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Epitaxial growth of CeO_2 on (100) InP using reactive r.f. magnetron sputtering

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ABSTRACT The epitaxial growth of CeO_2 thin films has been realized on (100) InP substrates using reactive r.f. magnetron sputtering. Oxide films were nucleated in the presence of molecular hydrogen (4% H_2/Ar sputtering gas) in order to reduce the native oxide formation on the InP surface, which interferes with CeO_2 epitaxy. 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. Crystallinity of the oxide films was examined using θ–2θ X-ray diffraction, ω-rocking curves, and in-plane ϕ-scans. The best results were obtained when the initial nucleation layer was deposited with $P(H_2O) < 10^{-5}$ Torr, followed by deposition at $P(H_2O) = 10^{-3}$ Torr. The epitaxial growth of CeO_2 on InP could prove enabling in efforts to integrate functional oxides with InP-based optoelectronic and microwave technologies.

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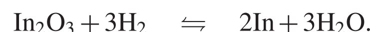
1 Introduction

In recent years, significant effort has focused on the integration of complex oxides with compound semiconductor technologies [1–3]. Compound semiconductor materials are used in a variety of electronic and optoelectronic applications, including light-emitting diodes and lasers of tunable wavelengths, as well as high-speed bipolar transistors. Since many ferroelectric and dielectric oxides are key functional components in discrete electro-optic and microwave systems, it would prove enabling to integrate electronic oxides on compound semiconductor wafer platforms. Among the compound semiconductor materials, indium phosphide (InP) and related alloys are particularly important in the areas of optical communications and high-speed integrated circuits [4, 5]. Diode lasers and optical waveguides, operating in the 1.55-µm dispersion minimum of silica fibers, can be constructed by growing lattice-matched layers of InGaAsP material on InP substrates. In many cases, it will be advantageous to have epitaxial oxides grown directly on the InP substrate surface for fully integrated microwave or electro-optic systems.

In order to explore the potential integration of functional oxides with III–V electronics, we have investigated the epitaxial growth of CeO_2 on InP substrates using reactive sputter deposition. CeO_2 has several material characteristics that make it attractive as a dielectric buffer layer for subsequent epitaxial oxide growth on InP, including a moderately high dielectric constant ($\varepsilon_r \cong 17$), a simple cubic crystal structure and a reasonable lattice match 8%. There are significant challenges in growing epitaxial oxide films on InP. At temperatures above 365 °C, the crystallinity of the InP surface degrades due to phosphorus evaporation from the substrate [3]. For epitaxial oxide growth, one also needs to prevent native oxide formation on the surface, as native oxides will interfere with the nucleation of crystalline material. In this work, molecular hydrogen was used during the oxide nucleation process in order to actively reduce the native oxide from the InP surface. The reduction mechanism can be seen from the chemical reaction of H_2 with In_2O_3:



$$In_2O_3 + 3H_2 \leftrightharpoons 2In + 3H_2O.$$

From Le Châtelier's principle, an increased amount of H_2 will drive the equation to the right, effectively dissociating the In_2O_3 native oxide. This can be quantified by the use of Ellingham diagrams that are derived from the change in the Gibbs free energy of formation for specific temperatures and pressures of products and reactants [6]. Figure 1 shows the oxide stability curve for In_2O_3 in the presence of water vapor and hydrogen. By controlling the ratio of water vapor and hydrogen partial pressure, conditions can be realized where the In_2O_3 native oxide is thermodynamically unstable while the CeO_2 is stable. Thus, without the presence of a native oxide, epitaxial growth of CeO_2 on InP should be possible.

2 Experimental methods

Radio frequency magnetron sputtering was used in our experiments for the deposition of CeO_2 films. Previous work in hydrogen-assisted physical vapor deposition of oxides has focused

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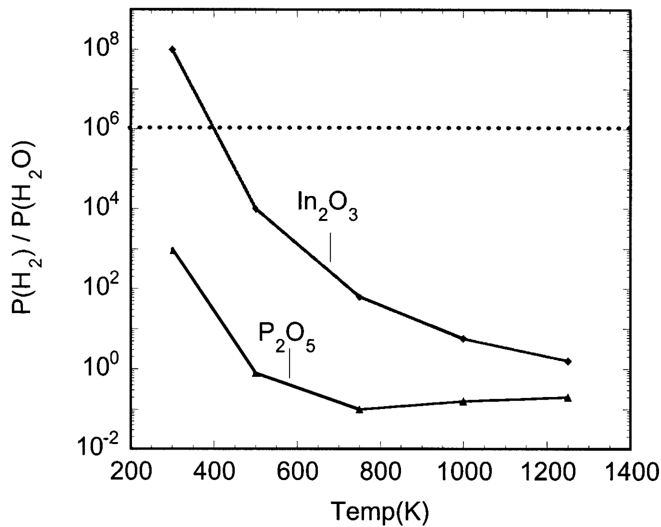

FIGURE 1 Oxide stability curves for In_2O_3 and P_2O_5 as a function of $P(H_2)/P(H_2O)$ and temperature. The *dashed line* indicates the technical limit for hydrogen-to-water-vapor ratios

on pulsed-laser deposition as the means for film growth [7]. In comparison, reactive sputtering is much more amenable to large-area deposition, and is routinely used in semiconductor processing. The experiments were performed in a stainless steel UHV sputter deposition system that was equipped with four sputter guns, two DC sputter guns and two r.f. sputter guns, an attached load-lock chamber and a radiant tungsten-wire 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 deionized 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. As compared to oxygen, the use of water vapor as the oxidizing species had the additional benefit of being reasonably compatible with the tungsten filament heater for oxide growth.

InP (100) substrates were ultrasonically cleaned in sequential baths of trichloroethylene, acetone, and isopropyl alcohol for 5 min each. 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 approximately 1 h, the samples were loaded into the load lock for transfer into the film-growth chamber. In order to outgas the solvent and binder in the silver paint, the sample platen was heated to 100 °C for an additional 30 min. 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. The heater temperature was quickly heated to the deposition temperature. A fast ramping rate for the temperature is crucial in minimizing the phosphorus evaporation from the InP substrate. The r.f. sputtering gun was set to 100 W power. The water vapor pressure was then adjusted by opening the leak valve. The deposition time was 1.5 h for all experiments.

3 Results

In order to identify the conditions necessary for the epitaxial growth of CeO_2 using Ce metal and H_2O, preliminary studies focused on ceria growth on (100) yttria-stabilized zirconia (YSZ) substrates. Oxide epitaxy on single-crystal oxide surfaces is easier to achieve than oxide growth on semiconductors due to the absence of an amorphous native oxide. Experiments were performed at 550 °C in water vapor pressures ranging from 5×10^{-5} to 10^{-3} Torr. Films deposited at 10^{-3} and 10^{-4} Torr were epitaxial, showing high-

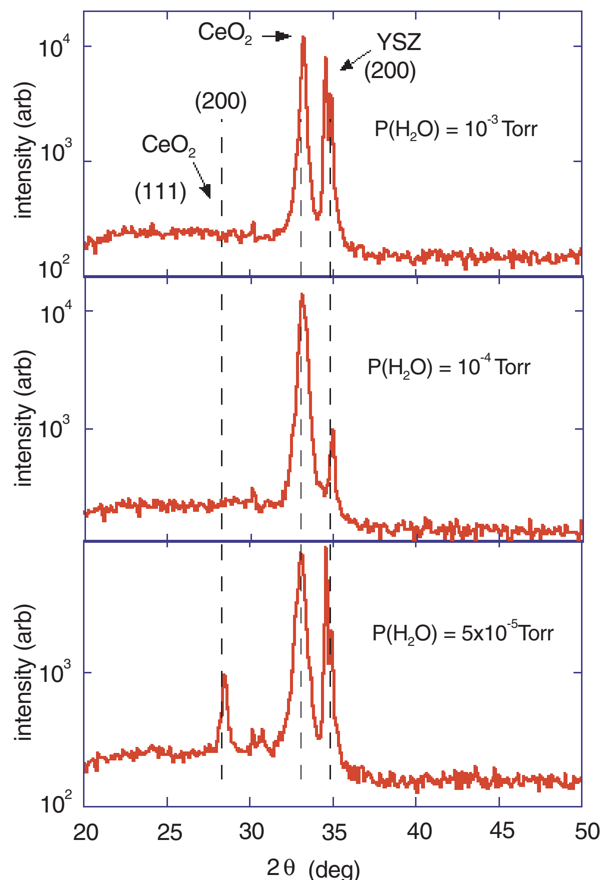

FIGURE 2 X-ray diffraction data for CeO_2 sputter deposited on (001) YSZ using water vapor as the oxidization source. The films were deposited at 550 °C

intensity (200)-oriented CeO_2 peaks, as seen in Fig. 2. Ceria films deposited at $P(H_2O) = 5 \times 10^{-5}$ Torr showed both (111) and (200) CeO_2 peaks, indicating polycrystalline growth.

After identifying conditions for CeO_2 film growth on the YSZ substrates, CeO_2 films were deposited onto the (100) InP substrates. Significant degradation of the InP surface was observed for film-growth temperatures greater than 600 °C. Epitaxial oxide films on InP 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. Figure 3 shows the X-ray diffraction data taken of the films grown under these conditions. The films deposited at 10^{-3} Torr show a strong (200) peak, indicating excellent growth oriented with the surface of the InP substrate. For films deposited at $P(H_2O) = 10^{-4}$ Torr, both (111)- and (200)-oriented CeO_2 is evident in the diffraction pattern, signifying polycrystalline growth.

Further X-ray diffraction characterization of films was done using in-plane φ-scans and ω-rocking curves. Figure 4a shows the ω-rocking curve data for the film grown at 10^{-3} Torr. The film exhibits excellent out-of-plane alignment of the (100) planes, with a full width half maximum of only 0.9°. While this mosaic spread is much larger than that for the InP substrate, it is small relative to other oxides grown on semiconductor substrates [6]. A four-circle X-ray diffraction φ-scan through the CeO_2 (202) plane is shown in Fig. 4b. The data indicate that the CeO_2 film is completely in-plane aligned, with a cube-on-cube orientation relative to the InP lattice. The in-plane peak width is 1.4°. The lattice constants for the CeO_2 film exhibit a slight tetragonal distortion with $a = b = 5.436$ Å and $c = 5.401$ Å, but are 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 excellent epitaxial growth of the CeO_2 layer on the InP substrate.

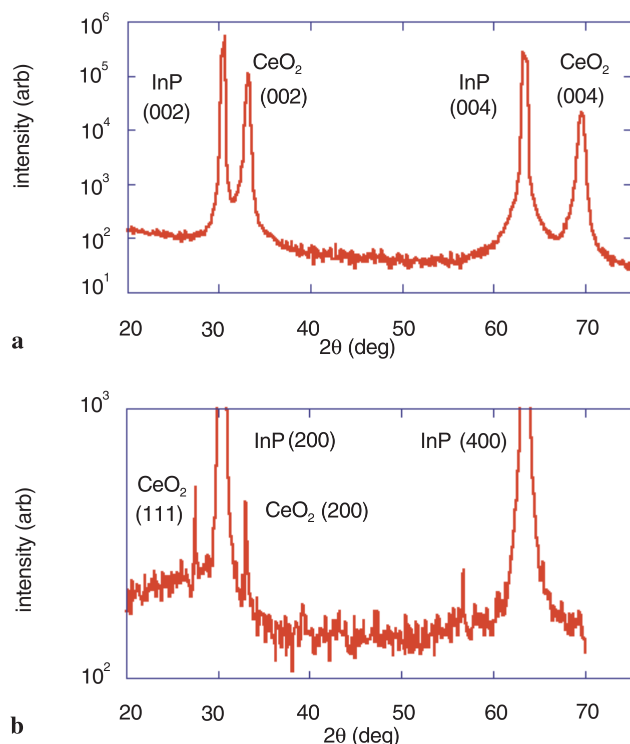

FIGURE 3 X-ray diffraction data: **a** for an epitaxial CeO_2 film grown at $P(H_2O) = 10^{-3}$ Torr; and **b** a polycrystalline film grown at $P(H_2O) = 10^{-4}$ Torr on (001) InP

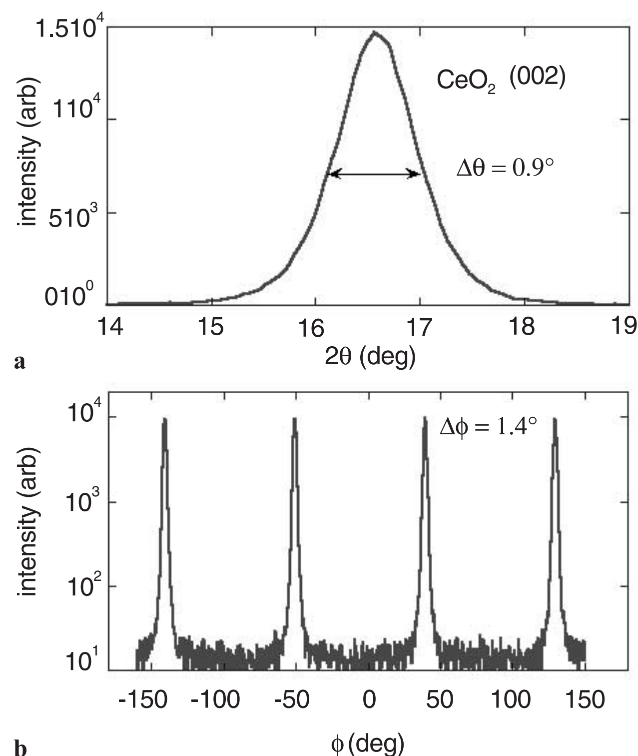

FIGURE 4 Plot showing: **a** an ω-rocking curve; and **b** an in-plane φ-scan for an epitaxial CeO_2 film on (001) InP

4 Conclusions

In conclusion, this work has shown that reactive r.f. magnetron sputtering is a suitable method for the growth of epitaxial CeO_2 films on (100) InP substrates using hydrogen-assisted nucleation. 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, surface and optical properties

of the CeO_2 films, as well as the properties of the InP/CeO_2 interface.

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