Hydrogen-assisted pulsed-laser deposition of epitaxial CeO_2 films on (001)InP

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We report on the growth of epitaxial CeO_2 on (001) InP using hydrogen-assisted pulsed-laser deposition. Epitaxy is achieved via laser ablation of a CeO_2 target in the presence of molecular hydrogen that is introduced during nucleation to reduce native In_2O_3 from the InP surface. X-ray diffraction scans confirm a cube-on-cube epitaxial relationship between the oxide film and the InP substrate. Rapid heating to the deposition temperature proved important in avoiding significant decomposition of the InP surface prior to film growth. This result should enable the integration of electronic oxide functionality with InP-based semiconductor technologies, and provide a means to explore InP metal–oxide–semiconductor field-effect transistor structures. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1431696]

In recent years, significant attention has been directed at the integration of enhanced functionality on semiconductor platforms. The possibility of achieving digital switching, optical signal processing (emission, waveguiding, modulation, and detection), piezoelectric actuation, and even magnetic field sensing on a single substrate would provide an unprecedented system-on-a-chip capability in which present-day instrumentation based on discrete components could be integrated on a single semiconductor structure. Of the inorganic materials that could be integrated with semiconductors, electronic oxides represent an attractive class of compounds in terms of complementary functionality. This is particularly evident as one considers the integration of oxides with compound semiconductors important for photonic and microwave applications, such as InP and GaAs. The development of next-generation electro-optic and/or microwave semiconductor systems would greatly benefit from the nonlinear optical response in ferroelectrics for optical switching, and/or the tunable rf response of paraelectric oxides. In addition, the use of deposited oxides as gate dielectrics in metal–oxide–semiconductor field-effect transistor (MOSFET) structures for III–V compound semiconductors is a topic of significant interest, as native oxides of these materials are unsuitable.[1]

For many of these applications, the superior crystallinity of epitaxial oxide films is either enabling or required for device performance. The growth of oxide films on nonoxide substrates, such as semiconductors, represents a significant challenge due in part to the potential of forming native oxides that interfere with epitaxial growth.[2] The thermodynamic stability of the semiconductor/oxide interface will largely determine whether epitaxy or secondary phase formation occurs.[3] For III–V compound semiconductors, such as InP, the volatility of the Group V element offers an additional complexity that may require control of the kinetics of surfaces decomposition.[4] Of course, lattice matching of the film and substrate will also be a factor in determining how epitaxy may proceed. Among the compound semiconductor materials, InP is one of the most important for microwave and optoelectronics.[5] InP-related alloy devices include laser diodes and high-speed transistors, and are key components in state-of-the-art fiber optic and microwave systems. While the growth of oxide films has been widely reported on several elemental and compound semiconductors, including Si,[6] GaAs,[7] and GaN,[8] very few studies have addressed epitaxial oxide growth on InP.[9] In this letter, we report on the epitaxial growth of CeO_2(001) thin films on InP(001) using a hydrogen-assisted pulsed-laser deposition method. Hydrogen gas in introduced to assist with the reduction of native oxide on the InP surface during nucleation. We find that accelerated heating of the substrate to the growth temperature is sufficient in limiting surface degradation due to phosphorus loss, thus permitting epitaxial oxide growth. In addition, epitaxy is achieved at a sufficiently low temperature so as to enable oxide growth on InP either before or after semiconductor device fabrication.

The films were grown using pulsed-laser deposition, with a KrF(248 nm) excimer laser serving as the ablation source. (001)InP substrates were ultrasonically cleaned with trichloroethylene, acetone, and methanol. They were blown dry with nitrogen and mounted on a substrate heater using silver paint. No attempt was made to remove any surface layers prior to loading into the deposition chamber. Upon loading the substrates, the chamber was pumped to a base pressure of $\sim 2\times 10^{-6}$ to 10^{-5} Torr. Several pregrowth heating cycles were investigated, subjecting the substrate to different temperature transients and preanneals prior to CeO_2 deposition. During the heating and nucleation steps, a 4% H_2/96% Ar background gas mixture was introduced to a pressure of 100 mTorr. This was done in order to suppress or eliminate In_2O_3 native oxide from the InP surface. With a base pressure (mostly water vapor) that ranged from 2

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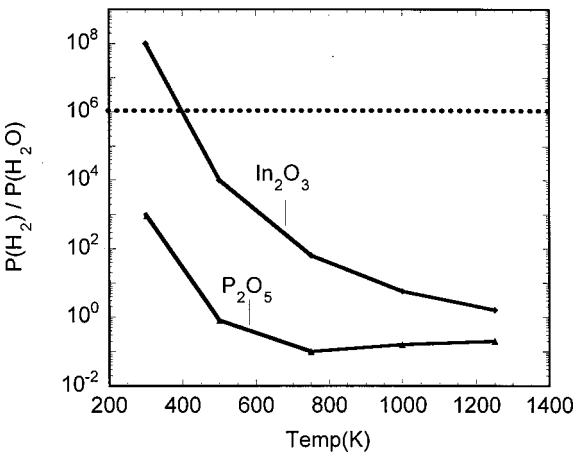

FIG. 1. Oxide stability curves for In_2O_3 and P_2O_5 in the presence of hydrogen. The phase space above the curves represents the conditions for which the given oxides are thermodynamically unstable.

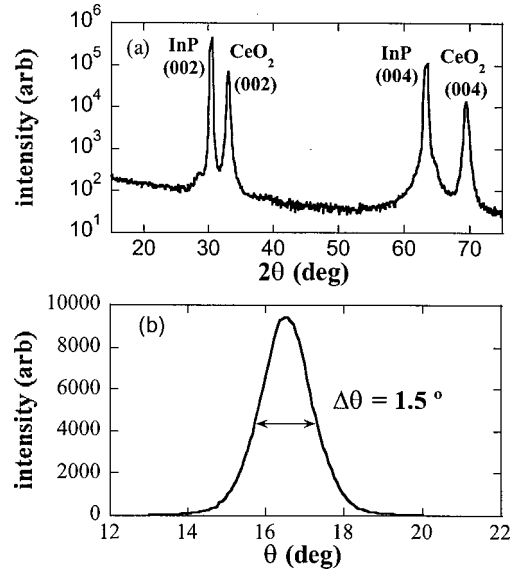

FIG. 2. X-ray diffraction data for (a) a 2-θ scan along the surface normal showing that the CeO_2 film is *c*-axis oriented, as well as (b) a rocking curve for the $CeO_2(002)$ peak showing the mosaic spread for the epitaxial CeO_2

$\times 10^{-6}$ to 10^{-5} Torr and a H_2 partial pressure of 4 mTorr, a $P(H_2)/P(H_2O)$ ratio of 2×10^3 to 4×10^2 was maintained during heating and nucleation. Based on the thermodynamics of In_2O_3 (and P_2O_5) decomposition in hydrogen, the native oxides should be unstable under these conditions. Figure 1 shows the oxide stability curves, derived from the Gibbs free energy for oxide decomposition, for In_2O_3 and P_2O_5 in the presence of H_2 and H_2O.[10] In this plot, the native oxides will be thermodynamically unstable for conditions that lie above the curve, and stable for conditions below. Of course, these curves indicate little about the kinetics of this decomposition process. The dashed horizontal line at $P(H_2)/P(H_2O)=10^6$ represents an approximate technical limit for this ratio using physical vapor deposition. Also note that a similar stability curve for CeO_2 lies orders of magnitude above the In_2O_3 curve shown, indicating that CeO_2 remains stable for conditions where In_2O_3 and P_2O_5 are unstable. Most importantly, the $P(H_2)/P(H_2O)$ ratio chosen for heating and nucleation corresponds to conditions where the native oxides in question are unstable. These conditions offer an opportunity to achieve CeO_2 epitaxy on a native oxide-free InP surface despite lack of UHV conditions. This assumes that the kinetics of oxide decomposition are sufficiently rapid.

The initial investigation of the growth of CeO_2 on InP focused on the effects of substrate heating rates on oxide nucleation. Substrate temperatures as high as 600 °*C* were investigated. Previous results have shown that the InP(001) surface begins to lose P at temperatures above 365 °*C*.[4] The creation of an In-rich surface would presumably interfere with oxide epitaxy. Our results indicate that heating rates on the order of 10 °C/min do not result in an InP surface conducive with oxide epitaxy. Significant degradation of the InP surface appeared to be the origin for the lack of epitaxy. In addition, we also investigated the use of a short (5 min) *in situ* preannealing step at 550 °C prior to nucleation. Previous work for yttria-stabilized zirconia growth on InP (with no background hydrogen) showed that short preanneals were necessary in order to desorb native oxide for subsequent oxide epitaxy.[9] Our results indicate that this is not effective, at least when hydrogen gas is introduced to assist in native oxide reduction. Apparent decomposition of the InP surface led to rough surfaces and polycrystalline film deposition under these conditions.

Fortunately, the degree to which the surface degrades appears to be kinetically limited at the growth temperatures considered, as a rapid substrate heating rate of 120 °C/min circumvented this limitation and resulted in epitaxy. The best results obtained for CeO_2 epitaxy were realized when the substrate temperature was raised to 550 °C at a heating rate of 120 °C/min. This relatively rapid increase in substrate temperature appears necessary in order to avoid significant decomposition of the InP surface. The first 200 Å of CeO_2 were grown at 550 °C in a H_2/Ar partial pressure of 100 mTorr. The laser energy density was approximately 2 J/cm^2 with a target to substrate distance of ~6 cm. The laser repetition rate was 3 Hz, yielding a deposition rate on the order of 1.5 Å/s. After depositing this nucleation layer, the H_2/Ar mixture was evacuated while continuing CeO_2 film growth in a vacuum at the same deposition rate. The total CeO_2 film thickness was ~100 nm. The sample was then cooled in a vacuum at ~120 °C/min.

Under conditions of rapid heating and nucleation in a hydrogen background, epitaxial CeO_2 films were realized. The x-ray diffraction data taken along the surface normal for a CeO_2 film grown at 550 °C under the conditions described are shown in Fig. 2(a). The film is (001) oriented with virtually no (111)-oriented material apparent from the diffraction pattern. The film surface was optically smooth. Detailed analysis of the film morphology is in progress. Figure 2(b) shows a rocking curve for the (002) CeO_2 peak. The mosaic spread (rocking curve width) is measured to be 1.5°. While this is significantly larger than that of the substrate, it is comparable to that observed for epitaxial CeO_2 films grown on (001) Ge as reported earlier.[11] The in-plane φ-scan shown in Fig. 3 indicates that the film is completely in-plane aligned with a cube-on-cube orientation. The scan was taken through the $CeO_2(202)$. The in-plane mosaic of the diffraction peaks is $\Delta\varphi=2.2°$. With a bulk lattice constant of 5.411 Å, CeO_2 presents a lattice mismatch of 8.5% on InP($a=5.869$Å). The

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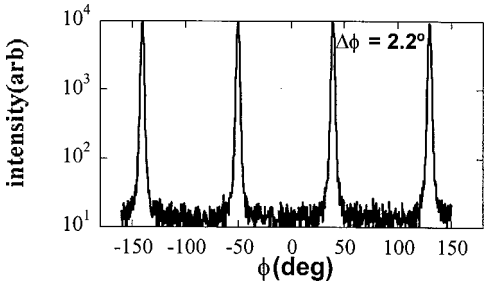

FIG. 3. Four-circle x-ray diffraction scan through the (202) reflection showing that the CeO_2 film is in-plane aligned with the (001)InP substrate.

measured lattice constants of the CeO_2 film indicate a slight tetragonal distortion with $a=b=5.424$ Å and $c=5.409$ Å. This may indicate strain due to the lattice mismatch between CeO_2 and InP, which would place the film in tension.

In conclusion, we have investigated the use of hydrogen-assisted pulsed-laser deposition for the nucleation of epitaxial CeO_2 on InP(001). Under conditions that minimize P loss and decomposition of the InP surface, epitaxial films were obtained. These results should prove enabling in exploratory efforts to integrate functional oxides on InP circuit platforms, as well as to develop InP-based MOSFET structures. Future experiments will investigate the properties of the CeO_2/InP interface. In particular, it will be important to determine whether In_2O_3 forms at the interface after oxide epitaxy. This will directly impact the viability of these structures for InP-MOSFET structures. In addition, the morphology of the surface and stability of the interface will determine the usefulness of CeO_2-buffered InP substrates for subsequent growth of ferroelectric films.

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