X-Ray Diffraction Recognition of Cadmium Borate Nanostructures Prepared by Physical Vapor Deposition

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Abstract

In this work, an attempt to prepare cadmium borate nanostructures is presented. These nanostructures were prepared by reactive magnetron co-sputtering technique. The cadmium and boron targets were mounted in a geometrical configuration allowing to produce a stoichiometric compound. The growth of crystal planes in the prepared samples could be reasonably controlled by tuning the operation parameters and preparation conditions. The structural characterization showed that the prepared nanostructures were highly pure.

Keywords*:* Cadmium borate; Nanostructures; Magnetron sputtering; Reactive sputtering
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1. Introduction

Many industrial applications are employing metal borate compounds due to their mechanical, chemical and thermal properties [1]. Metal borates nanostructures have added new and unique features allowing for new uses and applications such as magnetoelectronics, tunable and optical fiber communication systems [2-5]. Ohmic photoconductivity is one of most important features exhibited by metal borates nanostructures [1]. Among all metal borates, cadmium borate has attracted intensive research interest due to its different chemical compositions, structures and stoichiometry those result in a variety of physical and chemical properties [6-9]. For example, due to excellent luminescence properties, cadmium borate was used as a coating for fluorescent tubes [10,11]. It was used in the fabrication of localized hopping conductors (LHCs) due to the dependencies on frequency and temperature [12]. Also, cadmium borate nanoparticles were effectively used as additives in tribology [13]. In general, the BO_4 (tetrahedral) and BO_3 (triangular) groups in cadmium borate can form polyborate anions by linking to cadmium atoms or cadmium oxide groups via common oxygen atoms [14]. Consequently, the CdO_6 (octahedral) and BO_3 groups share the corners and edges in the crystalline structure to form a 3D structures [15].

Cadmium borate nanostructures are advanced materials with unique physical and chemical properties, making them suitable for applications in optoelectronics, catalysis, and energy storage. These nanostructures typically exhibit high thermal stability, excellent optical properties, and good electrical conductivity. Cadmium borate ($Cd_3(BO_3)_2$) is characterized by its wide bandgap, which makes it a promising candidate for ultraviolet (UV) light-emitting devices and photocatalysis. Its chemical stability in various environments further enhances its utility in harsh conditions. The active sites of cadmium borate structure may produce different reactive species as a result of the structural composition [16]. As nanoparticles, the production of reactive species is dependent on the physicochemical properties of cadmium borate, mainly the dominant crystal phase, average nanoparticle size, mean and average surface roughness, agglomeration and stability [17-19].

In this work, highly-pure stoichiometric cadmium borate nanostructures were prepared by reactive magnetron co-sputtering technique and their structural properties were investigated.

2. Experimental Part

A dc sputtering system was used to prepare cadmium borate thin films on glass substrates. Two highly-pure targets of cadmium and boron were mounted on the cathode to perform the co-sputtering process. The dimensions of targets were mainly determined by an empirical model that takes into account several parameters of the target materials, such as sputter yield, surface binding energy, atomic mass, and material density, in addition to the configuration of the magnetrons maintained on the cathode. The diameters of boron and cadmium targets were 80 and 16.5 mm, respectively. This configuration can ensure the stoichiometric reaction of boron and cadmium with oxygen atoms available in the discharge volume. The discharge power was ranging in 35-40 W as the discharge current was maintained at 20 mA. Consequently, the evaporation of target materials is not expected as the temperature was not raised to the melting points of them (594.1 °C for Cd and 2349 °C for B).

The mixing ratio of argon and oxygen in the gas mixture can be precisely controlled by premixing these gases in a mixer before pumped into the discharge chamber. Several mixing ratios were used (1:1, 2:1, 3:1, 4:1, 1:2, 1:3, 1:4), but the results of only two mixtures (1:1 and 4:1) were presented herein. The total gas pressure was 0.1 mbar. The cathode was cooled down to 4 °C in order to prevent thermal heating of the target – and hence the uncontrolled evaporation – as well as to minimize the thermoionic emission, while the anode was left to heat up to about 150 °C in order to induce the reaction producing the required compound (cadmium borate). More details on the preparation conditions can be found elsewhere [20-23].

The nanopowders were extracted from thin film samples by conjunctional freezing-assisted ultrasonic extraction method. In this method, the thin film sample deposited on glass substrates was cooled down to -20° inside an evacuated chamber and then left to restore its initial temperature gradually. Accordingly, the adhesion between the thin film and the substrate is reduced and the film material can be extracted by applying ultrasonic waves at frequencies ranging in 3-50 MHz. One of the advantages of this method is the extraction of nanopowder from nanostructured thin film samples with no increase in the nanoparticle size. Another advantage is no other material than of the thin film is extracted (e.g., from the substrate) [24,25].

The crystallographic phases of prepared samples were determined by a Bruker, 1.545Å CuKα radiation x-ray diffractometer (XRD), and the Fourier-transform infrared (FTIR) spectrometry was carried out using Shimadzu FTIR-8400S instrument.

3. Results and Discussion

Figure (1) shows the simulated XRD pattern of the cadmium borate samples prepared in this work. Figure (1a) shows the XRD pattern of the sample prepared using gas mixture of 1:1 and deposition time of 60 s. All peaks belonging to the polycrystalline structure of cadmium borate are observed while no peaks belonging to other compounds are seen in this pattern [26]. This is an initial indication of the structural purity of the prepared samples. Further tuning of the operation parameters and preparation conditions may lead to suppress some peaks and allow fewer number of crystal planes to grow. Using gas mixture of 4:1 and after 30 s of deposition, three small peaks were suppressed as shown in Fig. (1b). This result can be attributed to decreasing the amount of oxygen in the reaction volume as well as the time required for growth of more crystal planes.

Figure (2) shows the FTIR spectrum of the cadmium borate sample prepared using Ar:O_2 mixing ratio of 4:1. Three bands are observed around680, 1000 and 1400 cm^{-1}, which ascribed to the vibrations of B-O-B, BO_4 and BO_3 bonds, respectively [27-29]. A wide band was observed in the range 2400-2800 cm^{-1}, which is ascribed to the vibration of O-H bond in water molecules. This may be attributed to the possible adsorption of water by the prepared sample. In the samples prepared using gas mixtures other than 4:1, poisoning of the targets is very possible due to higher amount of oxygen in the gas mixture. Some vibrational bands ascribed to the Cd-O and B-O bonds were observed in the FTIR of the deposited films as a result of formation of CdO and B_2O_3 compounds.

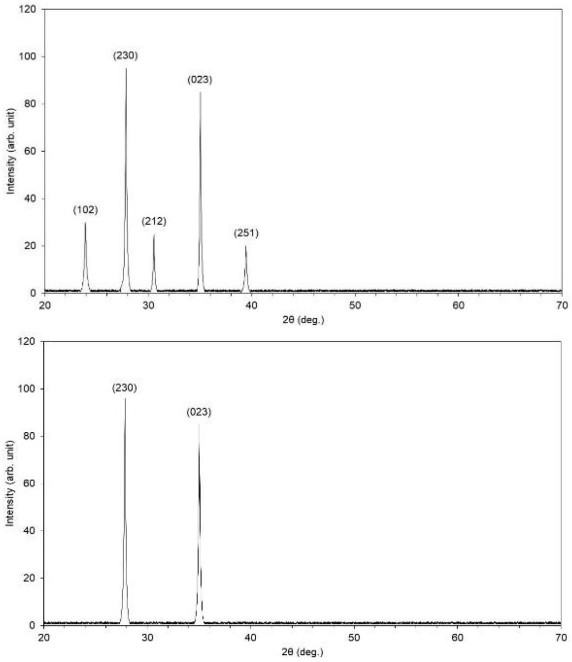

Fig. (1) XRD patterns of the cadmium borate samples prepared in this work using Ar:O_2 mixing ratio of 1:1 and deposition time of 60 s (upper) and 4:1 and 30 s (lower)

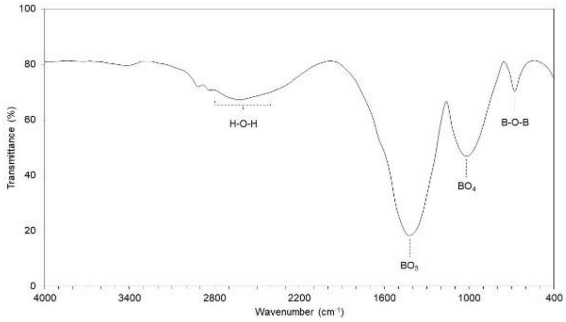

Fig. (2) FTIR spectrum of the cadmium borate samples prepared in this work using Ar:O_2 mixing ratio of 4:1 and deposition time of 30 s

4. Conclusion

In concluding remarks, an attempt to prepare cadmium borate nanostructures by reactive magnetron co-sputtering technique was presented. A new geometrical configuration was used for co-sputtering process depending on the surface binding energies as well as dimensions of cadmium and boron targets with respect to each other. The prepared nanostructures were highly pure as no elements other than cadmium, boron and oxygen were found in the final sample and no crystal planes belonging to other compounds than cadmium borate were recognized.

The growth of crystal planes in the prepared samples can be controlled by tuning the operation parameters and preparation conditions, especially gas mixing ratio and deposition time.

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