

Hydrothermal growth and photoluminescence property of textured CdWO₄ scintillator films

H. M. Shang and Y. Wang

Department of Materials Science and Engineering, University of Washington, Seattle, Washington 98195

M. Bliss

Pacific Northwest National Laboratories, Richland, Washington 99352

G. Z. Cao^{a)}

Department of Materials Science and Engineering, University of Washington, Seattle, Washington 98195

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Cadmium tungstate (CWO) films on glass substrate have been first prepared by hydrothermal method at temperatures ranging from 120 to 180 °C from cadmium nitrite and tungstic acid in hydrogen peroxide solution. Crack free and dense CWO films with textured structure and thickness up to 8 μm were formed at 150 and 180 °C as revealed by x-ray diffraction (XRD) and scanning electron microscopy (SEM) studied. Photoluminescence (PL) measurements revealed that highly textured CWO thick films possess better PL property. The growth mechanism and preferred orientation or textured structure as well as the relations between textured structure and PL property have been discussed. © 2005 American Institute of Physics. [DOI: 10.1063/1.2001133]

Cadmium tungstate (CdWO₄, hereafter referred to as CWO) is one of the most important scintillator materials with high density (7.9 g/cm³), high atomic number (Z), non-hygroscopicity, and inherent optical properties, such as high light output, low intrinsic background and few afterglows. It has been widely studied and used in x-ray computer tomography and introscopy, in spectrometric and radiometric devices, for creation of small-sized detectors with photodiodes or photoelectronic amplifiers and multielement detecting assemblies for computer tomography (CT).¹ CWO has many other applications, such as, oil well logging,² industrial processing control and inspection,³ dosimetry,⁴ and nuclear weapons and waste monitoring.^{5,6} Most studies and applications of CWO are limited to single crystals grown by Czochralski method at high temperatures.⁷ It is difficult to incorporate single crystal into microdevice fabrication process. High temperature processing also renders defects due to stress, contamination, and loss of volatile constituents.⁸

CWO films are also investigated for their coverage in a large area. CWO films have been prepared by sol-gel method,^{9–11} pulsed laser deposition (PLD),¹² and spray pyrolysis.¹³ All these methods produce films with thickness less than 1 μm and relatively poor quality. Hydrothermal growth offers a good possibility for producing high quality and thick CWO films. Hydrothermal process is the heterogeneous reaction in an aqueous media carried out above room temperature and at pressure greater than 1 atm.¹⁴ It has been garnering interest for synthesis of a wide variety of materials,^{15,16} such as, ceramics (lead zirconate titanate,¹⁷ alumina,¹⁸ zirconia,¹⁹ barium titanate,²⁰ and bioceramics²¹), composites,²² ultrafine particles with a desired shape,²³ and epitaxial growth of crystalline films.²⁴ Hydrothermal technology has also been used for the synthesis of CWO, but only millimeter sized single crystals²⁵ and fine powders^{26,27} were prepared. In this letter we report the first hydrothermal

growth of textured CWO thick films and their photoluminescence (PL) properties.

Hydrogen peroxide based solution was first prepared by dissolving 1.35 g tungstic acid powder (WO₃·H₂O, 99%, Aldrich) into 35 ml hydrogen peroxide (H₂O₂, 30 wt %, Aldrich) by stirring at 40 °C for 3 h, and then, 1 ml cadmium nitrite [Cd(NO₃)₂·4H₂O, 99.99%, Alfa Aesar] ethanol solution (0.875 M) was added into the colorless clear tungstic acid solution with a Cd:W molar ratio of 1:1. For the film growth, the resultant solution was transferred into a 23 ml Teflon inline digester and a clean 1.5 × 1.5 cm² glass substrate (microslides, VWR Inc.) was suspended horizontally inside the digester, which was subsequently heated at 120, 150, and 180 °C for 9 h. CWO films were found to grow on both sides of the substrate, with a much thicker film on the top side of the substrate, which was a loose packing of crystalline CWO powder and easily washed away by water. On the down side of the substrate, a dense thick CWO film was formed, and was subjected to further characterization by means of x-ray diffraction (XRD, PW 1820, Phillips), scanning electron microscopy (SEM, JSM 5200, JEOL), and photoluminescence (PL) spectra obtained with an Oriel Instaspec current-voltage charge-coupled device camera using a mercury lamp (100 W) for excitation. All the films used for PL test was 1.5 × 1.5 cm and the excitation wavelength for PL was 298 nm.

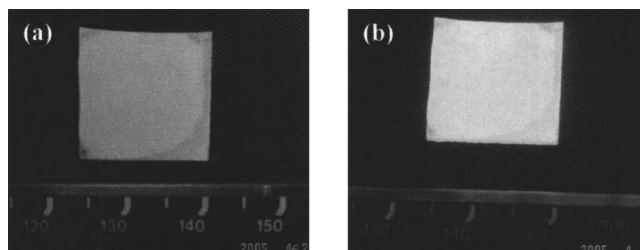


FIG. 1. Images of CdWO₄ hydrothermal films heat-treated at 180 °C (a) without UV light excitation, (b) with UV light excitation luminescence. The size of the film is 1.5 × 1.5 cm.

^{a)}Electronic mail: gzcao@u.washington.edu

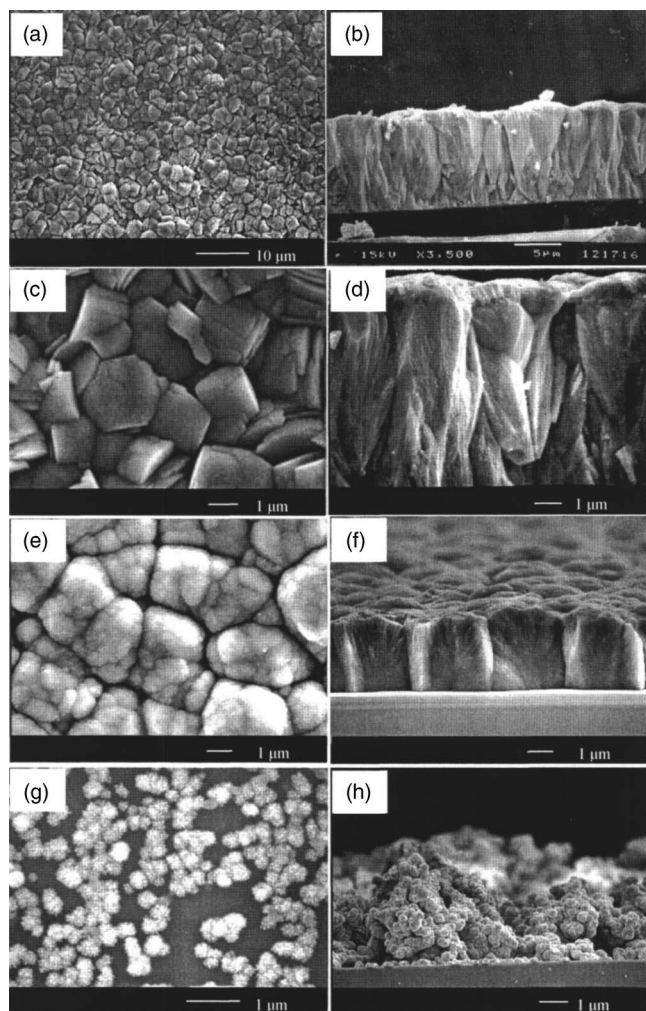


FIG. 2. Morphologies of CdWO_4 hydrothermal films: (a), (b), (c), (d), and (h) were hydrothermal treated at 180 °C; (a) and (b) were high magnification images of (c) and (d); (e) and (f) were treated at 150 °C; (g) was treated at 120 °C. (a), (c), (e), and (g) were top-view of the films; (b), (d), (f), and (h) were side-view of the films.

Uniform and crack free crystalline films were found to cover the entire bottom surface of glass substrates (1.5×1.5 cm) as shown in Fig. 1, which compares the entire CWO film without [Fig. 1(a)] and with UV light excited photoluminescence [Fig. 1(b)]. CWO films heat treated at 150 and 180 °C were polycrystalline as determined by XRD to be discussed in next section, whereas only scattered islands were formed at 120 °C and are amorphous in nature from XRD. Figure 2 shows the SEM images of films grown at various temperatures. Surface morphologies of both films grown at 150 and 180 °C are similar and consist of equal-axes grains with average grain size of $\sim 4 \mu\text{m}$ though 180 °C film is pinhole free whereas 150 °C film consists of some large pinholes. Cross sections revealed that both films have a columnar structure, suggesting that the initial nucleation occurred at the substrate surface and no appreciable secondary nucleation took place during the subsequent growth process. However, secondary nucleation did form on the other side of substrates upward exposed to solution; such secondary nucleation may be resulted from homogeneous nucleation and precipitation from the solution. The film grown at 180 °C has a transgranular fracture cross section, whereas the film grown at 150 °C, has an intergranular fracture cross section. Furthermore, one can easily notice that in the 150 °C

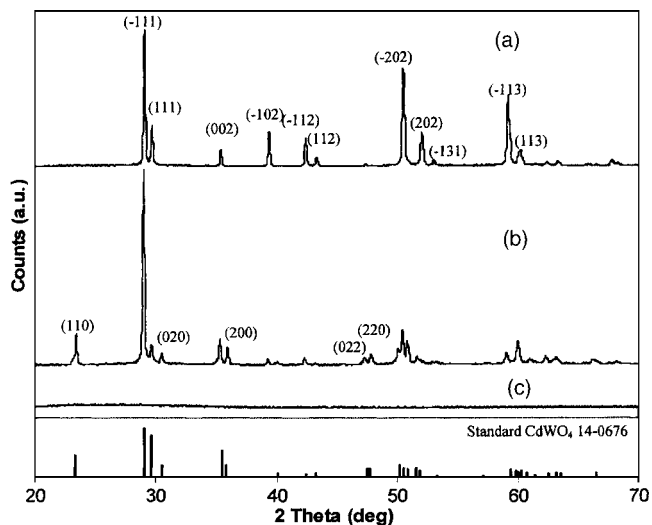


FIG. 3. X-ray diffraction patterns of CdWO_4 hydrothermal films treated at 180 °C (a), 150 °C (b), and 120 °C (c) the standard diffraction peaks are shown on the bottom for comparison. The missing peaks of 180 °C hydrothermal film were indexed in 150 °C hydrothermal film.

film, the grain size near the substrate was almost the same as that at the growth surface; however, in the 180 °C film, the grain size changed noticeably: much larger number of smaller grains near the substrate surface and less number of much larger grains near the growth surface. This observation reveals that there was a much lower nucleation density at 150 °C than that at 180 °C, which is in a good agreement with the scattered island deposits formed at 120 °C as shown in Fig. 2(g). There was sufficient free space for nuclei to grow in both lateral and perpendicular to substrate surface at 150 °C, but almost no free space for nuclei to grow laterally at 180 °C, which may explain the fact that there were pinholes between grains in 150 °C film, but grains were densely packed in 180 °C films. The same reason can be applied to explain the intergranular fracture in 150 °C film due to its weak grain boundaries, whereas the transgranular fracture in 180 °C film resulted from its close packing and strong grain boundary. Similar cross-section morphology to Fig. 2(b) is also often observed in films grown by vapor phase depositions.²⁸

Figure 3 is the XRD patterns of hydrothermal films grown at 120, 150, and 180 °C for 9 h. All the peaks of hydrothermal films were identified to belong to CWO, and no extra peaks were detected. Furthermore there was no detectable shift of peak positions. Deposits formed at 120 °C are amorphous and did not demonstrate any XRD peaks, suggesting that the lowest growth temperature of crystalline CWO be higher than 120 °C, but below 150 °C. It should also be noticed that although the CWO film grown at 150 °C demonstrated an XRD pattern identical to that of CWO powder sample and the standard pattern, several XRD peaks of CWO film grown at 180 °C were missing and these included peaks of (110), (020), and (200). The XRD pattern of 150 °C film indicated that the initial nuclei formed at the substrate surface had random orientation. Since there were no or little constrain on the subsequent growth process, the resultant film demonstrated an XRD pattern similar to that of powder sample and the standard. However, the situation in 180 °C film is rather different. Although the initial nuclei formed on the glass substrate would have random orientation, the same

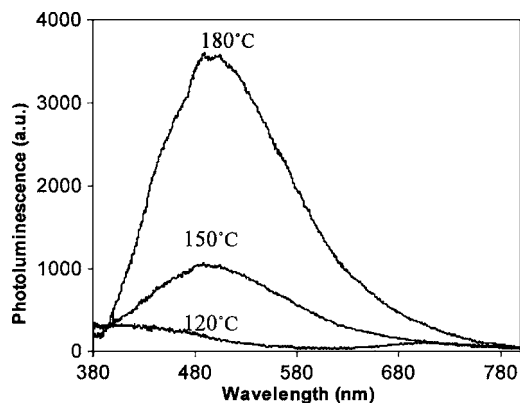


FIG. 4. Photoluminescence (PL) spectra of CdWO₄ hydrothermal films. (Excitation wavelength was 298 nm.) Films had redshift by 14 nm.

as that in 150 °C case, the nuclei density was much higher and the subsequent growth as permitted only perpendicular to the substrate surface, as discussed in the previous paragraph. In this case, only these crystal orientations with the high growth rate and perpendicular to the substrate or growth surface can continue to grow, other orientations will be terminated. Consequently, textured polycrystalline film with a columnar structure with smaller grains near substrate and larger grains near the growth surface is formed. Such a growth process is known as evolution selection growth, and has been well documented in literature.^{29,30} CWO has a monoclinic wolframite-type structure and its thermodynamically equilibrium crystal consists of (100), (010), (110), (-111), (102), and (-102) facets.³¹ All of these facets possess relatively lower surface energy and have low growth rates. According to the evolution selection growth mechanism,²⁹ none of these orientations would survive the competitive growth. Figure 3(a) obviously agrees well with the theory. Although the exact surface energy and growth rates of various facets of CWO are not known to us, the presence of peaks with strong intensity such as (-111), (-102), (-202), and (-113), suggests they have high growth rates and low surface energy.

Figure 4 compares the photoluminescence (PL) spectra of 180, 150, and 120 °C films measured at room temperature, with the PL peaks from glass substrates subtracted. This result suggested that the blue-green emission apparently originated from the WO₄²⁻ complex.³² The presence of this intrinsic PL peak in both 180 and 150 °C films is indicative that both films are crystalline CWO. However, 120 °C film is amorphous and consisted of only scattered deposits on glass substrate according to the SEM and XRD results discussed in previous section, it is not surprised to see there was no PL peak emitted from this film. However, there was a redshift in hydrothermal films by 14 nm to 494 nm. The redshift emission may be caused by the oriented growth of the CWO crystals as reported in literature.²⁵ 180 °C film had higher emission intensity and broader emission spectra. The higher emission intensity was due to greater thickness, higher density, and perfection of the crystal. The broader shape emission of hydrothermal film might be explained by considering the Jahn-Teller active vibrational modes of t_2 symmetry which influence the WO₄²⁻ complex anion of slightly distorted tetrahedral symmetry to lead to a structure absorption band for the $A_1-T_{1(2)}$ transitions.^{33,34}

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