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Reactive sputter deposition of epitaxial (001) CeO_2 on (001) Ge

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Abstract

The growth of epitaxial (001) CeO_2 on a (001) Ge surface using a reactive sputter deposition method is reported. Hydrogen gas (4%H_2/Ar sputtering gas) is introduced during film growth in order to reduce or eliminate the presence of the GeO_2 from the semiconductor surface during the initial nucleation of the metal oxide film. A metal cerium target was used as the cation source, with water vapor serving as the oxidizing species. Epitaxial films were sputter deposited at a substrate temperature of 550 °C in a H_2O vapor pressure of approximately 10^{-3} Torr. The hydrogen partial pressure and substrate temperature were selected to be sufficiently high such that the germanium native oxides are thermodynamically unstable. The Gibbs free energy of CeO_2 is larger in magnitude than that of the Ge native oxides, making it more favorable for the metal oxide to reside at the interface in comparison to the native Ge oxides.
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1. Introduction

Metal/oxide/semiconductor field-effect transistor (MOSFET) structures are key elements in microelectronic applications [1,2]. While silicon MOSFETs dominate microprocessor and memory technologies, other semiconductor materials would be attractive for MOS-type device applications given a method to form well-defined oxide/semiconductor interfaces suitable for functional structures. Of particular interest are Ge and SiGe alloys, which are attractive semiconductor materials for electronic applications, possessing higher carrier mobilities and thermal conductivities than that of silicon. Unfortunately, thermally grown germanium oxide is not stable at elevated temperatures, and as such is not suitable for metal-oxide-semiconductor (MOS)-type device structures [3,4]. The formation of a stable dielectric on Ge could prove instrumental in the development of Ge and/or SiGe alloy field-effect technologies. For applications involving sensors, detectors, and optoelectronics, the formation of well-defined metal oxide/semiconductor interfaces for semiconductor materials other than silicon is attractive for current and future device architectures. In addition, a method to grow epitaxial oxides on semiconductor surfaces would enable the integration of various epitaxial oxide materials and device structures with semiconductor electronics by providing a crystalline oxide template for additional epitaxial oxide film growth. In many cases, one would prefer to have a well-defined metal oxide/semiconductor structure devoid of any native oxide at the interface, as the presence of native oxide at the interface often limits the performance of these structures. This has been demonstrated for the case of silicon, in which molecular beam epitaxy was used to grow a crystalline oxide as a monolithic, commensurate structure on silicon [5].

In order to explore the formation of Ge-based MOS device structures, as well as the integration of functional oxides with Ge, we have investigated the epitaxial growth of CeO_2 on Ge (001) substrates using reactive sputter deposition. CeO_2 has several material characteristics that make it attractive as a dielectric buffer layer for gate dielectrics or as a template for subsequent epitaxial oxide growth on Ge, including a moderately high dielectric constant ($\varepsilon_r \cong 17$), a cubic crystal structure, and a reasonable lattice match to Ge (4%). In order to eliminate the native GeO_2 on the Ge surface and achieve epitaxy, hydrogen was introduced as a background gas during the film nucleation [6,7]. Previous work in hydrogen-assisted physical vapor deposition of

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CeO_2 on Ge focused on pulsed-laser deposition as the means for film growth [8]. The use of hydrogen greatly relaxes vacuum requirements needed for the formation of a GeO_2-free surface.

2. Experimental details

RF magnetron sputtering was used in our experiments for the deposition of CeO_2 films. Reactive sputtering is amenable to large-area deposition, and is routinely used in semiconductor processing. The experiments were performed in a stainless steel ultra high vacuum (UHV) sputter deposition system that is equipped with two DC sputter guns, two RF sputter guns, an attached load lock chamber, and a radiant heater. A stainless steel vessel connected to the chamber through a vacuum leak valve served as the water vapor source. The purging procedure for the water vapor source consisted of freezing DI-water inside the vessel while evacuating residual air and other airborne impurities. This procedure was done twice in order to eliminate most of the impurity gases from the water vapor source.

Ge (001) substrates were ultrasonically cleaned in sequential baths of trichloroethylene, acetone, and isopropyl alcohol for 5 min each. The native oxide was then removed by a 30 s dipping in a 1:10 HF/H_2O solution. The samples were then blown dry with N_2. A sample platen was ultrasonically cleaned in nitric acid and solvents. The samples were attached to the sample platen using silver paint. After allowing the Ag paint to dry for ~ 1 h, the samples were loaded into the load lock for transfer into the film-growth chamber. The background pressure in the chamber was then set to 25 mTorr of forming gas (4%H_2/Ar), providing a hydrogen partial pressure of 1 mTorr, which is sufficient to yield GeO_2 unstable. In order to outgas the solvent and binder in the silver paint, the sample platen was heated to 100 °C for 30 min. The substrate was then heated to the growth temperature in the 4% H_2/96% Ar background. As the substrate is heated, the hydrogen reduces any GeO_2 that resides or forms on the substrate surface, resulting in the gas-phase etching of the native oxide. The final growth conditions (temperature, water vapor partial pressure, hydrogen partial pressure) must satisfy the requirement that the formation of GeO_2 is thermodynamically unfavored. The most reproducible results were obtained when a 2–3 nm thick Ce metal nucleation layer was deposited prior to introducing the water vapor. The RF sputtering gun was set to 100 W power. The water vapor pressure was adjusted by opening the leak valve. The deposition time was 1.5 h for all experiments.

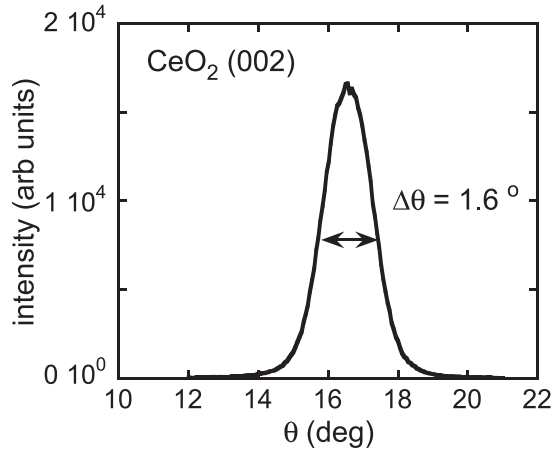

Fig. 2. Rocking curve of the CeO_2 (002) peak showing good out-of-plane alignment.

3. Results and discussion

Epitaxial CeO_2 films on Ge were realized for deposition at 550 °C in H_2O vapor pressures of 10^{-3} Torr. The thickness of the films was approximately 200–300 nm. Fig. 1 shows θ–2θ X-ray diffraction data taken with a film

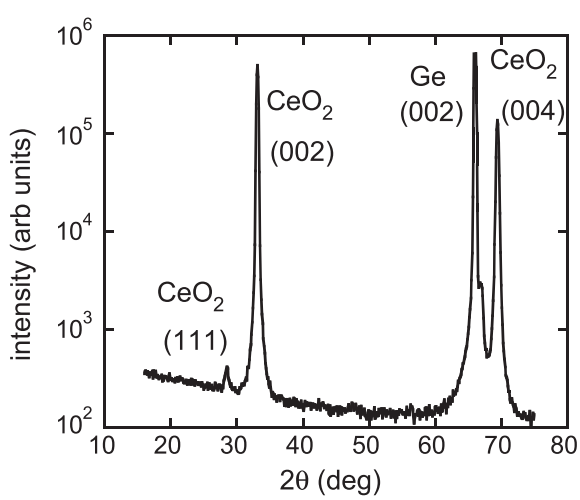

Fig. 1. X-ray θ–2θ diffraction scan along the surface normal showing c-axis orientation for the CeO_2 epitaxial film.

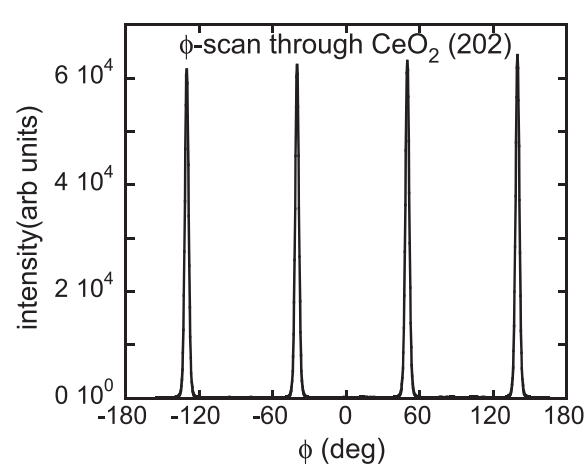

Fig. 3. In-plane ϕ-scan through the CeO_2 (202) peak showing in-plane alignment of the CeO_2 film.

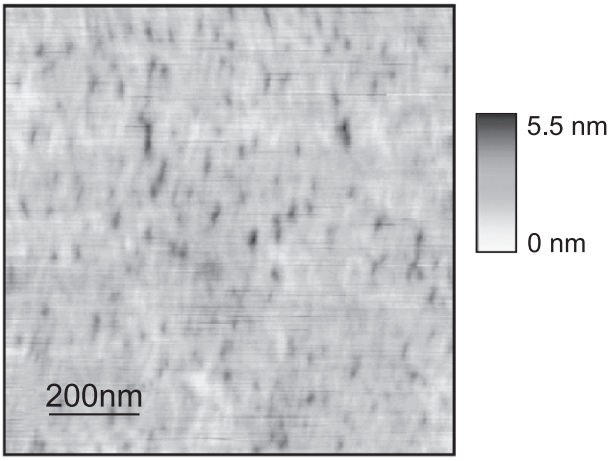

Fig. 4. Atomic force microscopy image of the CeO_2 film.

grown under these conditions. The films deposited at 10^{-3} Torr show a strong (002) peak, indicating excellent growth oriented with the surface of the Ge substrate. Further X-ray diffraction characterization of films was done using in-plane ϕ-scans and ω-rocking curves. Fig. 2 shows the ω-rocking curve data for the film grown at 10^{-3} Torr. The film exhibits good out-of-plane alignment of the (001) planes, with a full-width-half-maximum of only 1.6°. Note that (001)-oriented CeO_2 thin films were obtained on the (001) Ge surface. These results differ from that reported for CeO_2 on (001) Si, where the film was (110)-oriented with significant SiO_2 formation at the film/substrate interface [9–11]. While this mosaic spread is larger than that for the Ge substrate, it is comparable to that achieved for other oxides grown on semiconductor substrates. A four-circle X-ray diffraction ϕ-scan through the CeO_2 (202) is shown in Fig. 3. The data indicate that the CeO_2 film is in-plane aligned with a cube-on-cube orientation relative to the Ge lattice. The in-plane peak width is 3.6° FWHM. The lattice constants for the CeO_2 film are $a = b = 5.411$ Å, and $c = 5.412$ Å, which is remarkably close to those of bulk CeO_2. This suggests that the oxide film does not possess significant oxygen deficiency, as this would be reflected in an expanded unit cell. All of these results indicate good epitaxial growth of CeO_2 layer on the Ge substrate.

In addition to crystallinity, the surface morphology was also investigated using atomic force microscopy. Fig. 4 shows an image taken on a film grown at 550 °C. Note that the surface is somewhat rough, with a RMS roughness of 0.43 nm. This may reflect a tendency for the Ge (001) surface to facet upon heating as has been observed in cross-section TEM images taken for CeO_2 epitaxial films on Ge grown by pulsed-laser deposition. Lower temperature processing may help to alleviate this roughening of the surface.

4. Conclusion

In conclusion, the growth of epitaxial CeO_2 films on (001) Ge substrates using reactive RF magnetron sputtering is reported. A key to obtaining reproducible results is to control the water vapor partial pressure both during nucleation and oxide film growth. Future work will focus on characterizing the dielectric and optical properties of the CeO_2 films, as well as the properties of the Ge/CeO_2 interface.

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