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MOCVD growth of CdO very thin films: Problems and ways of solution

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ABSTRACT

In this paper the growth of CdO by the MOCVD technique at atmospheric pressure has been studied in order to achieve very thin films of this material on r-sapphire substrates. The growth evolution of these films was discussed and the existence of a threshold thickness, below which island-shaped structures appear, was demonstrated. Some alternatives to reduce this threshold thickness have been proposed in the frame of the analysis of the crystal growth process. The morphology and structural properties of the films were analyzed by means of SEM and HRXRD. High-quality flat CdO samples were achieved with thicknesses up to 20 nm, which is five times thinner than the values previously reported in the literature.

1. Introduction

Cadmium oxide (CdO) is an n-type semiconductor with a Γ- Γ bandgap of 2.16 eV at room temperature in the rocksalt structure [1]. Over the last few years, CdO has attracted extensive attention due to its potential interest in gas sensor applications and optoelectronic technologies like transparent electrodes in touch panels, organic light emitting diodes and photovoltaic devices, among others. In some of its industrial applications as transparent conductive oxide (TCO), high optical transparency is needed. In TCO layers their thickness is one of the most important factors conditioning their properties [2], because the optical transparency increases as the thickness of the layer decreases. Chan et al. [3] have reported significant improvements related to the optical properties and the production costs of indium tin oxide (ITO) films below 40 nm. A real challenge is, consequently, to achieve very thin films maintaining a good crystalline quality in the crystal structure in order to reduce the presence of interface defects in the heterostructures, when needed for device applications.

Many techniques have been used to grow CdO films such as spray pyrolysis [4], thermal evaporation [5], sputtering [6], pulsed laser deposition [7], molecular beam epitaxy [8] or metal organic chemical vapor deposition (MOCVD) [9,10].

Nevertheless, the growth of films thinner than 100 nm of this material has been less studied or at least to the best of our knowledge, no results can be found in the current literature, despite its strong potential.

The lack of reports could be explained taking into account the difficulties to control the growth parameters to stimulate the lateral growth when growing onto substrates [11], key point to have flat surfaces where different growth rates are present.

On the other hand, some studies about the growth of this material show the difficulties to obtain high density of isolated nanoparticles of CdO on substrates, due to their particular nucleation properties and the absence of a significant amount of nucleation points on the substrate [12]. This difficulty can also be the origin of some limits on the growth of flat thin layers with high crystalline quality.

By using MOCVD method –for its ability to industrial scale- we have deepened in the study of obtaining CdO very thin films while maintaining its quality so as to extend the knowledge in this subject.

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2. Experimental procedure

In order to develop this work, CdO films were grown at atmospheric pressure in a horizontal vent-run type MOCVD reactor (Quantax 226 refurbished by EMF Ltd). Tertiary butanol (TBA) and dimethylcadmium (DMCd) were used as oxygen and cadmium precursors respectively. They were transported from temperature controlled stainless steel bubblers to the reaction chamber via nitrogen carrier gas. Both precursors were introduced into the reactor through two separated inlets, so that they started to mix on the heated substrate wafer in the reaction chamber.

Sapphire substrates have been our choice for this study for their technological interest along with the previous experience of our group on the growth on these substrates by MOCVD. More specifically, r-plane sapphire was shown to be one of the most suitable substrates in order to achieve high structural quality CdO films [9].

HRXRD measurements were performed in a Philips X'Pert MRD X-ray diffractometer with monochromatic Cu $K\alpha_1$ radiation (λ = 1.54056 Å), which impinged on the sample after having traversed a curved graded multilayer mirror and a Ge (220) monochromator. For the structural characterization of the samples, rocking curves, 2θ-ω scans, pole figures and reciprocal space maps (RSMs) were carried out.

The morphology of the samples was studied by using a Hitachi S-4800 field emission electron microscope with an acceleration voltage of 20 kV. A gold-palladium thin conductive film (≈2 nm) was deposited over the CdO films using dc-sputtering prior to the scanning electron microscopy (SEM) analysis. It is worth to note that, in SEM images taken in a low scan mode to improve the image quality, the scale is only valid for horizontal dimensions. A drift effect in the vertical axis makes inaccurate quantification of the distances in this direction on the pictures. Thus, the thickness of the samples was determined on a faster scan mode where drift effect is minimized.

The optical transmittance of the films was determined at room temperature using a Jasco V-650 spectrophotometer spanning the energy range from 1.5 to 5 eV and normalizing by the sapphire substrate transmittance.

Finally, electrical transport properties were determined at room temperature by Hall effect measurements in the Van der Pauw configuration using In contacts.

3. Results and discussion

In order to find the optimal growth temperature conditions, a series of experiments varying the temperature were carried out in the range of 260–410 °C. Layers with thicknesses around 1 μm were obtained after 60 min of growth with flows of 71.76 and 13.86 μmol/min for the TBA and DMCd precursors, respectively.

Fig. 1 shows the full width at half maximum (FWHM) of the rocking curve for the CdO layers depending on the temperature. It can be seen that the FWHM depends slightly on the growth temperature in the range from 260 °C to 380 °C, but it worsens noticeably for higher temperatures, when desorption occurs. From all the samples studied within the range 260–414 °C, the ones corresponding with a growth temperature of 277 °C were found to provide the flattest morphologies without grain boundaries, as can be compared with the top-view inset images.

Once established the substrate temperature and with a view to achieve very thin films of CdO, other parameters were modified. In concrete terms, both the deposition time and the precursor flows play a significant role, as is well known.

Maintaining that temperature, first, we have investigated the influence of the deposition time on the thickness of the grown layer. The studied films showed a high flatness independently of the deposition time in the range 5–60 min. However, we detected the existence of a time which leaded to a threshold thickness of 80 nm. Below this time, corresponding to 5 min under flows of 71.76 and 13.86 μmol/min for the TBA and DMCd precursors, films with discontinuous structures appeared. Within this range, the thickness of the films resulted to decrease linearly with time, as expected considering that there are no further changes in the morphology of the grown structures.

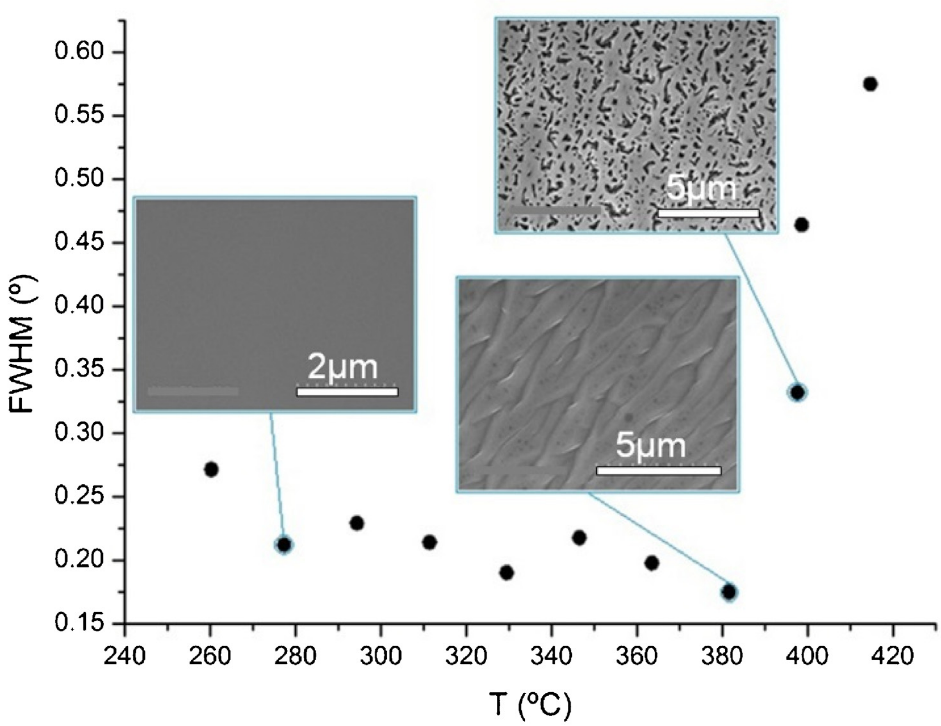

Fig. 1. FWHM of CdO layers around 1 μm thick depending on the growth temperature, T. Inset top-view SEM images of the corresponding layers.