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Physical properties of a non-transparent cadmium oxide thick film deposited at low fluence by pulsed laser deposition

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ABSTRACT

A stable non-transparent CdO film was grown by pulsed laser deposition. The sample was thermally annealed at 500 °C in air. A (2 0 0) highly oriented polycrystalline film was obtained. The annealed sample has not preferred orientation. Scanning electron micrographs show a grain size reduction for the annealed sample. By Raman spectroscopy, the defects related second order vibrational modes of CdO were observed. Chemical composition analysis shows the presence of CdO together with a substoichiometric CdO_x phase for the as-grown sample. For the annealed sample a compensation of oxygen vacancies was observed. Electrical resistivity measurements give a value of 8.602×10^{-4} (Ω cm) for the as-grown film. For the annealed sample the electrical resistivity increased to a value of 9.996×10^{-3} (Ω cm). Zero transmission has never been reported for CdO films. The photoluminescence spectra were measured in order to shed some light on the origin of the zero transmission.

1. Introduction

Cadmium oxide (CdO) has been intensively studied mainly due to its applications as transparent conductive oxide (TCO) because of its high optical transmission and low electrical resistivity values [1–4]. CdO is a cubic (FCC) *n*-type semiconductor with reported values of direct band gap energy ranging from 2.16 to 2.5 eV, depending on the preparation technique and deposition conditions [5–7]. Higher energy values for band gap have been reported for doped CdO [5,8–10] as a result of the Burstein–Moss effect.

The discrepancy on the reported bandgap values in the literature for undoped CdO samples lies in the defects. They can be composition related defects such as oxygen vacancies or cadmium interstitials producing energy levels within the band gap yielding deep levels. The presence of these levels will affect both optical absorption and electrical conductivity making CdO sensitive to stoichiometry variations [11].

CdO thin films have been grown using both chemical and physical deposition techniques. Among the chemical deposition techniques are: spray pyrolysis [2,6,12,13], sol–gel [1,14], chemical bath deposition [15] and metal organic vapor phase epitaxy [16,17]. The typical physical deposition techniques for CdO thin films are: pulsed laser deposition [3,8,9,18–20], magnetron sputtering [21,22] and thermal evaporation [7,23]. Chemical deposition techniques involve the use of different reactants to form CdO, and thus experiments have to be performed under extreme care conditions in order to avoid accidents. Meanwhile, for physical deposition processes a commercial CdO target can be used inside a vacuum chamber allowing reduction of health risks during films growth.

Among the physical deposition techniques for growing CdO, pulsed laser deposition is widely used due to the high-quality

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samples that can be obtained; however most of the works reported on CdO by pulsed laser deposition used fluence values ranging from 10 up to 60 J/cm^2 and different substrate temperatures and oxygen pressures [8,9,18–20]. It has been reported that the physical properties of films grown by pulsed laser deposition depend on the energy and density of the ions present in the laser produced plasma, which in turn depends on the laser fluence impinging on the target [24]. Thus a measurement of the plasma characteristics could be an important tool in order to understand the properties of the grown films.

It has also been reported that CdO buffer layers can be grown to enhance optoelectronic properties of ITO, electron beam evaporation has been used for this purpose [25], obtaining polycrystalline films with low electrical resistivity. The control of deposition conditions is crucial for CdO films growth. Pulsed laser deposition offers a precise control in film properties.

In the present work a CdO film has been deposited at room temperature using a plasma formed by low energy ions. Notoriously, the film exhibited negligible transmittance in the UV–visible range, a phenomenon that has not been reported before. The effects of a heat treatment on this sample are discussed.

2. Experimental details

A 2 μm CdO film was grown on a glass substrate by means of the pulsed laser deposition technique. A high purity CdO target (2.54 cm diameter) was fabricated compressing CdO powders (99.99% from Sigma–Aldrich) at a pressure of 15 t during 30 min.

The deposition chamber was evacuated to a base pressure of 5×10^{-6} mbar with a turbomolecular pump. The film deposition was carried out at a working pressure of 1×10^{-2} mbar, using a gas mixture of 80/20 Ar/O_2 as reactive atmosphere to compensate oxygen loss during deposition. For the ablation process a high power Nd:YAG laser with 500 mJ of maximum output energy, wavelength of 1064 nm, 5 ns pulse width, and frequency of 10 Hz was used. The CdO target was placed in front of the substrate at a distance of 5 cm. The incident energy density on the target was 2 J/cm^2. The target was rotating during ablation in order to avoid drilling. The deposition time was 40 min.

Using the time of flight technique (TOF), the plasma parameters such as mean kinetic ion energy and plasma density were measured. Plasma parameters measurements were carried out using a 6 mm diameter planar Langmuir probe biased at −50 V placed in the exact position of the substrate prior to deposition. The probe current was obtained by measuring the voltage drop across an 18 Ω resistor; this voltage was measured using a Tektronix 500 MHz digital oscilloscope. The average kinetic energy of the ions, E_k, present in the plasma was estimated using the TOF curve data and the procedure described by Bulgakova et al. [26].

The plasma density was calculated from the maximum value of current of the TOF curve [27]. The thickness of the sample was measured by means of profilometry with a KLA Tencor D-120 profilometer.

After deposition, the sample was divided into two parts; one of the parts was thermally annealed in air at $T_a = 773$ K for 90 min using an electric furnace. The as-grown film changed its color from black to brown-red after thermal treatment.

The films were structurally characterized by X-ray diffraction (XRD) using a Rigaku Dmax2100 diffractometer. Transmission electron micrographs (TEM) were taken using a Jeol JEM 2010 microscope with a lanthanum hexaboride filament at an acceleration voltage of 200 kV. Scanning electron micrographs (SEM) were recorded in a Tescan Mira3 field-emission gun scanning electron microscope at 20 kV. The Raman spectroscopy measurements were carried out on a Horiba Jobin Yvon HR 800 Raman spectrometer with a 532 nm excitation line, the beam was focused using a 50× objective lens. Electrical resistivity measurements were obtained with a Keithley 4200-SCS apparatus in the four point collinear probe resistivity configuration. X-ray photoelectron spectroscopy (XPS) measurements were carried out in a K-alpha Thermo Scientific system with an Al Kα (1486 eV) X-ray source. The binding energies were referenced to C 1s at 285 eV.

UV–vis transmission measurements were carried out in a PerkinElmer Lambda 35 spectrophotometer. Photoluminescence (PL) spectra were acquired in a Dilor LabRam microspectrometer equipped with a Si CCD detector and a 488 nm Ar^+ laser line as excitation source.

3. Results and discussion

Fig. 1 shows the TOF curve of the Langmuir probe plasma measurements, the values for energy and density of ions calculated using the procedure described in the Section 2, are $E_k = 75.3$ eV and $N_p = 13.5 \times 10^{12}$ cm^{-3}, respectively, as indicated in the graph. This mean kinetic ion energy value is considered to be low for laser produced plasmas.

For pulsed laser deposition, growth rates are affected by both energy and plasma density. For high energy plasmas re-sputtering on the film surface becomes important due to the ions impinging the surface at high velocity. When using low energy plasmas re-sputtering does not affect considerably the growth rate allowing it to increase. For the case of the present experiment a 2 μm thick film was grown, which means that the growth rate was 50 nm/min; a considerable high growth rate for pulsed laser deposition.

Fig. 2 shows the diffractograms of the as-grown film and the thermally annealed sample. It can be observed that the as-grown film is polycrystalline cubic CdO with a preferred orientation in the (2 0 0) direction, in agreement with literature when the pulsed laser deposition technique is used [8,9,18–20]. Using Scherrer's equation and the procedure described in reference [28] for the instrumental broadening, the average crystallite size was calculated. For the calculation of the FWHM due to size effects a calibration plot (not shown here) was constructed from measurements of a silicon standard sample using the exact same measurement conditions than those used for the samples in order to eliminate the instrumental broadening. The FWHM values corresponding to the diffraction angles of the CdO planes where obtained using the relation $\beta^2(2\theta) = \beta_i^2(2\theta) + \beta_s^2(2\theta)$. Where β_i stands for the FWHM from the instrument, β_s is the FWHM of the sample and β is the FWHM obtained from the Gaussian fittings of the peaks. The

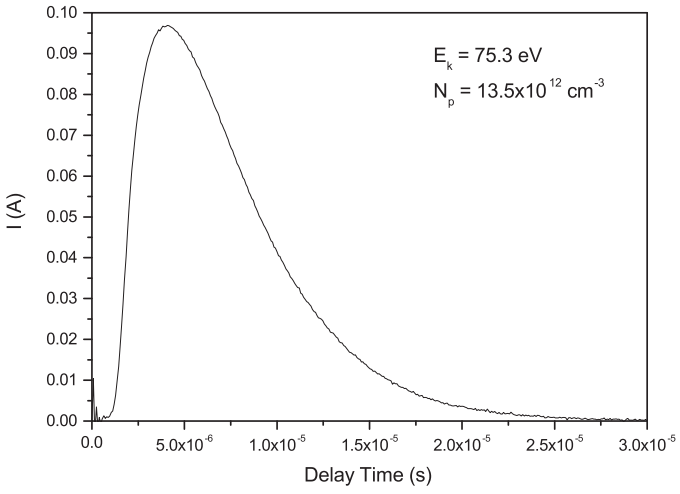

Fig. 1. Time of flight curve obtained from Langmuir probe measurements.