used.^{1,3,4,7,9)} VLSI devices may suffer thermal damage and internal stress during CVD process so long as a relatively high substrate temperature is necessary.

Homma et al. recently reported that they had firstly succeeded in preparing silicon oxide film at room temperature by CVD process using fluorotriethoxysilane (FTES; $\text{FSi}(\text{OC}_2\text{H}_5)_3$) and water.¹²⁾ Such low temperature CVD process might be very attractive and important for the development of VLSI devices, however, the range of CVD conditions for obtaining films has not been made clear because they have not varied the CVD conditions; i. e., the substrate temperature, the pressure in chamber and so on. In order to confirm their result, it is significant to collect more detailed experimental data under wide conditions. Thus, in this work, the present authors tried to clarify more detailed experimental conditions concerning with the substrate temperature, the total pressure in CVD chamber and so on.

2. Experimental procedure

FTES (Shin-Etsu-Kagaku; 95%, b.p.=406.5 K) and water (H_2O) were used as source materials. FTES and H_2O were vaporized in oil baths, which were kept at temperatures between 298 and 308 K. The reactant vapors were transported into the CVD chamber by N_2 flow at the rate of $5 \times 10^{-7} \text{ m}^3 \cdot \text{s}^{-1}$ (30 sccm). The transport lines were heated at 323 K by ribbon heaters in order to prevent the source

vapors from recondensing. Each source vapor was separately guided onto the substrate by a coaxial nozzle to avoid the reaction by mixing of each component before arriving at the substrate. The distance between the coaxial nozzle and the substrate (D_{noz}) was varied from 5 to 50 mm. The substrate used was of commercially pure iron ($20 \times 20 \times 0.5 \text{ mm}$) which had been polished beforehand by abrasive paper with silicon carbide particles ($40 \mu\text{m}$ in diameter). The substrate temperature (T_{sub}) and the total pressure in the CVD chamber (P_{chm}) were varied from 298 to 308 K and from 4 to 13 kPa, respectively. All deposition experiments were carried out for 3600 s. The deposition conditions are summarized in Table 1.

The crystal structure and the composition of the films were examined by X-ray diffractometer (XRD), infrared (IR) reflection spectroscopy and X-ray photoelectron spectroscopy (XPS), using Phillips PW1800, JASCO FT/IR-7000 spectrophotometer and Shimadzu ESCA-850, respectively. To evaluate the electrical resistivity of the film as an insulator, the leakage current density of the film in a direction perpendicular to the substrate was measured by the two-terminal method (Advantest R8340 & R12701).

Table 1. Deposition Conditions for the Preparation of Silicon Oxide Films by Using Fluorotriethoxysilane

Source materials	$\text{FSi}(\text{OC}_2\text{H}_5)_3$ H_2O
Substrate temperature	298~308 K
Pressure in CVD chamber	4~13 kPa
Distance between the tip of nozzle and substrate	5~50 mm
Temperatures of oil baths	298~308 K
N_2 gas flow rate	$5 \times 10^{-7} \text{ m}^3 \text{ s}^{-1}$
Deposition time	3600 s

3. Results and discussion

No film was obtained at the condition of the shorter distance between the nozzle tip and the substrate (D_{noz}) than 15 mm. It seems that enough distance is necessary from the nozzle to the substrate for mixing source gases. Since uniform and dense films were deposited at $D_{\text{noz}} > 25$ mm, the experiment was carried out at $D_{\text{noz}} = 25$ mm unless otherwise stated.

Figure 1 shows the effects of substrate temperatures and the total pressures in the CVD chamber on the formation of films at the fixed bath temperatures (303 K) of FTES (T_{bf}) and H_2O (T_{bh}). From Fig. 1, it is found that the following two points are significant to obtain the uniform and dense films on the substrates.

(1) Total pressure in CVD chamber (P_{chm}) should be equal to or more than 6.7 kPa.

The effect of the total pressure in CVD chamber (P_{chm}) is hard to be evaluated quantitatively, but it seems that the flow conditions of source gases has an important role for deposition.

(2) Substrate temperature (T_{sub}) should be equal to or lower than the bath temperatures of source materials (T_{bf} , T_{bh}).

$$\therefore T_{\text{sub}} \leq T_{\text{bf}} = T_{\text{bh}}$$

Since powder production by a homogeneous nucleation in the gas phase reaction was not found, the adsorption or the condensation of source gases onto the substrate seems to be essential and favorable to the reaction between the two source components in this case.

In order to examine the deposition rate based on the above results, the substrate temperature was set as low as 298 K and the temperatures of source materials (T_{bf} , T_{bh}) were independently varied between 298 and 308 K. P_{chm} and D_{noz} were fixed at 13 kPa and 25 mm, respectively. The deposition rate was determined by measuring the gain in weight. Figure 2 shows the relation between the deposition rate and the bath temperature of H_2O (T_{bh}). As is clearly seen from this figure, the deposition rate is strongly affected by the bath temperature of water vapor supply (T_{bh}), but not dependent on that for FTES (T_{bf}). It is certain that a sufficient supply of water vapor is necessary for the CVD reaction using FTES vapor. The deposition rate in the present work increased with an increase of the bath temperature of water (T_{bh}), and reached $0.22 \text{ nm} \cdot \text{s}^{-1}$ at $T_{\text{bh}} = 308 \text{ K}$. Though $T_{\text{bh}} (= 308 \text{ K})$ of this work was lower than the value by Homma et al., the deposition rate of this work was comparable to Homma et al.'s result that was prepared at $T_{\text{sub}} = 298 \text{ K}$, $P_{\text{chm}} = 0.67 \text{ kPa}$ and $T_{\text{bh}} = 323 \text{ K}$.¹²⁾ The difference between Homma et al.'s and the present work in T_{bh} may be due to the difference in the flow rate of carrier gas. The flow rate of nitrogen gas used in their work was $1.25 \times 10^{-6} \text{ m}^3 \cdot \text{s}^{-1}$ whereas that of the present work was $0.5 \times 10^{-6} \text{ m}^3 \cdot \text{s}^{-1}$. Their higher flow rate of carrier gas may have brought about lower partial pressure of water vapor in carrier gas compared with the present work.

The higher deposition rate is expected because of extrapolation to higher T_{bh} in Fig. 2, however, it was not confirmed because the formation of water droplets around the nozzle at higher T_{bh} than 308 K. More precise temperature control of the nozzle is necessary.

Films deposited could not be identified by X-ray diffraction (XRD) because only halo-patterns reflecting amorphous structure were obtained. Thus, IR reflection spectra of films were measured. Figure 3 shows an IR reflection spectra of the film prepared at $T_{\text{sub}} = 300 \text{ K}$, $P_{\text{chm}} = 13 \text{ kPa}$, $D_{\text{noz}} = 25 \text{ mm}$, $T_{\text{bh}} = 308 \text{ K}$ and $T_{\text{bf}} = 303 \text{ K}$. In addition to absorption around 1075 cm^{-1} corresponding to Si-O bond,^{3),6),9)} strong absorption at 3500 and 1635 cm^{-1} corresponding to H_2O were observed.^{3),8),9)} Therefore, films ob-

Fig. 1. Effects of T_{sub} and P_{chm} on the deposition when T_{bf} and T_{bh} are set at 303 K.

Fig. 2. Effect of T_{bh} on the deposition rate of silicon oxide films prepared at $T_{\text{sub}} = 298 \text{ K}$, $D_{\text{noz}} = 25 \text{ mm}$ and $P_{\text{chm}} = 13 \text{ kPa}$.

Fig. 3. IR spectrum of deposit prepared at $T_{\text{sub}} = 300 \text{ K}$, $P_{\text{chm}} = 13 \text{ kPa}$, $D_{\text{noz}} = 25 \text{ mm}$, $T_{\text{bf}} = 303 \text{ K}$ and $T_{\text{bh}} = 308 \text{ K}$.

tained seem to include much unresolved water. If the content of water vapor in the source is decreased, the amount of water in the film might be decreased, however, the rate of deposition would be also decreased, as stated above. Weak absorption at 935 cm^{-1} considering as the Si-F bond¹²⁾ was also observed in Fig. 3. It was difficult to determine the content of fluorine in the film by XPS measurement because the signal corresponding to F1s increased with the etching of the film surface to remove the surface contamination by argon ion for unidentified reason, but the fluorine content of the deposit was estimated up to about 10 mol%. The result of XPS measurement is shown in Fig. 4.

Fig. 4. XPS profile of deposit prepared at $T_{\text{sub}}=300$ K, $P_{\text{chm}}=13$ kPa, $D_{\text{noz}}=25$ mm, $T_{\text{bh}}=308$ K and $T_{\text{bf}}=303$ K.

The leakage current density of the dense film was from 10^{-10} to 10^{-7} $\text{A}\cdot\text{cm}^{-2}$ at an electric field from 10^3 to 10^5 $\text{V}\cdot\text{cm}^{-1}$ though the film seemed to contain fluorine. This result was in the same order of the data previously reported at higher deposition temperature.^{8),12)} It will be necessary to examine the influence of fluorine on the leakage current density of the film and/or to detect the CVD conditions for decreasing the amount of fluorine in the films.

4. Conclusions

Silicon oxide films were prepared by CVD using FTES and H_2O vapors. Dense films could be obtained at the substrate temperature below 303 K and the total pressure in CVD chamber above 6.7 kPa. The deposition rate was

strongly affected by the bath temperature for water vapor, and the rate was reached about $0.2\text{ nm}\cdot\text{s}^{-1}$. Though as-deposited films included fluorine, the leakage current density was as small as 10^{-9} $\text{A}\cdot\text{cm}^{-2}$ under an electric field of 10^4 $\text{V}\cdot\text{cm}^{-1}$.

References

- 1) H. Sakaue, M. Nakano, T. Ichihara and Y. Horiike, *Jpn. J. Appl. Phys.*, **30**, L124-27 (1991).
- 2) K. Fujino, Y. Nishimoto, N. Tokumasu and K. Maeda, *J. Electrochem. Soc.*, **138**, 550-54 (1991).
- 3) I. T. Emesh, G. D'Asti, J. S. Mercier and P. Leung, *J. Electrochem. Soc.*, **136**, 3404-08 (1989).
- 4) M. Nakano, H. Sakaue, H. Kawamoto, A. Nagata and M. Hirose, *Appl. Phys. Lett.*, **57**, 1096-98 (1990).
- 5) J. Shirafuji, S. Miyoshi and H. Aoki, *Thin Solid Films*, **157**, 105-15 (1988).
- 6) A. C. Adams and C. D. Capio, *J. Electrochem. Soc.*, **126**, 1042-46 (1979).
- 7) C. Pavelescu and I. Kleps, *Thin Solid Films*, **190**, L1-3 (1990).
- 8) M. Matsuura, Y. Hayashida, H. Kotani and H. Abe, *Jpn. J. Appl. Phys.*, **30**, 1530-38 (1991).
- 9) S. K. Ray, C. K. Maiti, S. K. Lahiri and N. B. Chakraborti, *Semicond. Sci. Technol.*, **5**, 361-63 (1990).
- 10) K. Fujino, Y. Nishimoto, N. Tokumasu and K. Maeda, *J. Electrochem. Soc.*, **137**, 2883-87 (1990).
- 11) K. Fujino, Y. Nishimoto, N. Tokumasu and K. Maeda, *J. Electrochem. Soc.*, **139**, 1690-92 (1992).
- 12) T. Homma, R. Yamaguchi and Y. Murao, *J. Electrochem. Soc.*, **140**, 687-92 (1993).