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Precursor Control in ZrO_2-CVD for Better Characteristics as High-k Gate Application

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1. Introduction

ZrO_2 has been considered as a promising candidate for high-k gate dielectrics. Although it has superior thermodynamic stability in contact with Si, the interfacial structure between ZrO_2 and Si substrate are degraded by annealing at 900-1000 °C for source and drain region activation [1]. Damascene gate process can prevent these thermal damage [2] and it is an effective process in utilizing high-k materials. High-k gate CVD process may be an inevitable technology for this application for its good controllability in step coverage profile.

In the present work, we carried out kinetic study on ZrO_2-CVD using hot-wall tubular reactor to clarify the basic reaction mechanism that controls step coverage and film properties.

2. Experiment

Figure 1 shows schematics of experimental set up employed in this study. Zirconium-tetra-tertiary-butoxide (ZTB) was used as Zr source and introduced to the reactor using He as carrier gas. Small piece of Si wafer (6mm x 80mm), pre-cleaned by RCA method, was inserted into the reactor and used as substrate. The fractured surface of the sample was investigated by FE-SEM to obtain the growth-rate and step coverage. The chemical compositions of ZrO_2 films were investigated by XPS.

3. Result and discussion

Figure 2 shows the deposition profile in the tubular reactor. It showed an increase in the up-stream part, and then a decrease was observed in the down-stream part. Figure 3 shows step coverage on micro trenches. The step coverage became poor, as the distance from the inlet increased. These results suggest the contribution of gas phase reactions to form highly active intermediate species as shown fig.4. Figure 5 demonstrated the fitting to the experimental trench profiles. At the inlet point, the step coverage was well explained by one precursor model. The sticking coefficient of this precursor, may be ZTB itself, was estimated to be 0.0013. At 2 cm from the inlet, the step coverage became poor, and we have to consider second precursor that has η_2=0.06 to explain the profile. At 6 cm, the step coverage became much worse and we have to consider the third species with η_3 =0.4 to explain the profile. The relative contribution of these three species at each position is shown in fig.2.

The film characteristics may show difference by the film precursors. Figure 6 shows XPS O1s spectra and fig.7 demonstrates C-O/Zr area ratio of ZrO_2 samples obtained at different position in the reactor [3,4]. C-O bond existed more at the 0 cm position, where only ZTB contributed to the deposition. ZTB is so stable that it cannot undergo enough surface reaction to release alchoxyl ligands at the deposition temperature of 360°C. On the other hand, for the deposition at the down-stream, the carbon content was low because a large part of carbon had already been removed by gas-phase reactions, and the intermediate was highly reactive.

4. Conclusion

Kinetic studies on ZrO_2-CVD using hot-wall tubular reactor system revealed the deposition chemistry. The initial precursor, may be ZTB itself, has low sticking coefficient and the other two species formed by consecutive gas phase reactions have higher sticking probabilities. ZrO_2 films formed by reactive intermediates have less carbon contamination and may possess better electric characteristics as high-k gate application. By enhancing the gas phase reaction and precise control on aspect ratio of damascene structure, we can utilize these profitable chemical species.

Reference

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[2] A. Yagishita, et al., IEDM (1998) 29.3.1.
[3] M. J. Guittet, et al., Phys. Rev. B. (2001) **63** 125117-1.
[4] M. R. Turner, et al., Sur. Inter. Analysis. **25**. (1997) 917.

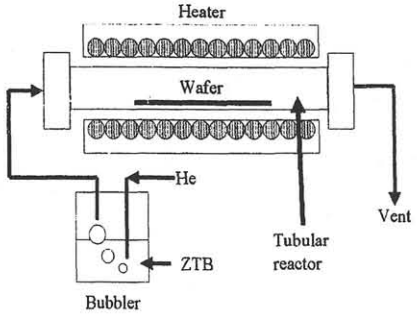

Fig.1 Hot-wall tubular reactor.

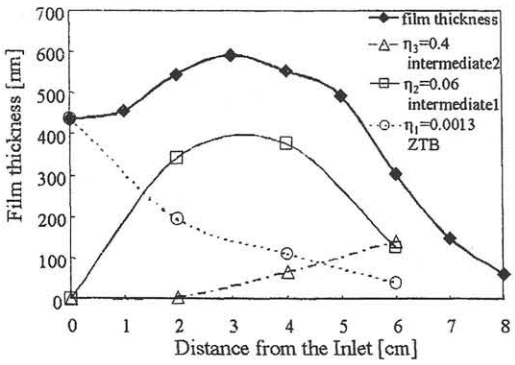

Fig.2 Deposition profile in the tubular reactor. The contribution of each precursor was estimated from step coverage analysis given in fig.5.

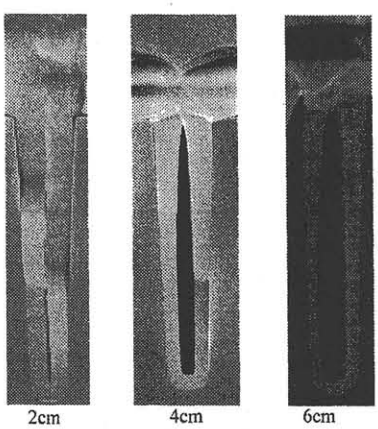

Fig.3 FE-SEM image of the deposition on micro trench at each position of the reactor.

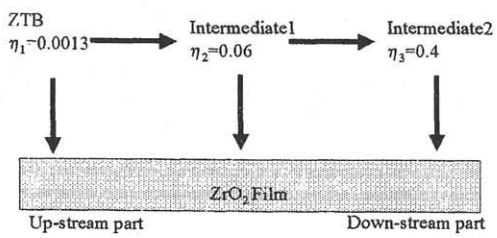

Fig.4 The consecutive reaction mechanism of ZTB.

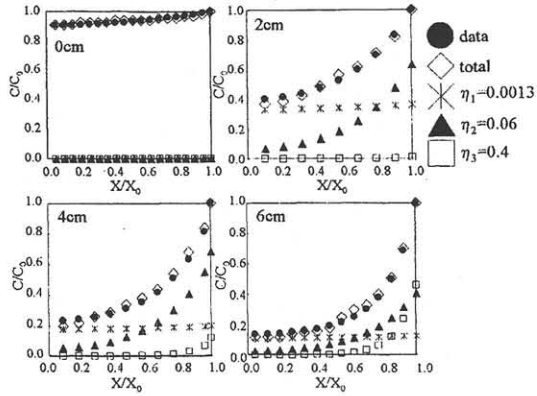

Fig.5 Step coverage profile and one-dimensional model fitting at each position of the reactor.

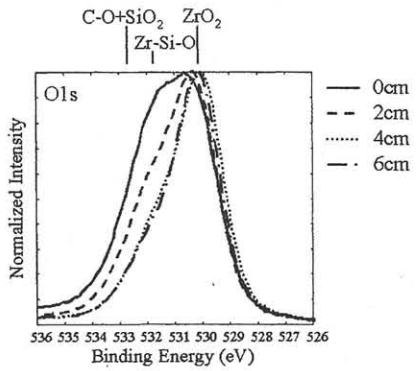

Fig.6 XPS O1s spectra at each position of the reactor.

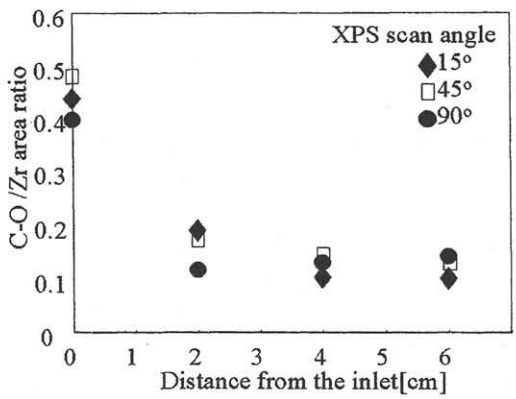

Fig.7 C-O/Zr area ratio in XPS spectra at each position of the reactor.