Hydrogen-assisted pulsed-laser deposition of (001)CeO_2 on (001) Ge

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The growth of epitaxial (001)CeO_2 on a (001) Ge surface using a hydrogen-assisted pulsed-laser deposition method is reported. Hydrogen 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. 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. © *2000 American Institute of Physics.* [S0003-6951(00)04413-2]

Metal–oxide–semiconductor (MOS) structures are key elements in microelectronic applications.[1,2] Much of the success of silicon in microprocessor and memory technologies can be directly attributed to the ability to form well-defined Si/SiO_2 interfaces for MOS-type structures, in which SiO_2 serves as the gate oxide. 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. 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 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 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 letter, we report on the epitaxial growth and properties of CeO_2 on (001) Ge using pulsed-laser deposition (PLD). 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] 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]

The deposition of (001) epitaxial cerium oxide on single crystal Ge (001) was performed by PLD using a KrF excimer laser. A (001) single crystal Ge substrate was cleaned by successive rinsing in trichloroethylene, acetone, and methanol, followed by rinsing in de-ionized water. The native oxide was then removed by a 30 s dipping in a 1:10HF: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 PLD of the oxide film. The chamber was evacuated to an initial base pressure that ranged from 5×10^{-6} to 2×10^{-9} Torr. The mounted Ge substrate was annealed in vacuum at 350 °C for 2–12 h 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 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

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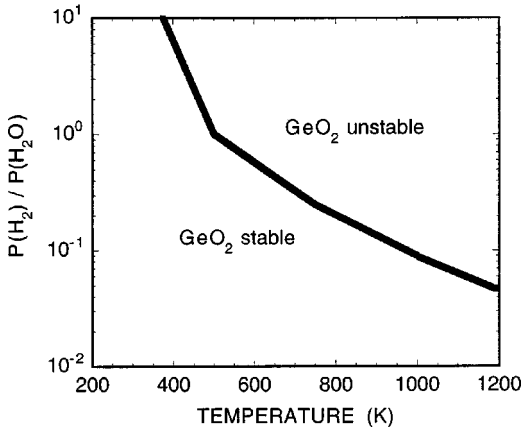

FIG. 1. Plot showing GeO_2 stability line with respect to the ratio of hydrogen gas to water vapor. The conditions for which GeO_2 is unstable are explicitly denoted.

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 PLD. 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 shows the x-ray diffraction data for a 50 nm thick CeO_2 film on (001) Ge deposited at 750° with $P(H_2) = 4\times10^{-7}$ Torr and a base pressure$=2\times10^{-9}$ Torr. Approximately 5 nm was deposited in the presence of hydrogen. The remaining 45 nm of CeO_2 was deposited with no hydrogen flow. The film is epitaxial with a (001) orientation. The out-of-plane rocking curve for this film yields a full-width-half-maximum of 2.8°. In-plane ϕ scans through the

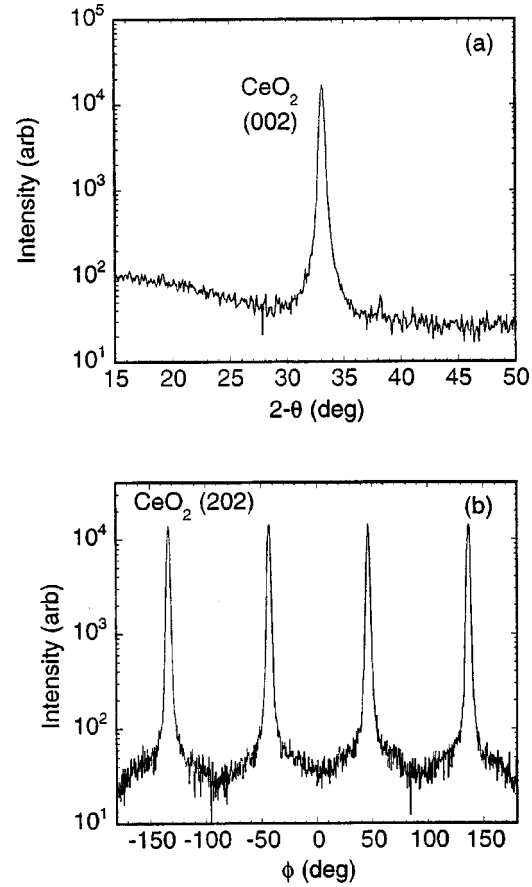

FIG. 2. X-ray diffraction scans along the surface normal (a) and in-plane ϕ (b) scans through the CeO_2 (202) peak.

$CeO_2(202)$ show that the $CeO_2(100)$ is rotated 45° with respect to the Ge (100) with an in-plane mosaic spread of ~2.7°. High-resolution scans also show that film is slightly tetragonal. The out-of-plane lattice constant is $c=5.406$ Å, with an in-plane lattice spacing of $a=b=5.420$ Å. This is consistent with the CeO_2 attempting to lattice match to the larger Ge lattice spacing. Similar results were obtained for CeO_2 films deposited in a system with a base pressure of 5×10^{-6} Torr using a hydrogen partial pressure of 4×10^{-3} Torr, although the x-ray diffraction peaks were slightly broader with higher base pressure.

Reflection high energy electron diffraction (RHEED) was used to characterize the development of crystallinity during nucleation. Figure 3 shows the RHEED patterns obtained from the Ge(001) surface along the (110) direction before growth (a), and after depositing ~ 1 nm (b) and 4 nm (c) of CeO_2 at 750 °C. In these experiments, the base pressure was 2×10^{-9} Torr with a H_2/Ar pressure of 10^{-5} Torr. Before deposition, a well-defined reconstructed (001) Ge sur-

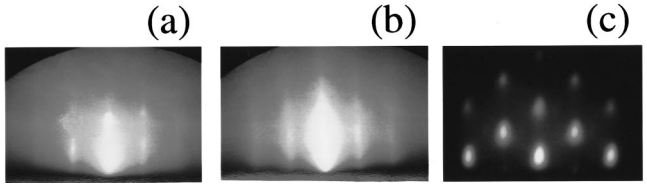

FIG. 3. RHEED images along the Ge(110) direction taken prior to film deposition (a), and after depositing 1 nm (b) and 4 nm (c) of CeO_2.

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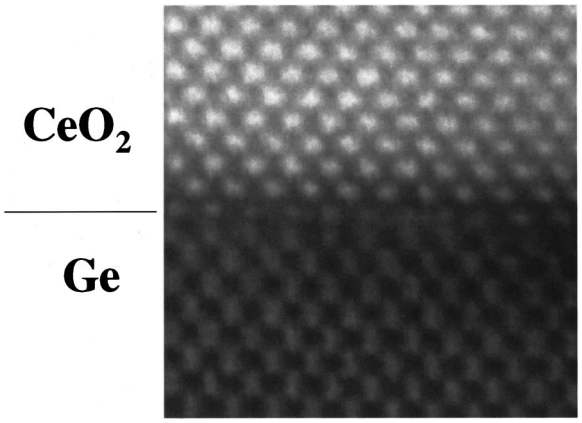

FIG. 4. High resolution STEM image of the atomically abrupt CeO_2/Ge crystalline interface.

face is observed. After depositing ~ 0.2 nm of CeO_2, a streaky RHEED pattern develops and remains until ~2–3 nm of CeO_2 is deposited. For film thickness greater than 3 nm, a distinctive spotty RHEED pattern emerges, indicative of the onset of island growth. This progression is expected due to the rather large (~4%) lattice mismatch between CeO_2 and Ge.

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 the CeO_2 film possesses a three-dimensional 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 was evident in the proximity of these defects. However, between the defects, the CeO_2/Ge interface is atomically abrupt and free of GeO_2 as is evident in Fig. 4. This result 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.

In conclusion, we report on the (001) epitaxial growth of CeO_2 on a (001) Ge surface using PLD in a hydrogen ambient. 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. By introducing hydrogen during film nucleation, the base pressure requirements are greatly relaxed as compared to conventional approaches that rely on the thermal desorption of the native oxides prior to film growth. In addition, the hydrogen-assisted approach will generally lend itself to processing temperatures that are lower than what would be required for conventional ultra-high vacuum oxide desorption. 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 MOS field-effect transistors, random-access memory devices, and optical waveguide structures.

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