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ABSTRACT

We describe the growth and properties of epitaxial (001) CeO_2 on a (001) Ge surface using a hydrogen-assisted pulsed-laser deposition method. Hydrogen gas is introduced during film growth to eliminate the presence of the GeO_2 from the semiconductor surface during the initial nucleation of the metal oxide film. The hydrogen partial pressure and substrate temperature are 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. By satisfying these criteria, the metal oxide/semiconductor interface is shown to be atomically abrupt with no native oxide present. Preliminary structural and electrical properties are reported.

INTRODUCTION

Metal/oxide/semiconductor (MOS) structures are key elements in microelectronic applications. [1,2] Various semiconductor materials would be attractive for MOS-type device applications given a method to form well-defined oxide/semiconductor interfaces suitable for functional structures. For example, Ge and SiGe alloys are attractive semiconductor materials for electronic applications, possessing higher carrier mobilities and thermal conductivities than that of silicon. Germanium possesses a simple cubic crystal structure with $\mu_n = 3900$ cm^2/V-sec, $\mu_p = 1800$ cm^2/V-sec, and a thermal conductivity of 0.6 W/cm-K. Unfortunately, the native germanium oxides are not suitable for MOS-type device structures.[3,4] The formation of stable metal oxides on Ge could prove instrumental in the development of Ge and/or SiGe alloy integrated circuits. For applications involving sensors, photovoltaics, and optoelectronics, the formation of well-defined metal oxide/semiconductor interfaces for semiconductor materials other than silicon is vital to current and future device architectures. 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 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 addition, a method to form oxides that are epitaxial on semiconductors 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 this paper, we report on the epitaxial growth and properties of CeO_2 on (001) Ge using pulsed-laser deposition (PLD). Hydrogen is introduced as a background gas during the film nucleation in order to eliminate the native GeO_2 on the Ge surface and achieve epitaxy.[6,7] The use of hydrogen greatly relaxes vacuum requirements needed for the formation of a GeO_2-free surface. Using this approach, (001)-oriented CeO_2 thin films were obtained on the (001) Ge surface. The resulting metal oxide/semiconductor interface is atomically abrupt, with no apparent native oxide present at the semiconductor /metal oxide interface. These results differ from that observed for CeO_2 on (001) Si, where the film is (110)-oriented with significant SiO_2 formation at the film/substrate interface.[8-10]

EXPERIMENTAL DETAILS

The deposition of (001) epitaxial cerium oxide on single crystal Ge (001) was performed by pulsed-laser deposition using a KrF excimer laser. Single crystal (001) Ge substrates were cleaned by successive rinsing in trichloroethylene, acetone, and methanol, followed by rinsing in deionized water. The native oxide was then removed by a 30 sec dipping in a 1:10 HF:H_2O solution. The substrate was blown dry with dry nitrogen and mounted on the heater platen using silver paint. The sample was loaded into the vacuum chamber for pulsed-laser deposition of the oxide film. The chamber was evacuated to an initial base pressure that ranged from 5×10^{-6} Torr to 2×10^{-9} Torr. The mounted Ge substrate was annealed in vacuum at 350°C for 2-12 hrs in order to decompose the organic binder in the silver paint. Prior to heating, the ablation target was in situ cleaned by laser ablation with a shutter between the substrates and ablation target.

In order to minimize or eliminate any native germanium oxide on the substrate surface prior to growth, hydrogen gas was introduced into the chamber to a sufficient pressure such that the ratio of hydrogen to water vapor partial pressure $P(H_2)$ / ($P(H_2O)$ was approximately at or above the GeO_2 stability curve at the anticipated oxide film growth temperature as shown in Fig. 1. This curve was derived from Ellingham diagrams for oxide materials.[11,12] The oxide stability line can be estimated from the temperature-dependent Gibbs free energy of the chosen native oxide when compared to the H_2O/H_2 equilibrium behavior. Depending on the anticipated metal oxide deposition temperature, the

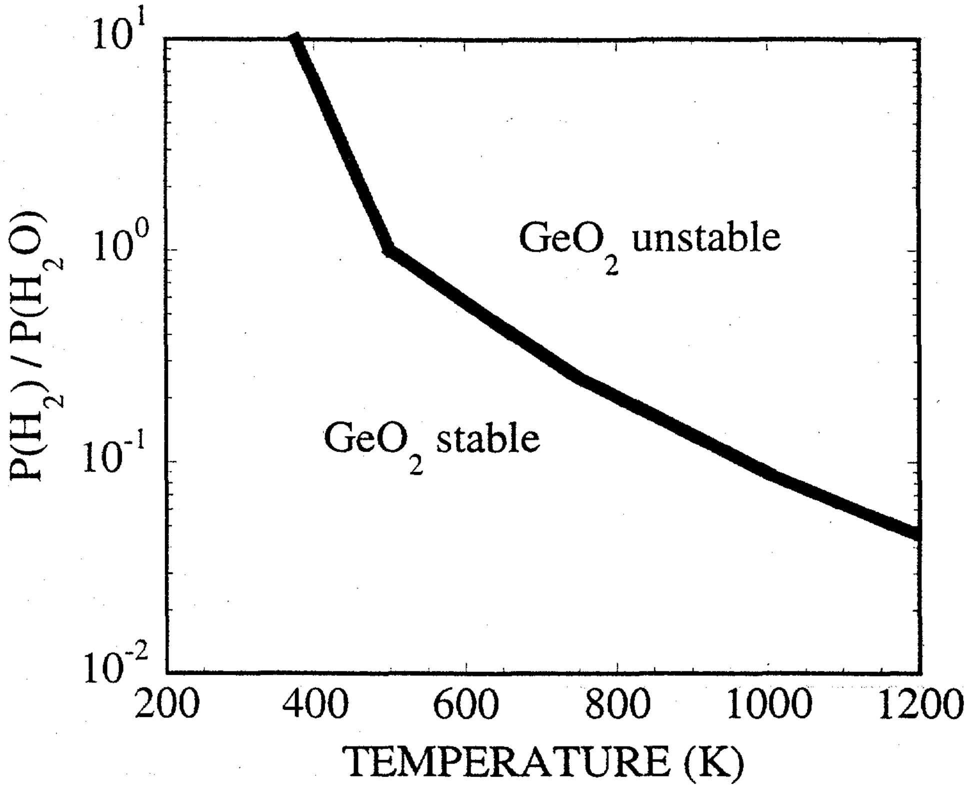

Figure 1. *Plot showing GeO_2 stability line with respect to the ratio of hydrogen gas to water vapor. The conditions for which GeO_2 is unstable are explicitly denoted.*

GeO_2 instability criterion translates into a value of $P(H_2)/P(H_2O) > 0.04$, preferably greater than 1.0. As a practical matter, the base pressure of the vacuum systems consists mostly of H_2O.

For the experiments reported here, a flow of 4% H_2 / 96% Ar was introduced into the chamber with the H_2/Ar pressure ranging from 10^{-5} to 10^{-1} Torr, depending on the base pressure. For example, an H_2/Ar pressure of 0.1 Torr yields a hydrogen partial pressure of 4×10^{-3} Torr, and a value of $P(H_2)/P(H_2O)$ of 8×10^{2} for a base pressure of 5×10^{-6} Torr. 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 temperature must be consistent with the requirement that the conditions (temperature, water vapor partial pressure, hydrogen partial pressure) be above the GeO_2 stability line where the formation of GeO_2 is thermodynamically unfavored. Under these conditions, a metal oxide material that is stable for the chosen temperature/water vapor/hydrogen conditions can be deposited onto the heated substrate by means of pulsed-laser deposition. This oxide material should be thermodynamically stable in contact with Ge.[13] Cerium oxide satisfies this criterion.

After heating to the selected growth temperature, a CeO_2 film was deposited on the Ge surface. The KrF excimer laser energy density was ~ 1.5 J/cm^2 with a laser repetition rate of 1 Hz. These conditions yielded a deposition rate of ~ 0.1 nm/laser pulse when using a pressed and sintered CeO_2 ablation target. Both the metal cation and oxygen atoms are provided by laser ablation as short, discreet pulses. Between the laser pulses, the metal oxide / semiconductor system can relax to the conditions that thermodynamically favor instability of the native oxides. After the initial film nucleation, additional CeO_2 could be deposited on the initial oxide film template using deposition conditions that do not necessarily coincide with the requirements of GeO_2 thermodynamic instability as outlined for the template oxide layer, thus allowing the CeO_2 stoichiometry to be controlled. After film growth, the germanium substrate was typically cooled in vacuum.

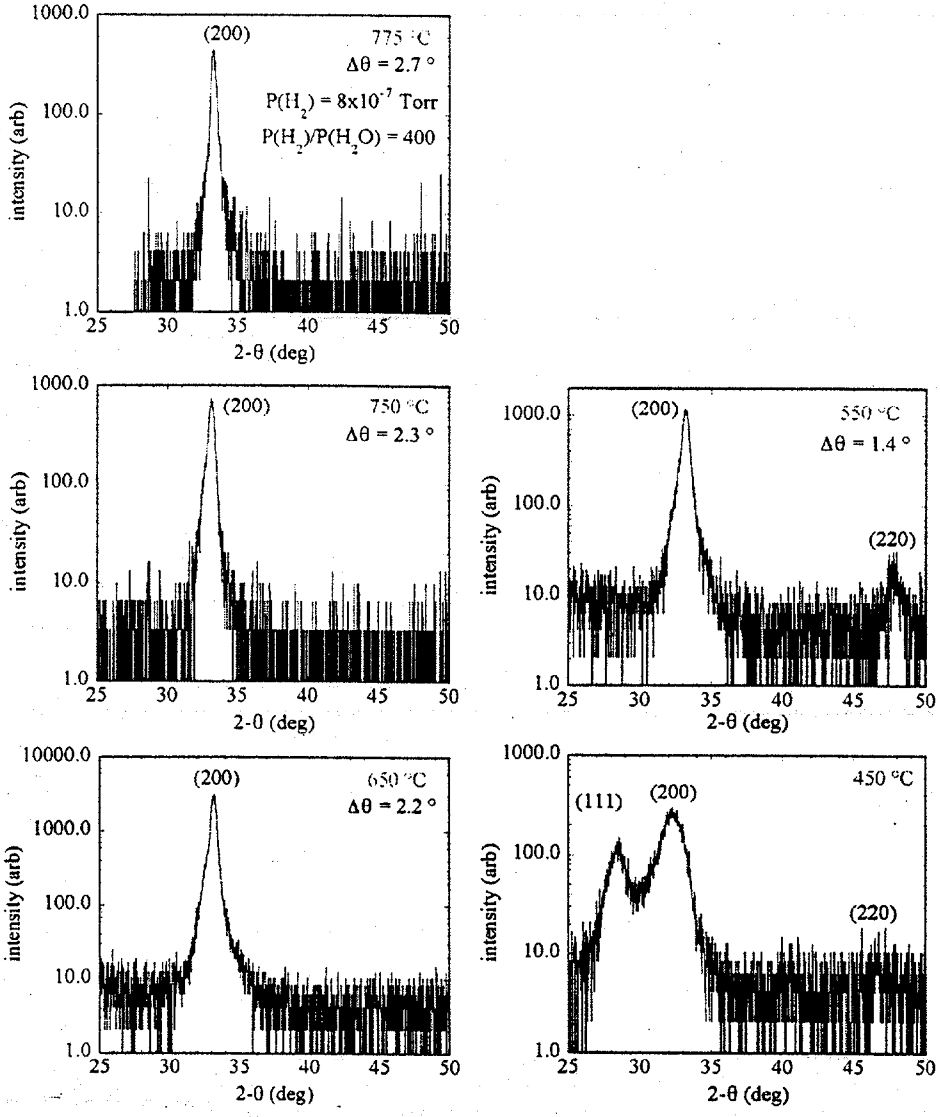

Figure 2 *X-ray diffraction scans along the surface normal for CeO_2 films grown on (001) Ge at various temperatures.*

RESULTS

Figure 2 show x-ray diffraction data for a series of 50 nm thick CeO_2 films on (001) Ge grown at temperatures ranging from 450 to 775°C. The CeO_2 films were deposited with $P(H_2) = 4x10^{-7}$ Torr and a base pressure = $2x10^{-9}$ Torr. Approximately 5 nm was deposited in the presence of hydrogen. The remaining 45 nm of CeO_2 was deposited with no hydrogen flow. Note that for temperatures greater than 550°C, only the (001) orientation is observed. In-plane XRD scans confirm that the CeO_2 films are in-plane aligned. Note that some broadening in 2θ is observed at the lower growth temperature, indicating that strain is present in the film.

In addition to x-ray diffraction, the properties of the CeO_2 / Ge interface were investigated using high-resolution scanning transmission electron microscopy (STEM). Cross-section images reveal that CeO_2 films deposited at 750°C possesses a 3D island-like morphology that is faceted, with extended defects (pinholes) extending to the substrate at some of the faceted boundaries. Disruption of the CeO_2/Ge interface in the form of etched holes or amorphous material

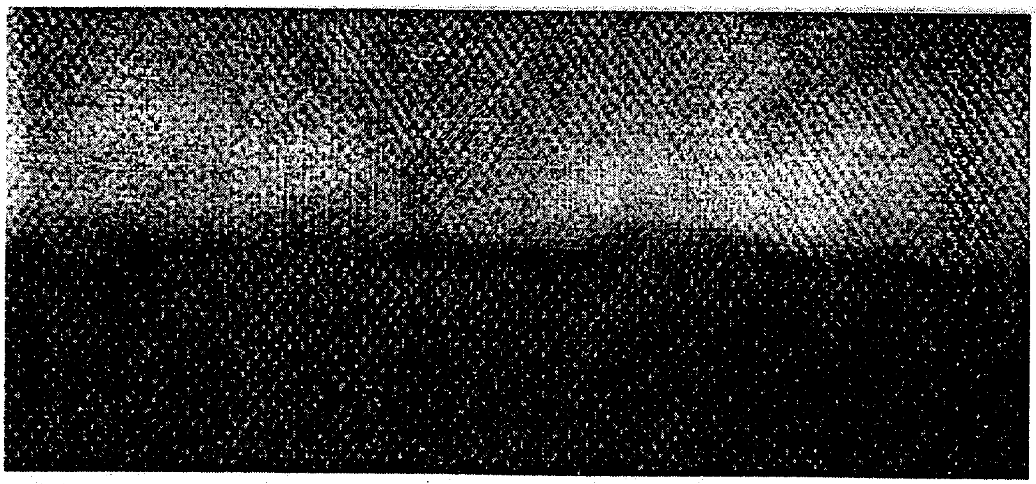

Figure 3 *High resolution STEM image of the atomically abrupt CeO_2/Ge crystalline interface.*

was evident in the proximity of these defects. Between the defects, the CeO_2/Ge interface is atomically abrupt and free of GeO_2. At slightly lower temperatures, faceting is significantly diminished. Figure 3 shows a cross-section Z-contrast STEM image of a CeO_2 film that was grown at 650°C. The absence of an amorphous native oxide layer at the interface differs from that observed for CeO_2 films on Si, where significant SiO_2 is observed at the film/substrate interface. The fact that GeO_2 is thermodynamically less stable than SiO_2 suggests that the formation of GeO_2 at the interface should be less likely. Figure 4 shows preliminary C-V data for a 1 mm diameter Au/CeO_2/Ge capacitor that was annealed at 500°C in oxygen. Note that accumulation is realized. The measurement was performed at 100 kHz.

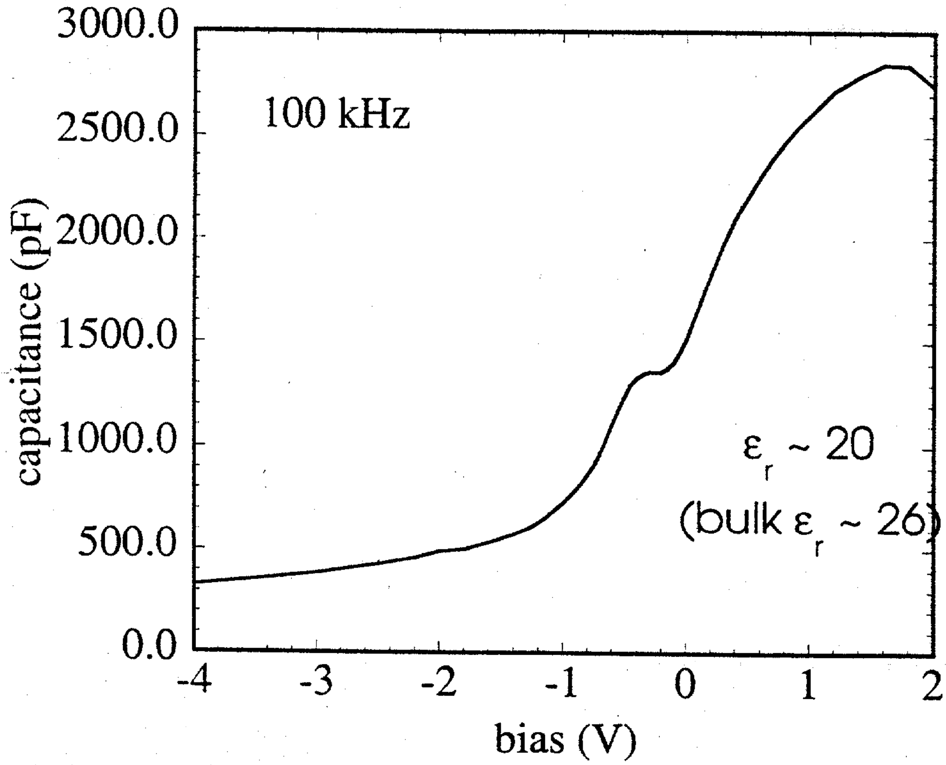

Figure 4 *A 100 kHz C-V measurement of 1 mm diameter Au/CeO_2/Ge capacitor.*

CONCLUSIONS

In conclusion, the growth of (001) epitaxial CeO_2 on a (001) Ge surface using pulsed-laser deposition in a hydrogen ambient has been realized. By using hydrogen to eliminate GeO_2 from the surface during film nucleation, a CeO_2 / Ge interface that is essentially free of GeO_2 can be formed. The use of hydrogen to promote the epitaxial growth of oxides on semiconductor surfaces should be applicable not only to CeO_2 on Ge by PLD, but to other material systems and physical vapor deposition techniques. The resulting epitaxial metal oxide film should be useful as a crystalline oxide template for subsequent growth of additional epitaxial oxide layers on the semiconductor surface. These structure may prove useful for numerous electronic and optoelectronic devices, including metal-oxide-semiconductor field-effect transistors, random-access memory devices, and optical waveguide structures.

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