Pr-Si-O Gate Stack with an Ultrathin Interfacial Layer Grown by MOCVD and PDA under Low O_2 Partial Pressure

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1 Introduction

Praseodymium silicates/oxides (Pr-Si-O) high-k dielectrics have been considered as promising materials to overcome the gate leakage issue in MOSFET[1]. We have studied the growth of Pr-based materials by using metal-organic chemical vapour deposition (MOCVD) [2], focusing particularly on an issue of thick interfacial layer (IL) which might be formed during both deposition and annealing. In this paper, we performed post deposition annealing (PDA) of Pr-Si-O thin films under low partial pressure of O_2 to realise Pr silicate gate stack with an ultrathin IL. We also discuss the effects of PDA in detail based on the data of angular-resolved X-ray photoelectron spectroscopy (AR-XPS).

2 Experimental

We used p-type Si (100) substrates with a 0.9-nm-thick thermal oxide layer. Pr-Si-O thin films were grown on the substrates by MOCVD using $Pr(DPM)_3$ as a precursor at the deposition temperature of 350 °C. We transferred to the sample to the UHV chamber which is connected to the AR-XPS measurement system (ESCA-300, Scienta Instruments AB) in vacuum and performed PDA in the temperature range of 300-900 °C for 20 min in N_2 with the pressure of 1.0 Torr. The partial pressure of oxygen was kept below 10^{-8} Torr throughout annealing. The AR-XPS measurements were subsequently performed after annealing without any air exposure.

3 Results and Discussion

First we show the cross-sectional TEM images of the as-deposited sample in Fig. 1(a) and of the sample with PDA at 900 °C in Fig. 1 (b). A 1.0-nm-thick SiO_2 IL shown in Fig. 1 (a) indicates that an additional IL was not grown during the deposition at 350 °C. Obviously thickness of IL decreased to below 0.5 nm after PDA at 900 °C. This result strongly suggests that PDA under low partial pressure of O_2 is quite effective to control the thickness of IL.

In order to discuss the detailed mechanism of reduction of the IL thickness, we analysed the O 1s photoelectron spectra for the samples before and every after PDA at from 300 to 900 °C with a step of 100 °C as shown in Fig. 2. With increasing the PDA temperature up to 500 °C, the intensity of peaks related to Si-O-Si and Pr-O-H bonds at 533 eV gradually decreased, while the intensity of peak related to Pr-O-Pr bonds at 530 eV increased. Angle-resolved O 1s photoelectron spectra for the sample with PDA at 500 °C (Fig. 3(a)) were deconvoluted as shown in Fig. 3(b) and then the normalised Pr-O-Pr and Si-O-Si intensities were plotted as a function of take-off angle (TOA) in Fig. 4. Formation of Pr oxide on the Pr silicate/SiO_2 stack (see Fig. 7, left) was indicated from the analysis. Pr hydroxide formed by water absorption during the air exposure would be a possible origin.

In the O 1s spectra of the sample with PDA at temperatures above 600 °C in Fig. 2, on the other hand, the Pr-O-Pr peak intensity decreases with increasing the PDA temperature, and the intensity of the peak related to Pr-O-Si bonds at 531.5 eV was enhanced. The Si $2p_{2/3}$ spectra of the sample after PDA were deconvoluted using seven peaks as shown in Fig. 5. The normalised intensities N_{Pr}/N_{SiO2} and N_{Si}/N_{SiO2} were plotted as a function of PDA temperature in Fig. 6, where a rapid increase in N_{Pr}/N_{SiO2} and a decrease in N_{Si}/N_{SiO2} above 600 °C are observed. The analyses of the normalised intensities as a function of TOA indicate formation of Pr silicate/SiO_2 stack due to inter-diffusion of Pr, Si and O atoms (schematically in Fig. 7). The IL thicknesses extracted from the AR-XPS analyses are well consistent with the TEM results.

4. Conclusions

We have succeeded in the growth of the Pr-Si-O gate stack with an ultrathin IL with the thickness of less than 0.5 nm by MOCVD followed by PDA under the low partial pressure of O_2. The AR-XPS analyses indicated that Pr silicate was grown by the inter-reaction between Pr oxide, Pr silicate and SiO_2 with PDA in the temperature range from 600°C to 900°C so that the IL thickness could be reduced.

Acknowledgments

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References

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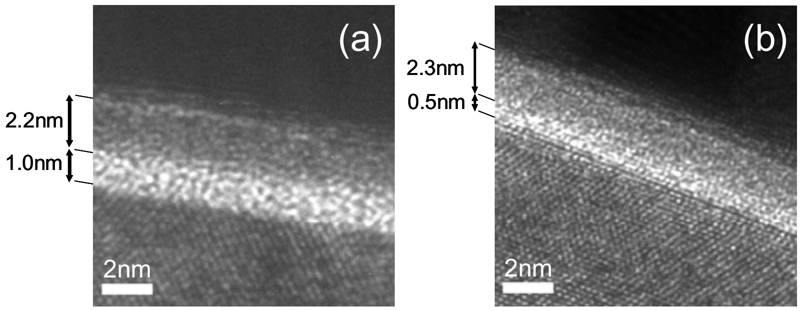

Fig. 1. Cross sectional TEM images of (a) the as-deposited sample and (b) the sample after PDA at 900 ºC.

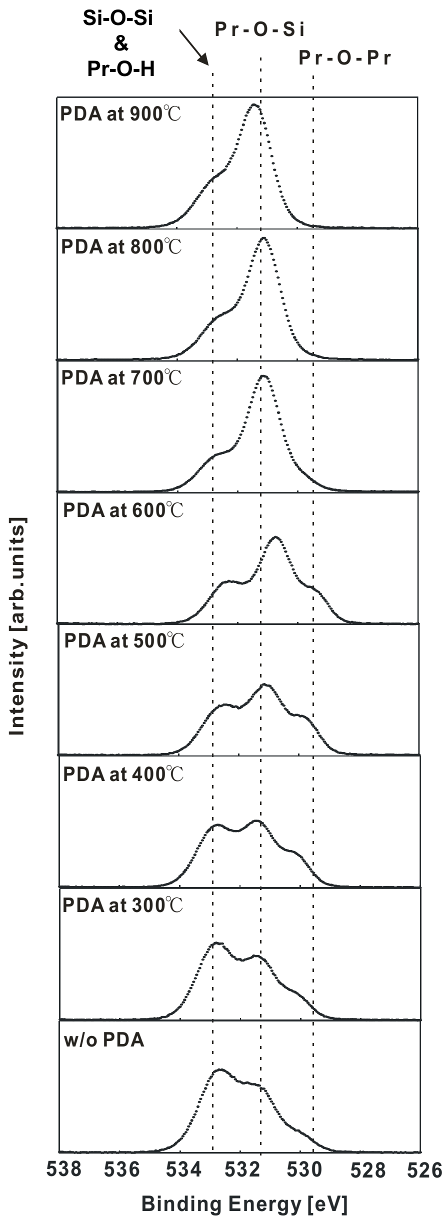

Fig. 2. XPS O 1s spectra of the sample before and after PDA at 300-900 ºC (TOA = 52º).

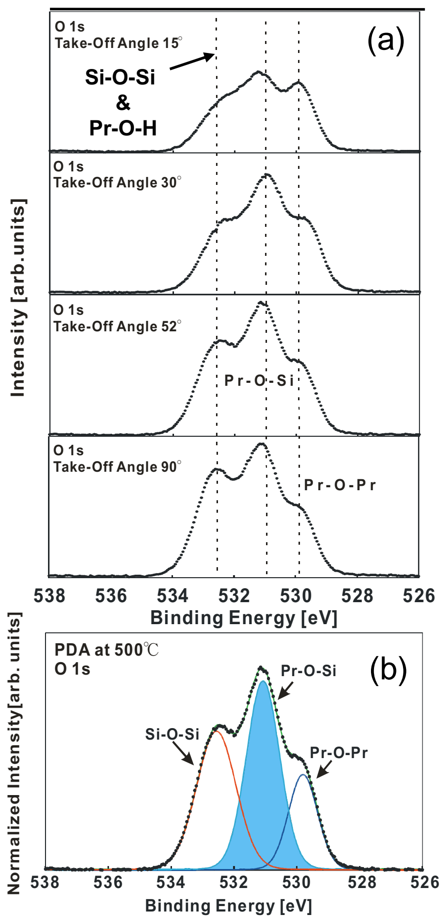

Fig. 3. (a) XPS O 1s spectra of the sample after PDA at 500 ºC at TOA of 15, 30, 52, and 80 degrees, respectively. (b) Deconvoluted O 1s spectra at TOA of 52 degree.

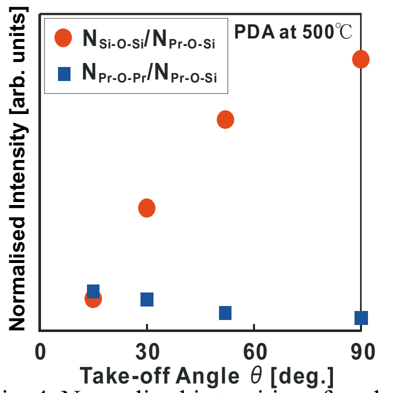

Fig. 4. Normalised intensities of peaks related to Si-O-Si ($N_{Si\text{-}O\text{-}Si}/N_{Pr\text{-}O\text{-}Si}$) and Pr-O-Pr ($N_{Pr\text{-}O\text{-}Pr}/N_{Pr\text{-}O\text{-}Si}$) as a function of TOA.

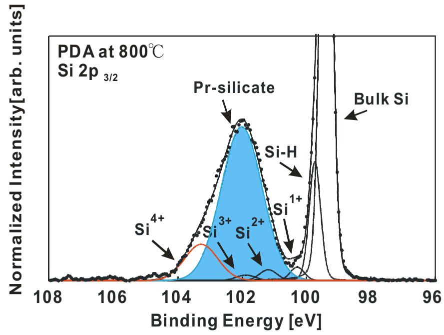

Fig. 5. XPS Si $2p_{3/2}$ spectra of the sample after PDA at 800 ºC , deconvoluted by using seven peaks.

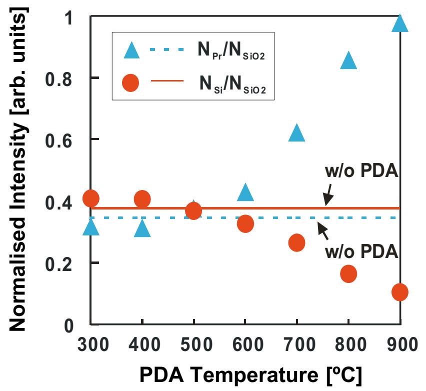

Fig. 6. Normalised intensities N_{Pr}/N_{SiO_2} and N_{Si}/N_{SiO_2} as a function of PDA temperature extracted from Si $2p_{3/2}$ spectra.

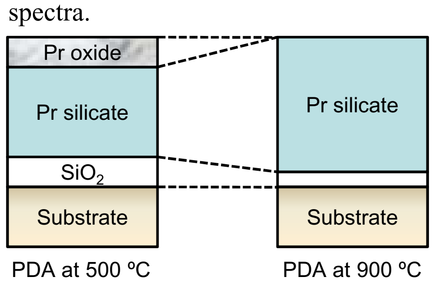

Fig. 7. Schematics of Pr-silicate/SiO_2 stack formation after PDA.