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Theoretical Calculations for the Elimination of Silanol and Decrease in Dielectric Constant

Akira Fujimoto and Osamu Sugiura

Department of Physical Electronics, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8552, Japan Phone: +81-3-5734-2696 e-mail: afujimot@o.cc.titech.ac.jp

1. Introduction

The multilevel interconnection process is important for fabricating sub-quarter-micron devices. Water (silanol) desorption from interlayer dielectrics, sipn-on-glass and SiO_2 film affects the devices' reliability by contributing to MOSFET hot-carrier degradation, void formation in interconnections and increase in the leakage current. The purpose of this study is to reduce silanol by annealing and decrease in dielectric constant.

In this paper we have investigated by the theoretical calculation that gas sources which could be expected the elimination of silanol and by annealing and annealing properties were evaluated experimentally.

2. Calculation

As shown Fig.1, we proposed that S-F and Si-CH₃ bond were substituted for silanol by annealing. As annealing gas sources, Si-F bond formation choose HF and CF4, and Si-CH₃ bond formation choose CH₃Cl, and CH₃CHO. We carried out reaction mechanisms in semiempirical molecular method. MO calculations were used by the MOPAC7 program package. The geometry of the reactant and product and transition state (TS) were optimized by PM3 method[1]. It thought about ((OH)₃Si)₃Si-OH as cluster of silanol in SiO2. Here, Si-OH except for Si-OH to use for the calculation is for the terminal. After the structure optimization the Si-O distance, Si-O-Si bond angle, and the O-O nearest neighbor distance was 1.64Å, 140-144°, and 2.75 Å respectively, and the experimental value was 1.62 Å, about 144°, and 2.62 Å respectively[2]. Thus the calculation value is suitable.

Figure 2 shows that the formation of Si-F bond was calculated. The reaction between silanol and HF produced Si-F and H_2O , and the activation energy was 1.53eV. It was found from calculations that the reaction between silanol and CF₄ was two reaction paths of Si-F+CF₃OH and Si-OCF₃+HF and that the activation energy was 2.82eV, 2.96eV respectively.

Then the formation of Si-CH₃ bond was calculated. The

reaction between silanol and CH_3Cl produced Si-OCH₃ bond and Si-Cl bond, and the activation energy was 2.25eV, 2.28eV respectively. But the transition state that Si-CH₃ bond was formed was not found. Figure 3 shows the reaction between silanol and CH₃CHO. It produced Si-CH₃ bond and Si-OOCH₂CH₃ bond by the addition reaction, and the activation energy was 3.10eV, 3.83eV respectively. Therefore Si-CH₃ bond is formed by CH₃CHO because the activation energy of Si-CH₃ bond formation is lower than that of the addition reaction.







Figure 2 Energy diagrams of reactions and transition structures of Si-F formation



Figure 3 Energy diagram of reactions and transition structure Si-CH₃ formation

3. Results and discussion

Actually CH₃CHO that Si-CH₃ bond was able to form annealed the film. SiO₂ films deposited by CVD using tetraisocyanate silane (TICS, Si(NCO₄)) and water[3]. The FT-IR spectra of the deposited film are shown in Fig. 4. As deposited, absorption peaks around 1100 cm⁻¹, 800 cm⁻¹ and 400 cm⁻¹ related to SiO₂ are observed, and the peaks of H₂O around 1600 cm⁻¹ and 3300 cm⁻¹, and the peaks of Si-OH around 950 cm⁻¹ and 3500 cm⁻¹ are observed in the film. This film annealed by CH₃CHO ambient for an hour between 200°C and 450°C. After annealing, the peaks of the water, and silanol were decreased and were almost eliminated in more than 300°C. Figure 5 shows the FT-IR spectra around 2800-3000cm⁻¹ after 300 ℃ annealing. Absorption peaks corresponding to C-H were observed by 2880 cm⁻¹, 2940 cm⁻¹ and 2970 cm⁻¹, since Si-CH₃ bond was formed. As deposited, water content was about 18 wt%, but after annealing it was decreased lower than 1wt% in more than 300°C. On the other hand at 450°C annealing in N₂ ambient, water content was included about 7wt%. This can be explained that CH₃CHO diffuses into the film and that the reaction between CH₃CHO and Si-OH bond produces Si-CH₃ bond. The peaks of C-H with FT-IR were the largest in 300 $^{\circ}$ C, and those became small when annealing temperature was in more than 300°C. Because there is 2Si-OH→Si-O-Si+H₂O of the dehydration reaction except for Si-OH+CH₃CHO → Si-CH₃+HCOOH reaction of Si-CH₃ formation, the former reaction occurs easily with aneealing temperature increasing and thus the formation of Si-CH₃ decreases. Figure 6 shows the resistivity and dielectric constant after CH₃CHO. The resistivity of the film increased with anneling temperature increasing, and it was higher than $10^{15}\Omega$ cm in more than 300° C. The electric constant decreased with annealing temperature increasing to 3.6 at 450℃. Although it seems that the dielectric constant is small in 300°C whose peak of C-H is the largest, it becomes large because a few silanol is included in the film. Therefore, the dielectric constant is small at the high temperature which silanol decreases to further.

4. Conclusions

For the elimination of silanol we calculated semiempirical molecular method the reactions between silanol and some gas sources. It was found from calculations that the formation of Si-F bond was possible by HF and CF_4 and that the formation of Si-CH₃ was possible by CH₃CHO. Actually when the film included silanol annealed by CH₃CHO ambient, silanol was eliminated and Si-CH₃ bond

was formed. The resistivity was $10^{16}\Omega$ cm and the dielectric constant was 3.6 at 450°C.

References

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Figure 5 FT-IR of Si-CH₃ bond for CH₃CHO annealed film at 300° C.



Figure 6 Dielectric constant and resistivity for CH₃CHO annealed films as a function of the annealing temperature