Structural and Electrical Properties of Praseodymium Silicate Ultrathin Gate Dielectrics Grown by MOCVD

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1. Introduction

An extensive study of high-*k* gate dielectrics has been conducted to overcome a leakage current issue with ultrathin gate SiO_2 used for silicon-based sub-100 nm semiconductor devices [1]. Further device scaling may require other gate dielectrics with dielectric constants higher than that for HfO_2 (k ~ 20). Rare earth oxides are attractive candidates for the next generation high-*k* gate dielectrics [2]. In Ref. [3], a dielectric constant as high as ~31 was reported for the Pr_2O_3 film grown epitaxially on the Si substrate. It was showed that the praseodymium oxide and related composites are potential materials. Among various methods, metal-organic chemical vapor deposition (MOCVD) is a leading deposition technique because of its good surface coverage and large-area uniformity. In this paper, the preparation of praseodymium silicate (Pr-silicate) ultrathin films using MOCVD, and structural and electrical properties of the films are discussed.

2. Experiments

In the present work we used a p-type Si(100) substrate (1 – 10 Ωcm), on which a 1 nm-thick chemical oxide layer was prepared. Pr-silicate thin films were deposited by MOCVD using $Pr(DPM)_3$ as a precursor. Since oxygen atoms are contained in this precursor, we do not use any oxidizing agent in this study, and the source was continuously supplied to the chamber. Total pressure in the reaction chamber during deposition was kept at 1.5 Torr. Films were grown at 770 °C. The chemical structure and the band energy profile at the Si/Pr-silicate interface were studied using the high-resolution x-ray photoelectron spectroscopy (HRXPS). Photoelectrons were excited by the monochromatic AlKα radiation with an acceptance angle of 3.3°, using ESCA-300 (Scienta Instruments AB). Capacitance-Voltage (*C*-*V*) characteristics and the leakage current densities (J_gs), were studied for the Au/Pr-silicate/Si/Al MIS diode structure.

3. Results and discussion

Angle-resolved O 1s spectra for the film with the thickness of 7.5 nm are shown in Fig. 1(a). Two peaks around 530 eV and 533 eV in the spectra with the take-off angles (TOAs) of 8° and 15° can be attributed to the Si-O or H-O, and Pr-O bonds, respectively. Note that a peak between the above two peaks develops in the spectrum with the TOA of 90 ° and can be attributed to the Si-O-Pr bonds, which imply the formation of praseodymium silicate. In the spectra for a thinner (5.5 nm) film (Fig. 1(b)), the Pr-silicate peak is clearly observed even in the spectrum with the lowest TOA, while the peak at 530 eV is not identified.

A cross-sectional TEM image of the 5.5 nm-thick film is shown in Fig. 2. A thin Pr-silicate layer maintains amorphous structures in spite of the growth at rather high temperature of 770 °C.

From the analysis of O1s energy loss spectrum and angle-resolved valence band spectra shown in Fig. 3, the band gap of Pr-silicate was estimated to be 6.3 eV and the valence and the conduction band offsets at the Pr-silicate/Si interface to be 2.3 eV and 2.9 eV, respectively.

The *C*-*V* and J_g-*V* curves for the MIS diode are shown in Fig. 4. The film with a capacitance equivalent thickness (CET) of ~1.5 nm and J_g of ~ 9.6×10^{-6} A/cm^2 at V_{fb}-1 V was obtained.

4. Summary

The Praseodymium silicate ultrathin film formed on the Si(100) substrate by MOCVD was studied by using the HRXPS measurement. Both the valence and conduction band offsets at the Pr-silicate/Si interface are larger than 1 eV, which meets a general criterion for deciding whether the material can be used as a gate dielectric for reducing the leakage current.

Reference

[1] G. D. Wilk, R. M. Wallace, and J. M. Anthony, J. Appl. Phys. **89**, 5243 (2001).

[2] H. Iwai, S. Ohmi, S. Akama, C. Ohshima, A. Kikuchi, I. Kashiwagi, J. Taguchi, H. Yamamoto, J. Tonotani, Y. Kim, I. Ueda, A. Kuriyama, and Y. Yoshihara, IEDM Tech. Dig., 625 (2002).

[3] H. J. Osten, J. P. Liu, P. Gaworzewski, E. Bugiel, and P. Zaumseil, IEDM Tech. Dig., 653 (2000).

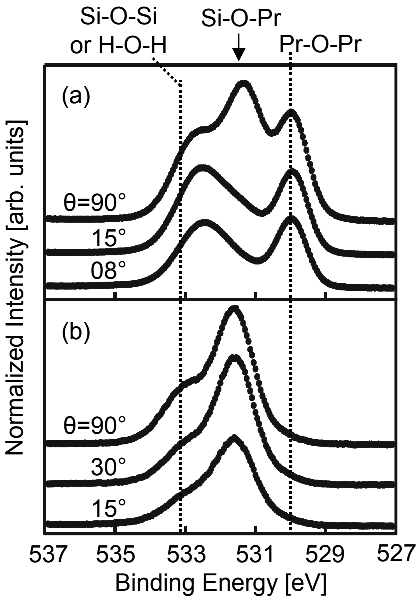

Fig. 2 Angle-resolved XPS spectra of the film deposited at 770 °C with the thickness of (a) 7.5 nm, and (b) 5.5 nm.

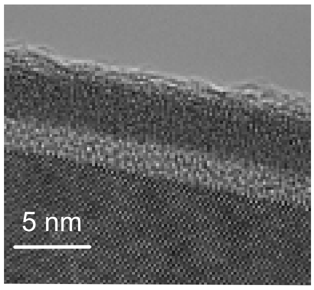

Fig.2 A cross-sectional TEM image of the Pr-silicate thin film.

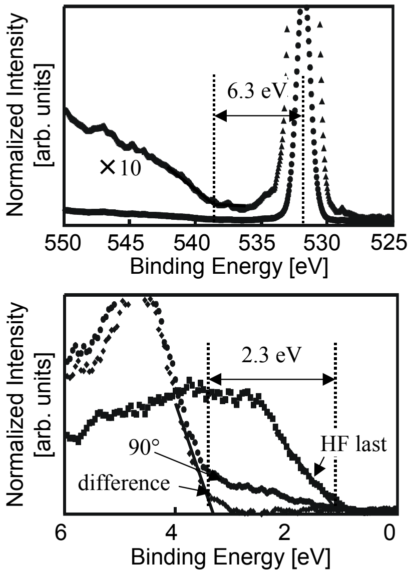

Fig. 3 The O1s energy loss spectrum (a) and angle-resolved valence band spectrum (b) of the Pr-silicate thin film.

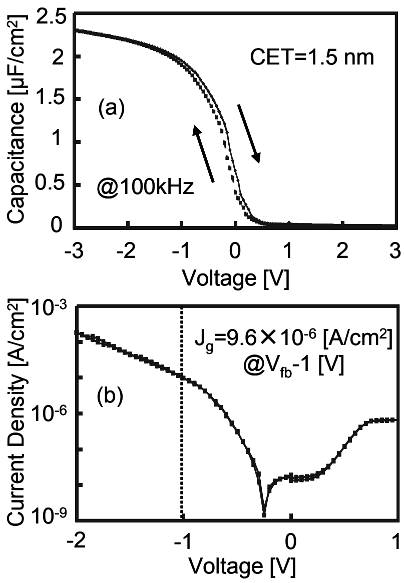

Fig. 4 Electrical properties of the sample: (a) *C*-*V* curve; (b) J_g –*V* curve.