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Importance of control of oxidant partial pressure on structural and electrical properties of Pr-oxide films

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ABSTRACT

For formation of gate dielectrics with higher permittivity (higher-k) using rare-earth oxide thin film, we have investigated the effect of H_2O partial pressure (P_{H_2O}) during the Pr-oxide film formation and annealing on the Pr valence states and the amorphous and crystalline phase structures of the Pr-oxide films. The amorphous structure of Pr-oxide is dominantly formed in the film formed by metal–organic chemical vapor deposition (MOCVD) at a low temperature of 300 °C. The decrease in P_{H_2O} during MOCVD leads to the formation of Pr_2O_3 (Pr^{3+}) composition compared with PrO_2 (Pr^{4+}) composition. It achieves the increase in the permittivity of the Pr-oxide films. The P_{H_2O} value drastically changes the grain size of crystal Pr-oxide in the amorphous film, and the crystalline structure is identified to be hexagonal Pr_2O_3 without depending on the Pr-oxide composition in the amorphous region. The annealing of the Pr_2O_3 film in vacuum at 500 °C promotes the crystallization of the hexagonal Pr_2O_3 phase, although the annealing in N_2 ambient forms cubic Pr_2O_3 phase.

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1. Introduction

For improving a drive current and suppressing a short channel effect of metal-oxide-semiconductor field effect transistors (MOSFETs), gate dielectrics with higher permittivity than Hf-based oxides (higher-k) are strongly required. Recently, crystalline controlled HfO_2, ZrO_2, and rare-earth oxides have attracted attentions as candidates for higher-k oxide materials [1–3]. In these oxide materials, we focus on the praseodymium (Pr) oxide film, which is one of the rare-earth oxides, because Pr-oxide has high permittivity of 31 [4–6]. In addition, it is reported that the large effective masses of f-electrons in Pr contribute to the small gate leakage current of films [7].

The important issues for putting into practical use of Pr-oxide films are precise control of film structure of Pr-oxide and valence states of Pr with a low process temperature. The low temperature is one of the essential process conditions for the realization of gate stack structures with superior MOS interfacial structures using higher-k oxides and semiconductor materials with high mobility. This is because the degradation of MOS interfacial structures easily occurs even with a process temperature below 500 °C due to the decomposition reaction of Ge-oxides or group-V-oxides at the higher-k/semiconductor interface [8–10]. On the other hand, the low process temperature puts a restriction on the process window for the formation of the crystalline controlled higher-k film. In particular, some reports imply the formation of amorphous structure in the film formed at less than 750 °C [11,12]. Therefore, the control of the film structure such as crystal and amorphous at a low temperature will be an important technique, since the formation of the crystallized oxide film is one of the key factors to realize the permittivity more than 30 as introduced previously. In other words, importance of clarification of effect of formation method and post deposition annealing (PDA) at a low temperature below and around 500 °C on the Pr-oxide film and the Pr-oxide film property consisting of not only crystal structure but also amorphous structure becomes large for the application of Pr-oxide to gate stacks. Nevertheless, most works are biased toward the investigation of properties of crystallized Pr-oxides in the film, and annealing processes at high temperature more than 700 °C are often performed [11].

The other feature of Pr is that Pr is multi-valent element, and it has trivalent (Pr^{3+}) and tetravalent (Pr^{4+}). At the same time, crystalline Pr-oxide has some crystalline structures such as hexagonal Pr_2O_3 (hex-Pr_2O_3), cubic Pr_2O_3 (cub-Pr_2O_3), and cubic PrO_2 (cub-PrO_2). In these crystalline structures, hex-Pr_2O_3 is the crystalline phase with high permittivity compared to other structures [4–6,13]. Previously, it is reported that crystalline phase of the Pr-oxide films depends on formation techniques such as atomic layer deposition, chemical vapor deposition (CVD), and molecular beam epitaxy, and low oxidant pressure conditions tend to realize the hex-Pr_2O_3 crystalline phase [6,12–15]. In contrast, the Pr-oxide phase with high oxygen concentration compared with Pr_2O_3 phase such as PrO_2 and Pr_6O_{11} is preferentially formed with increasing the oxidant partial pressure [11,14], and the critical point of the oxidant partial pressure for the change in the phase structure of Pr-oxide should be particularly clarified. However, the rare-earth-oxide film properties such as the valence states of rare-earth elements or phase structures in the film consisting of

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amorphous or both amorphous and crystal structures have not been systematically clarified yet.

From these observing points, in this study, we have tried to clarify the effect of the H_2O partial pressure during the Pr-oxide film formation by metal–organic CVD (MOCVD) and annealing on the film structures of the Pr-oxide films. We have systematically investigated chemical bonding states, crystalline structures, and electrical properties of the Pr-oxide films with both amorphous and crystal phase structures.

2. Experimental details

After diluted-HF treatment of a p-Si(001) substrate, a SiO_2 layer with a thickness of 6 nm was formed by thermal oxidation at 1000 °C. Subsequently, Pr-oxide films were formed on the SiO_2 layer by using MOCVD method with $Pr(EtCp)_3$ and H_2O as precursor and oxidant, respectively. The partial pressure of H_2O (P_{H_2O}) was controlled to be 3, 20, and 240 Pa by an elaborate needle valve during the MOCVD process. The substrate temperature was set to be 300 °C. Thicknesses of the Pr-oxide films were in the range from 7 to 32 nm, which were evaluated by ellipsometry. Post deposition annealing (PDA) was performed at 500 °C or 700 °C for 15 min in N_2 ambient or in vacuum with a pressure less than 10 Pa for some Pr-oxide/SiO_2/Si samples. Finally, Al electrodes were formed using vacuum evaporation method, and MOS capacitors with Al/Pr-oxide/SiO_2/Si stack structure were fabricated.

Amorphous and crystalline structures in the Pr-oxide films were investigated by transmission electron microscopy (TEM) and in-plane 2θ measurement of X-ray diffraction (XRD) (Rigaku, ATX-G). TEM samples were prepared with Ar ion milling, and the operating voltage for the TEM observation (JEOL, JEM-2010 F) was 200 keV. Also, 2θ is a diffraction angle between incident X-ray and diffracted X-ray. Chemical bonding structures of the samples were investigated by hard X-ray photoelectron spectroscopy (HAXPES) using radiation light with photon energy of 7939 eV and angle resolved X-ray photoelectron spectroscopy (AR-XPS) methods with Al$K\alpha$ line ($h\nu = 1486.6$ eV) (Thermo VG Scientific, ESCALAB210). Here, HAXPES measurement was performed at the beamline of BL46XU in the Super Photon ring 8 GeV (SPring-8) in Japan. The permittivities of the Pr-oxide films were evaluated from capacitance–voltage (C–V) characteristics of the MOS capacitors.

3. Results and discussion

3.1. Impact of H_2O partial pressure on amorphous and crystalline structures and permittivity of Pr-oxide films

In this section, the physical structures of the Pr-oxide film formed with various P_{H_2O} are investigated focusing on the film structures of amorphous or crystal and Pr valence states, and its effect on the permittivity is discussed. Fig. 1 shows C–V characteristics of the Al/Pr-oxide/SiO_2/Si MOS capacitors measured at room temperature. The measurement frequency is 1 kHz, to suppress the influence of the parasitic resistance in the MOS capacitors on the C–V characteristics. The thicknesses of the Pr-oxide films formed at P_{H_2O} of 3, 20 and 240 Pa are 21, 19, and 21 nm, respectively. The accumulation capacitance increases with decreasing P_{H_2O}. This indicates the increase in the permittivity of the Pr-oxide film with decreasing P_{H_2O}, which is discussed in Fig. 2 more quantitatively, because the physical thickness of the Pr-oxide film is almost same in these samples. It is also found that the interface state density of these samples is less than 3×10^{11} eV^{-1} cm^{-2} from the conductance–voltage characteristics. On the other hand, the hysteresis voltage width in the C–V characteristics increases with P_{H_2O}. The polarity of the hysteresis indicates the ion drift in the Pr-oxide film or electron injection from the gate electrodes to the Pr-oxide film.

Fig. 2(a) shows the relationship between capacitance equivalent thicknesses (CET) evaluated from the accumulation capacitance in the C–V characteristics measured at 1 kHz and the physical thickness of the Pr-oxide film ($d_{Pr\text{-}oxide}$). The slope of the CET-$d_{Pr\text{-}oxide}$ relationship decreases with decreasing P_{H_2O}. Since the Pr-oxide film and the interlayers formed at Pr-oxide/Si and/or Al/Pr-oxide make a series capacitance, the relationship between CET and $d_{Pr\text{-}oxide}$ is expressed as Eq. (1).

$$\mathrm{CET} = \frac{\varepsilon_{SiO_2}}{\varepsilon_{Pr-oxide}} \times d_{Pr\text{-}oxide} + \mathrm{EOT_{IL}}, \quad (1)$$

here, ε_{SiO_2} and $\varepsilon_{Pr\text{-}oxide}$ are the permittivities of ideal SiO_2 and the Pr-oxide film, respectively, and $\mathrm{EOT_{IL}}$ is the total equivalent oxide thickness of the interlayers at Pr-oxide/Si and/or Al/Pr-oxide interfaces. The inverse of the slope of the CET-$d_{Pr\text{-}oxide}$ relationship corresponds to the permittivity of the Pr-oxide film. Fig. 2(b) shows the P_{H_2O} dependence of relative permittivity of the Pr-oxide film evaluated from the CET-$d_{Pr\text{-}oxide}$ relationship shown in Fig. 2(a). The relative permittivity of 3.9 was used for ideal SiO_2. It is found that the permittivities of the Pr-oxide film increases with decreasing P_{H_2O} during the MOCVD process, and that the relative permittivity of the Pr-oxide film formed at P_{H_2O} of 3 Pa is 15 ± 4. Also, the both intercepts of the CET axis of the CET-$d_{Pr\text{-}oxide}$ relationships of the samples formed at P_{H_2O} of 3 and 20 Pa are approximately 5 nm as shown in Fig. 2(a). That is in good agreement with the thickness of the thermally-oxidized SiO_2 film formed before the Pr-oxide film formation, suggesting that an insulating layer is hardly formed at the Al/Pr-oxide interface or it hardly affects on the CET values of the MOS capacitors even if the interlayer is formed at the Al/Pr-oxide interface. On the other hand, the $\mathrm{EOT_{IL}}$ value of the sample at

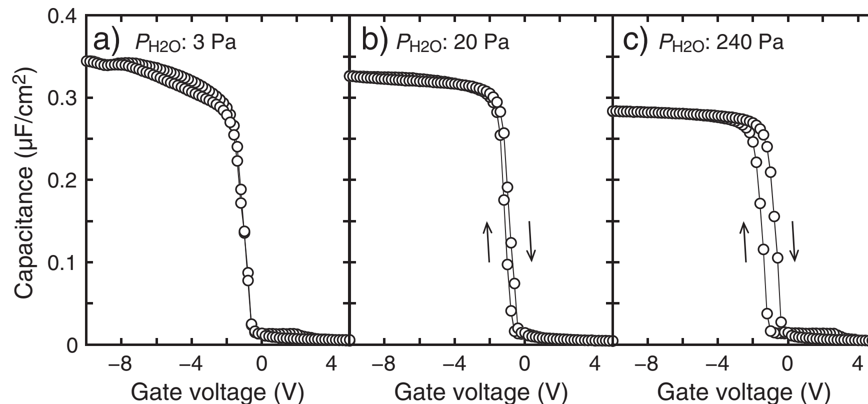

Fig. 1. Capacitance–voltage characteristics of Al/Pr-oxide/SiO_2/Si MOS capacitors before PDA measured at room temperature with a frequency of 1 kHz. P_{H_2O} are (a) 3 Pa, (b) 20 Pa, and (c) 240 Pa, and the thickness of the Pr-oxide film is 21, 19, and 21 nm, respectively.

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