The Behavior of Alkoxy-Functional Groups on Atmospheric-Pressure Chemical Vapor Deposition Using Alkoxysilane and Ozone

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The behavior of alkoxy-functional [RO-] groups in the APCVD reaction using alkoxysilane and ozone has been evaluated by alcohol adding. The RO- groups of the alkoxysilane source and the RO- groups supplied from the alcohol similarly affect the APCVD reaction. An increase of RO- groups, which are smaller than or equal to the RO- of the alkoxysilane molecule, accelerate the flowing-like step coverage formation. When the flow property enhanced, hydrogen and carbon from RO- groups incorporate into the film in a similar way. TDS (Thermal desorption spectroscopy) spectra for water desorption show shape change according to the flow property.

1. Introduction

Atmospheric-pressure chemical vapor deposition (APCVD) using tetraalkoxysilane [(RO)₄Si] and ozone deposits silicon dioxide film at low temperature and provides efficient step coverage from a conformal to a flowing-like step coverage with as-deposited films. This APCVD has been extensively developed for interlayer dielectric applications on multilevel interconnections in quartermicron VLSIs because this flow property ensures that deep gaps and holes are filled and planerized.^{1,2)} However, the details of the APCVD reaction are not yet completely understood. A few reports for reaction models have been proposed.3,4,5) but the application studies are ahead of reaction mechanism evaluations.

We previously reported the effects of alkoxy-functional [RO-] groups on the APCVD reaction.⁶⁾ Both the deposition rate and step coverage were found to be influenced by the RO- groups of alkoxysilane sources. Moreover, adding alcohol, which results in the formation of RO- adducts into the reaction system, also affects the step coverage.^{6,7)} Therefore, since RO- groups appear to play an important role in the APCVD reaction, an evaluation of their behavior is the first step toward clarifying the reaction mechanism.

The aim of this work is to clarify the role of RO- groups in the flowing-like step coverage formation. The amount and the configuration of the carbon and hydrogen, supplied to



Fig. 1 Experimental setup and CVD parameters.

the films from the RO- adducts, are evaluated, using deuterium-substituted alcohols.

2. Experimental

A modified CANON APT-1600 system was used. Alkoxysilane, oxygen with ozone, alcohols and nitrogen carrier gas were mixed and supplied uniformly through a gas dispersion head made of aluminum plates. The gap between the gas dispersion head and substrate was 6.0 mm. The total gas flow rate was kept at 26.5 slm. The experimental setup and parameters are shown in Fig. 1.

Tetramethoxysilane [(CH₃O)₄Si] was used as the silicon source. Methanol and ethanol were compared as adding alcohol. Moreover, deuterium-substituted alcohols (i.e., CD₃OD and C₂D₅OD) were used. Deuterium enables us to clarify the volume and the configuration of the hydrogen incorporated in the deposited films.

3. Results and Discussion

First, the relationship between RO- groups in reaction system and step coverage will be described. Adding alcohol either accelerates or inhibits the step coverage change, as shown in Fig. 2. With tetraethoxysilane source, for example, the flow property is accelerated at first by ethanol, but as more ethanol is added the flowing degree decreases.^{6,7)}





Fig. 3 Relationship between adding alcohol and the flow property for $(CH_3O)_4Si$ and $(C_2H_5O)_4Si$ source.

The results for $(C_2H_5O)_4$ Si were reported in Ref. (6).

Conversely, iso-propanol does not cause the flow property to accelerate.⁶⁾ In this study, the effect the added alcohol has on the tetramethoxysilane source was evaluated. SEM (Scanning Electron Microscopy) measurements of the step coverage change showed methanol accelerates the flow property, while ethanol suppresses it, as mentioned above, although ethanol accelerates the flow property for tetraethoxysilane source.

Figure 3 shows the relationship between the flow property and alcohol for tetramethoxysilane and tetraethoxysilane sources. When the added RO- group from the alcohol was smaller than or equal to the RO- of alkoxysilane source, the flow property was enhanced. Conversely, larger RO- groups suppressed the flow property. Moreover, between the silicon sources, the more flowing-like step coverage was obtained with tetramethoxysilane source. We previously reported that the flow property with alkoxysilane sources changes depending on the RO- groups (i.e., a decreasing flowing degree in the order of methoxy-, ethoxy- and iso-propoxy-).⁶ These results suggest that the RO- groups of alkoxysilane source and the RO- groups supplied from the alcohol similarly affect the APCVD reaction.

SIMS (Secondary Ion Mass Spectroscopy) analysis detects a uniform depth profile of hydrogen, deuterium and carbon in the deposited films. So, the added alcohol continuously contributes on the film formation process as a reactant. The amounts of carbon and deuterium in the deposited films are shown in Figs. 4 and 5. The amounts for the films with methanol- D_4 are larger than those with ethanol- D_6 over the entire range of ozone flow rates. For carbon incorporation, the ion intensity increase at low ozone flow rates because of the excess hydrocarbons supplied from the alcohol. With methanol- D_4 , there is an increase in carbon incorporation again at higher ozone flow rates. The amount of deuterium also increases in a similar way. These increases were not detected when ethanol- D_6 was added.

The relationship between the incorporated carbon and deuterium is plotted in Fig. 6. These plots are divided into two groups. The numbers in the brackets indicate the CVD condition; [20/200], for instance, means the methanol-D₄ flow rate is 20 sccm and the ozone flow rate is 200 sccm. It can be seen that the points on Group A plots have high ozone flow rates where flowing acceleration is obtained. The data for ethanol-D₆-added films are in Group B. Moreover, the ratio of deuterium to carbon is nearly constant in each group. Therefore, incorporation of these elements proceeded in the same way during film formation. It is considered that the structure of the RO- functional groups is important to affect the flowing-like step coverage formation.

Finally, it will be discussed that the configuration of terminal groups related to the flow property. The TDS (Thermal Desorption Spectroscopy) spectra of the M/e=18 and M/e=19 fragments assigned to water desorption are shown in Figs. 7 and 8. They are mainly assigned to H₂O⁺ and DHO⁺.⁸⁾ Four peaks were measured from as-deposited films. γ peak split to form the fourth peak, which is labeled a δ peak. The α and β peaks reflect the water molecules contained in the films. The water desorption shown by the γ and δ peaks is generated from residual terminal groups in the films (i.e., Si-H, Si-OH, Si-D and Si-OD).

By comparing in Figs. 7(a) and 8(a), it can be seen that a



Fig. 4 The amount of carbon in the films as a function of ozone flow rate detected by SIMS.



Fig. 5 The amount of deuterium in the film as a function of ozone flow rate detected by SIMS.



Fig. 6 Relationship between the amount of carbon and deuterium in the films.







Fig. 8 TDS spectra of the film with ethanol– D_6 . (a) as–deposited film. (b) 6 months after deposition.

shape δ peak is obtained from the film with methanol-D₄. This peak is associated with the flowing degree acceleration caused by the methanol. These spectral changes appeared clearly for M/e=19. For the films in Figs. 7(b) and 8(b), β and γ peak growth were observed and the δ peak disappeared. The residual terminal groups in the δ state changed their configuration to β and γ states. It is considered that hydrolysis occurred in the films. The δ peak is associated with flowing degree acceleration and indicates an unstable configuration.

4. Conclusion

There is a strong relationship between the behavior of RO- groups and the flow property. The behavior of ROgroups from alkoxysilane source and from the added alcohol was shown to be similar. An increase of RO- groups, which are smaller than or equal to the RO- of alkoxysilane source, in the reaction system accelerates the flow property. When the flowing degree is accelerated, carbon and hydrogen are incorporated into the deposited film from the RO- groups of the added alcohol. An unstable δ state was measured in associated with the incorporated hydrogen. The effects of the RO- groups reflect their chemical structure in the reaction system.

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