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Structural evolution and defect control of yttrium-doped ZrO_2 films grown by a sol–gel method

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ABSTRACT

Yttrium-doped ZrO_2 thin-films were prepared on Si substrates via sol–gel synthesis at a low temperature of 700 °C. During sol–gel synthesis, yttrium can easily take the place of the zirconium in ZrO_2, even at low ambient process temperatures. We were therefore able to successfully synthesize yttrium-doped zirconium oxide (Y-ZrO_2) with a clean interface without the generation of zirconium silicate, which is formed at high temperatures (~1000 °C). Doped yttrium can eliminate the interstitial oxygen contained in ZrO_2 thin films as O_2^{-1} states. The conduction band offset (CBO) is also increased via yttrium doping: from 1.69 eV for ZrO_2 to 1.99 eV for Y-ZrO_2 in the as-grown films, and from 1.27 eV for ZrO_2 to 1.35 eV for Y-ZrO_2 in the annealed films. The difference observed in the CBO of the as-grown films may be caused by interstitial oxygen, which is formed in the ZrO_2 films, while the annealed films have oxygen vacancies. The reported data show that yttrium doping of ZrO_2 induces the formation of a yttrium–oxygen vacancy pair, which can reduce the formation energy of oxygen vacancies. However, using the density-of-states analysis from the VASP code density functional theory (DFT) calculations, we confirm that the oxygen vacancy in the Y-ZrO_2 did not generate defect states within the silicon band gap, whereas in the ZrO_2 it did generate defect states within the silicon band gap. Using the conductance method, reductions in the interfacial trap charge densities of approximately 20% were observed near the mid-gap in Y-ZrO_2, as compared with undoped ZrO_2. Following the application of electrical stress, the reduction in interface states was found to be greater in the Y-ZrO_2 film, which is consistent with the DFT calculation.

1. Introduction

Improving the performance of semiconductor devices via methods such as minimization of power consumption and maximization of operational speed is an issue of equal importance to the downscaling of devices [1]. However, critical problems such as leakage current and unreliability have emerged as the device sizes approach physical limits, due to the thinness of the dielectric oxide film layer [2]. High-k insulators have been widely and intensively researched to replace SiO_2 as a dielectric layer [3]. Among the many candidate materials, zirconium dioxide (ZrO_2) is one of the most promising materials due to its band gap (E_g) (5.16–7.8 eV), proper conduction band offset (~1.5 eV) and high dielectric constant (k) (~25) [4]. The many interfacial states of ZrO_2, approximately $\sim 10^{13}$ electrons/ev cm^2 [5], present a critical barrier to the application of ZrO_2 as a dielectric layer. It is therefore vital to reduce the interfacial states by modifying the ZrO_2 film using a simple and low-cost method.

It has been reported that the doping of these rare earth materials reduces interfacial states and increases the dielectric constant in HfO_2/Si systems [6–8]. Since the chemical bonding properties of ZrO_2 are similar to those of HfO_2 due to a shared number of valance electrons, doping rare earth material to ZrO_2 is expected to have the same effect on electrical properties. Among many dopants, yttrium has been widely used to enhance thermal and mechanical barriers [9]. Wang et al. show that yttrium-doped zirconium oxide (Y-ZrO_2) deposited on a silicon substrate using molecular beam deposition has a low interface state density, approximately 2×10^{11} eV^{-1} cm^{-2} [10], though the application of molecular beam deposition in industrial fields is problematic due to its small deposition area

Abbreviations: XAS, X-ray absorption spectroscopy; HRXPS, high resolution X-ray photoelectron spectroscopy; REELS, reflection electron energy loss spectroscopy; DFT, density functional theory; CBO, conduction band offset; VBO, valance band offset.

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and high cost. In addition, the more economical method of synthesizing Y-ZrO_2, often called yttrium-stabilized zirconium (YSZ), requires a high-temperature doping process, including sintering (1200 °C) [11] and sputtering (800 °C) [12]. At these temperatures, ZrO_2 readily reacts with the silicon substrate to form zirconium silicate, which undesirably decreases the dielectric constant and increases the defect density [13]. The sol–gel process is a well-known method, useful because various films can be synthesized at low temperatures without the formation of an interfacial reaction. The sol–gel process has many advantages over the vacuum process, including large-area deposition, precise composition control, high homogeneity, simple processing for the incorporation of additional species and low cost [14]. Despite these advantages, Y-ZrO_2 film grown via the sol–gel process has not previously been verified.

In this study, Y-ZrO_2 produced via the sol–gel method shows improved electrical properties over undoped ZrO_2. We investigate the origin of the enhancement in electrical properties through chemical property analysis of the films. Various chemical properties of Y-ZrO_2 thin films grown via the sol–gel method are evaluated using combined spectroscopic, electrical and theoretical methods. High-resolution X-ray photoelectron spectroscopy (HRXPS) was performed to confirm the chemical bond states of yttrium in the doped thin films. The crystalline structure was investigated using high-resolution transmission electron microscopy (HRTEM), and more detailed structural changes are examined via X-ray absorption spectroscopy (XAS) using the O K_1-edge spectrum of undoped and Y-ZrO_2 films. The refraction electron energy loss spectroscopy spectra (REELS) and HRXPS valance band spectrum are analyzed to determine the electronic structure in the band gap. Electrical measurements were performed to investigate the charging and interface states. Finally, the energy levels and formation energy of the defect states were evaluated via density functional theory (DFT) calculations using the VASP code with the MEDEA program [15] to explain the electrical measurements.

We deposited 5-nm-thick ZrO_2 and Y-ZrO_2 films using sol–gel synthesis [16]. Zirconium-n-butoxide was used as a base solution for ZrO_2 and Y-ZrO_2. To incorporate the yttrium into the ZrO_2 film, approximately 10 mol% yttrium nitrate hexahydrate was added to the base solution. Acetic acid and nitric acid were used as the chelating agent and catalyst, respectively. Yttrium nitrate hexahydrate was added to zirconium-n-butoxide, and the mixture was stirred for 3 h to obtain a completely mixed solution. The sol was placed on the silicon substrate using a spin coater and subsequently heated at 100 °C. Finally, the sample was heated at 400 °C in air to finalize film synthesis. To confirm the suitability to a conventional post process, both films were annealed at 700 °C under a nitrogen ambient for 2 min. The quantity of Y in ZrO_2 was confirmed as 10% using XPS. To confirm the thickness, morphology and crystal structure of the films, the high resolution transmission electron microscopy (HRTEM) images shown in Fig. 1(a) and Fig. 2(a) were analyzed. The low magnified images of ZrO_2 and Y-ZrO_2 films indicate that the films synthesized by the sol–gel method were uniformly grown. The uniform morphology of films was preserved after annealing at 700 °C. For the ZrO_2 film, the thickness of the as-grown film, 5.5 nm, decreased to 5.0 nm through the crystallization process during the annealing process. The interface layer of the as-grown film, 1.8 nm, slightly increased after annealing at 700 °C. For Y-ZrO_2 film, an oxide thickness of 5.0 nm in the as-grown film was maintained after annealing at 700 °C. The 1.9-nm change in the interface oxide of Y-ZrO_2 was similar to the ZrO_2 film during the annealing process. The FFT image in the inset of Fig. 1(a) was obtained from the boxed yellow section of Fig. 1(b). The diffraction of the as-grown film shows a blurred ring shape that represents an amorphous structure. Alternatively, the image of the annealed film shows the specific diffraction pattern in the tetragonal [1 1 0] and [1 0 3] directions.

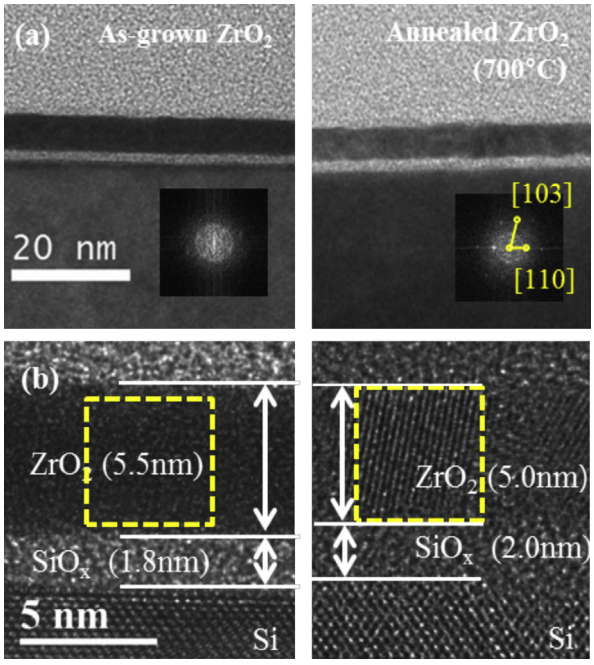

Fig. 1. (a) Low magnification TEM images of as-grown ZrO_2 and ZrO_2 annealed at 700 °C. The low magnification image shows uniformly grown films. Insets show FFT images of ZrO_2 films in the region marked by a rectangle in Fig. (b). The amorphous ring pattern for as-grown film and a typical diffraction of tetragonal structure for the annealed film are observed. (b) High magnification images of the ZrO_2 films. Amorphous and crystalline structures are clearly observed in the high magnification images of the films. (For interpretation of the references to color in the text of this figure citation, the reader is referred to the web version of this article.)

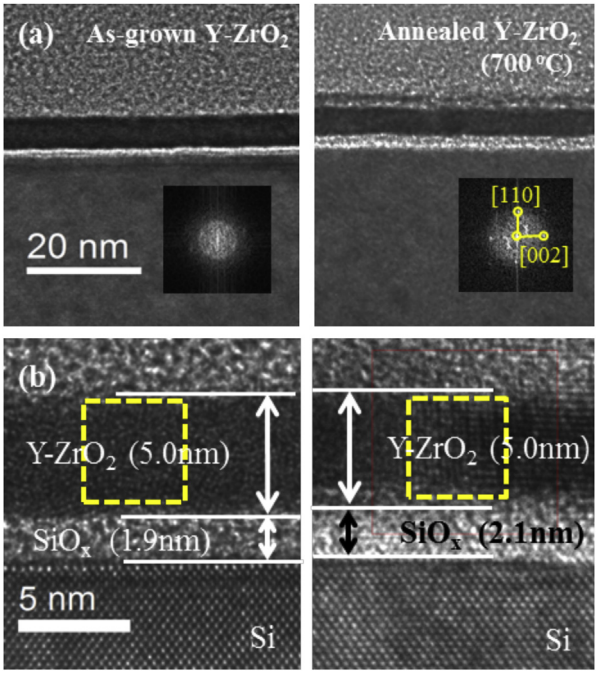

Fig. 2. (a) Low magnification TEM images of Y-ZrO_2 films. FFT images of Y-ZrO_2 films are represented in inset images of the region marked with a yellow rectangle in Fig. (b). Inset images show the amorphous ring pattern for as-grown and crystalline diffraction patterns for the tetragonal structure of the annealed film. (b) High magnification images of Y ZrO_2 films. Amorphous and crystalline structures are clearly observed in the high magnification images of the films, which are nearly the same changes in the crystalline structure and interfacial region as seen in the ZrO_2 film.