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Phase stability and strain accumulation in CdO as a function of Cd/O supply during MOVPE synthesis

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ABSTRACT

A prominent trend for the stabilization of zincblende or wurtzite phases in CdO is observed. Typically, CdO occurs in its "equilibrium" rocksalt phase when grown on r-plane oriented sapphire substrates employing Cd-rich growth conditions. Gradual decrease of Cd supply, i.e. moving towards O-rich condition, results in additional phases, firstly zincblende and secondly wurtzite. Importantly, the variation of Cd/O ratios at the reaction zone was tuned by changing both the precursor flow rates and the growth temperature affecting the precursor decomposition. Moreover, an interesting strain accumulation trend, correlating with the band gap variations was observed as a function of Cd/O supply ratios too. In particular, a gradual change towards O-rich conditions leads to a build-up of strain in the films and red-shifts the optical absorption edge.

1. Introduction

Cadmium oxide (CdO) is a promising semiconductor exhibiting a rocksalt (rs) crystal structure in equilibrium, but also being observed as a mixture of rs and wurtzite (w) phases [1]. The interest to CdO has recently been renewed by demonstrating its high potential as a transparent conducting oxide (TCO) in solar cells, light emitting diodes, flat panel displays, etc. [2–4]. Moreover, CdO can also perform as an active component in photovoltaics, e.g. n-CdO/p-Si solar cells were demonstrated with the efficiency reaching ~8.8% [5,6]. However, the understanding of phase stability, strain accumulation and defect formation in CdO is limited. Moreover, uncertainties with the energy band structure as well as scattering of electrical and optical data are long lasting issues related to CdO [7–10]. For example, the band structure calculations suggested the existence of two low energy indirect band gaps of 0.8 eV (L_3 and Γ_1) and 1.2 eV (Σ_3 and Γ_1), in addition to a direct band gap at 2.3 eV [11]. Surprisingly enough, apart from an early work by H. Kohler indicating the indirect transitions in the absorbance spectra of sputtered CdO films [12], so far there is no conclusive demonstration of the indirect band gaps in CdO.

Application of modern epitaxial film synthesis techniques opens a new possibility to study CdO. A variety of advanced methods, including molecular beam epitaxy (MBE) [13], metal organic vapor phase epitaxy (MOVPE) [14], and pulsed laser deposition [15] were already used to fabricate hetero-epitaxial CdO films. However, systematic understanding of the phase stabilization mechanisms in CdO is missing. Evenly, reliable correlations between the band gap variations, strain accumulation and/or phase transformations are missing. Concurrently, density functional theory (DFT) [16] predicts rs-, w- and zincblende (zb-) phases to have gradually decreasing stability in CdO. Ashrafi et al. [1], indeed observed mixed w- and rs-phases in laser ablated CdO on ZnO. Notably, w- and zb-phases are structurally similar and differ only by the stacking in (111) direction, while the atomic coordination in both zb- and w-

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is exactly the same through the second neighbor.

In the present work, we present a systematic structural and optical analysis of the bandgap modulation due to variable strain incorporated during the MOVPE growth of the CdO films by tuning Cd/O precursor ratios, and discuss the possible methods/routes for stabilization of w- and zb-phases.

2. Experimental

CdO thin films were fabricated on (1–102) plane of sapphire (r-Al_2O_3) by two-inlet MOVPE system (Titan, EMF Ltd.) operating in a vector flow epitaxy mode. The substrates were cleaned using acetone and ethanol in an ultrasonic bath, followed by etching in an H_2SO_4:H_2O_2:H_2O (1:1:6) solution. Prior to loading into the chamber, the substrates were rinsed with deionized water and dried in N_2. The chamber was pumped down to 600 Torr and a preheating stage at 700 °C for several minutes in N_2 atmosphere was employed, to minimize the substrate surface contamination. Afterwards, dimethyl cadmium (DMCd), N_2 gas, and tertiary butanol (t-BuOH) were used as the cadmium source, carrier gas, and oxidizing agent, respectively.

The flows of DMCd and t-BuOH were set at 70 and 150 sccm, respectively. DMCd bubbler bath temperature was maintained at 10 °C, while t-BuOH was kept at 30 °C. The chamber pressure was maintained at ~600 Torr, while the growth temperature was varied from 270 °C to 420 °C with an interval of 30 °C. The samples were labeled accordingly as AX, where X represents the actual temperature in °C and A-series represents the set of samples, where the carrier gas and bubbler flows were maintained to yield a II-VI molar ratio of 0.635. The deposition time was 60 min for all the samples resulting in thicknesses in the range of 400–700 nm. The second set of samples was fabricated by changing the N_2 carrier gas flow rate yielding different II-VI molar ratios at growth temperatures of 300, 330 and 360 °C, maintaining other process parameters constant. The samples were labeled as BX and CX, where X represents the growth temperature. While, B and C refer to II-VI ratios; B = 1.00 and C = 1.68.

Optical transmittance measurements were carried out at room temperature by employing a Shimadzu Solid Spec 3700 DUV double-beam spectrophotometer. The scanning wavelength range was 290–2500 nm and the baseline correction for the bare substrate was set to 100% light transmission. The measurement was done in a double beam mode with a bandwidth of 1 nm. A tungsten lamp was used as the light source for the visible (VIS) – near infrared (NIR) region of wavelengths. The photo-detectors were photo-multiplier tube and InGaAs for the UV-VIS and PbS photocell for the NIR region. The crystalline structure of the films was characterized by x-ray diffraction (XRD) measurement with Cu $K\alpha_1$ radiation (Bruker Advanced D8 x-ray diffractometer) in the locked-coupled mode (where the theta and 2theta goniometer moves in equal spacing without any offset in scaling). The surface morphology was monitored by scanning electron microscopy (SEM - FEI Quanta 200 FEG-ESEM) and aluminum (Al) & cadmium (Cd) depth profiles were also measured by secondary ion mass spectrometer (SIMS - Cameca IMS 7f microanalyzer) using 10 keV O^{2+} primary ions. The chemical composition of the CdO films was analyzed by Rutherford backscattering spectrometry (RBS) with 3.03 MeV $4He^{2+}$ ions backscattered into a detector at 165° relative to the incident beam direction. The energy of the incident He^{2+} ions was chosen in such away to exploit the O resonance ($^{16}O(\alpha, \alpha)\ ^{16}O$) and, therefore, to enhance the yield from O sublattice needed for accurate analysis of the film compositions. The stoichiometry of the films was determined from the experimental spectra using simulations performed with SiMNRA code [17]. Hall measurements were performed at room temperature (Lakeshore 7704A), employing a magnetic field of 10 kGauss in Van-der Pauw configuration of 10 × 10 mm square sample.

3. Results and discussion

Fig. 1 shows 2θ XRD scans taken from CdO films grown on r-Al_2O_3 at different growth temperatures (T_g). Starting from the sample grown at T_g = 270 °C (A270), a dominating signature of the rs-CdO (002) diffraction peak at 2θ ≈ 38.3° can be observed and the trend holds for the rest of the samples, indicating an epitaxial growth on r-Al_2O_3 [14]. Interestingly, for the samples grown at $T_g \geq 300$ °C, two additional diffraction peaks centered at 2θ ≈ 34.6° and at 73.24° are observed, not correlating with either of rs-CdO reflections. Indeed, the lattice parameter, as calculated from the CdO (002) diffraction peak is ~4.693 Å (sample A420 - shown as a dashed line in Fig. 1) consistently with that for rs-CdO [18]. However, additional diffraction peaks centered at 2θ ≈ 34.6° and/or 73.26° are not consistent with the rs-symmetry, suggesting other phases to form [1]. Meanwhile, theoretical calculations predict w- and zb-to be next stable structures; 0 and 0.12 eV respectively, energy difference higher than rs-phase [16]. In these terms, the peak at 2θ ≈ 73.26°, is consistent with w-phase assuming lattice parameters of a = 3.66 Å and c = 5.856 Å from literature and attributed to (104) w-CdO [1,16,19]. Further, no diffraction peaks at 2θ ≈ 34.6° for rs- or w-phases are envisaged. However, assuming zb-structure, the diffraction peak at 2θ ≈ 34.6° ascribed to (002) zb-CdO results in a lattice parameter of a = 5.15, which is very close to the value reported for zb-crystal structure [16,19]. Notably, the position of the dominating rs-peak shifts as a function of T_g indicating gradual strain accumulation and release.

In addition, two “shoulder” peaks around the CdO (002) diffraction are observed for samples A270 - A330. The two shoulder peaks are identified as highly strained rs-CdO (002) due to different in-plane lattice mismatch between CdO (002) and r-Al_2O_3. The lattice mismatch between [001] CdO along the [2-1-10] sapphire direction is of only 1.2%, while in the orthogonal [0$\bar{1}$11] sapphire direction the lattice mismatch increases up to 8.3%, assuming the formation of a 3:1 coincidence lattice [20]. Importantly, along with the T_g increase, the intensity of the CdO (002) diffraction peak increases, demonstrating better crystalline quality, while the intensities of the shoulder peaks decreases. J. Zuniga-Perez et al. studied growth of CdO thin films on r-plane sapphire substrates and demonstrated that at low temperatures, the CdO film exhibit mosaic structure and the layers are tilted with respect to the substrate [20]. The decrease in shoulder peak intensity may perhaps be attributed to the formation of a very thin mismatch-accommodating interfacial layer at the boundary with the substrate. The calculated strain (ε) [$\varepsilon = a_0 - a_{exp}$, where a_0 = 4.6953 Å] as well as the full