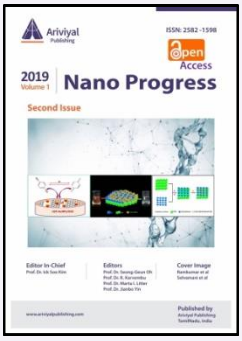
Nano Progress

Research Article

DOI: 10.36686/Ariviyal.NP.2020.02.03.008

Nano Prog., (2020) 2(3), 1-10.



Study of Thin Layers of Cadmium Oxide (CdO) Nanostructure

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ISSN: 2582-1598

Abstract: Thin layers of Cadmium Oxide with various volumes of Cadmium acetate solution (40, 50 and 70 ml) were deposited using spray pyrolysis technique over a glassy substrate. Samples were investigated using FESEM images, XRD and UV–Vis spectra as well as I–V characteristic. It was found that all samples were grew up with polycrystalline nanostructures along the preferred direction of (002). In addition, it was found that grew up sample in the volume of 50 (ml) are of optimum photoconductivity condition in visible range regarding optimum structural (largest crystallite size and lowest crystallite defect density) and optical (smallest band gap and highest light absorption) conditions.

Keywords: Cadmium Oxide; Spray Pyrolysis Technique; Photoconductivity; Nanostructure; Visible Light

Publication details
Received: 03rd March 2020
Revised: 07th May 2020
Accepted: 07th May 2020
Published: 15th May 2020

1. Introduction

Cadmium Oxide (CdO) is one of the rare inherent semi–conductors of type P with a narrow band gap of about 1.2–2.1 (eV) which has a monoclinic structure with limited transparency in the region of visible light.[1–11] Thin layers of this material are frequently dark brown to black. This darkness is due to narrow band gap and direct transitions between bands.[12–20] This fact leads to high absorption of visible light and can be used in optical pieces such as solar cells. In addition, this material is considered due to abundance of raw material, non–toxicity, easy production and ability to change and optimizing its physical properties using various physical and chemical methods such as chemical vapor deposition,[21–31] spray pyrolysis[32–43] and so on. This material is one of the important mineral Oxides for applying in pieces such as solar cells, electrochromic pieces and gaseous sensors due to its availability, high absorption rate and low cost.[44–56]

In the current research, cost effective spray pyrolysis technique was used to investigate photoconductivity of CdO thin layers with various volumes of spray solution.

Conventional electrical energy storage (EES) electrodes, such as rechargeable batteries, are mostly based on composites of monolithic micrometer sized particles bound together with polymeric and conductive carbon additives and binders.[94–127] The kinetic limitations of these monolithic chunks of material are inherently linked to their electrical properties, the kinetics of ion insertion through their interface and ion migration in and through the composite phase.[128–141] Redox chemistry of nanostructured materials in EES systems offer vast gains in power and energy. Furthermore, due to their thin nature, ion and electron transport is dramatically increased, especially when thin heterogeneous conducting layers are employed synergistically.[142–156] However, since the stability of the electrode material is dictated by the nature of the electrochemical reaction and the accompanying volumetric and interfacial changes from the perspective of overall system lifetime, research with nanostructured materials has shown often indefinite conclusions: in some cases, an increase in unwanted side–reactions due to the high surface area (bad). In other cases, results have shown significantly better handling of mechanical stress that results from lithiation/delithiation (good). Despite these mixed results, scientifically informed design of thin electrode materials, with carefully chosen architectures, is considered a promising route to address many limitations witnessed in EES systems by reducing and protecting electrodes from parasitic reactions, accommodating mechanical stress due to volumetric changes from electrochemical reactions, and optimizing charge carrier mobilities from both the "ionic" and "electronic" points of view. Furthermore, precise nanoscale control over the electrode structure can enable accurate measurement through advanced spectroscopy and microscopy techniques.[157–160]

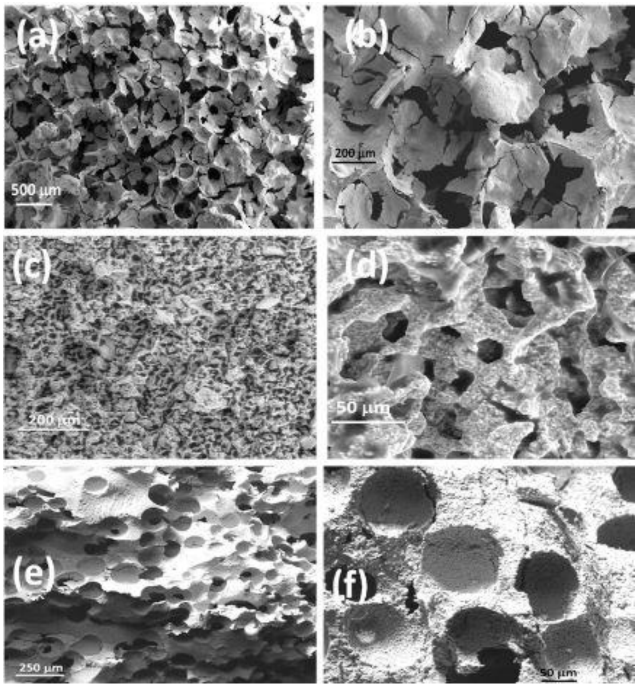

Fig. 1. SEM images of thin layers of Cadmium Oxide for samples prepared in various volumes.

This Account summarizes recent findings related to thin electrode materials synthesized by atomic layer deposition (ALD) and electrochemical deposition (ECD), including nanowires, nanotubes, and thin films. Throughout the Account, we will show how these techniques enabled us to synthesize electrodes of interest with precise control over the structure and composition of the material. We will illustrate and discuss how the electrochemical response of thin electrodes made by these techniques can facilitate new mechanisms for ion storage, mediate the interfacial electrochemical response of the electrode, and address issues related to electrode degradation over time. The effects of nanosizing materials and their electrochemical response will be mechanistically reviewed through two categories of ion storage: (1) pseudocapacitance and (2) ion insertion. Additionally, we will show how electrochemical processes that are more complicated because of accompanying volumetric changes and electrode degradation pathways can be mediated and controlled by application of thin functional materials on the electrochemically active interface; examples include conversion electrodes, reactive lithium metal anodes, and complex reactions in a Li/O2 cathode system. The goal of this Account is to illustrate how careful design of thin materials either as active electrodes or as mediating layers can facilitate desirable interfacial electrochemical activity and resolve or shed light on mechanistic limitations of electrochemical processes related to micrometer size particles currently used in energy storage electrodes.

Three–dimensional (3D) nanostructures are emerging as promising building blocks for a large spectrum of applications. One critical issue in integration regards mastering the thin, flat, and chemically stable insulating layer that must be implemented on the nanostructure network in order to build striking nano–architectures. In this letter, we report an innovative method for nanoscale planarization on 3D nanostructures by using hydrogen silesquioxane as a spin–on–glass (SOG) dielectric material. To decouple the thickness of the final layer from the height of the nanostructure, we propose to embed the nanowire network in the insulator layer by exploiting the planarizing properties of the SOG approach. To achieve the desired dielectric thickness, the structure is chemically etched back with a highly diluted solution to control the etch rate precisely. The roughness of the top surface was less than 2 nm. There were no surface defects and the planarity was excellent, even in the vicinity of the nanowires. This newly developed process was used to realize a multilevel stack architecture with sub–deca–nanometer–range layer thickness.

2. Sample Preparation

To prepare thin layers of Cadmium Oxide, Cadmium acetate powder was solved in deionized water and 0.15 (M) Cadmium acetate solution was prepared. Then, this solution was sprayed over glassy substrate in various volumes (40, 50, 70 ml) – corresponding to samples of V1, V2, V3 – to prepare the considered layers. It is expected that in pyrolysis process, the following chemical reaction mechanism happens:[57–63]

$$Cd(CH_2COO)_2.H_2O+H_2O \quad CdO+2CH_3COOH+H_2O$$

During each step, cleaned substrates were heated up to 440º C in spray device and then, solution was sprayed under air pressure (1.1 bar). In this process, distance of sprays from substrates was 35 (cm). Structural analysis of samples was performed by X–Ray Diffraction device (XRD, Brucker AXS) with CuKα spectral line emission (1.5405 Å) and the surface morphology of samples were investigated by Scanning Electron Microscopy (FESEM Hitachi S.4160). Optical characteristics of layers were measured using passed and absorbed spectra by optical spectroscopy (Shimadzu UV–Vis 1800) in the range of 300–1100 (nm).

3. Surface Morphology

Fig. 1 shows SEM images of samples in the scales of 5 microns and 500 (nm). Although the images for V1 and V3 samples show uniform surface along with some grains with 50 and 100 (nm), respectively, V2 sample is of porous surface along with woven fibers and mud–like particles that differentiate it from two other sample.

4. Structural Properties

XRD spectrum of samples is shown in Fig. 2. Diffraction curves of samples indicate that they are of polycrystalline structure with monoclinic structure and principal planes of (002) and (111) located at angles of 35.56° and 38.74°. The results indicate that V2 sample with solution volume of 50 (ml) is of weaker peaks at directions of (202) and (020) at angles of 48.86° and 53.85°, respectively. The presence of these peaks along with relative intensity of the major peaks indicates that crystalline structure improves compared to other samples.

Table 1. Calculated structural properties for the preferred peak (002).

Sample	D (nm)	$\delta\left(\times10^{-2}nm^{-2}\right)$	$\varepsilon\left(\times10^{-3}\right)$
V1	17.77	0.525	3.37
V2	27.23	0.333	3.56
V3	16.96	0.673	4.63

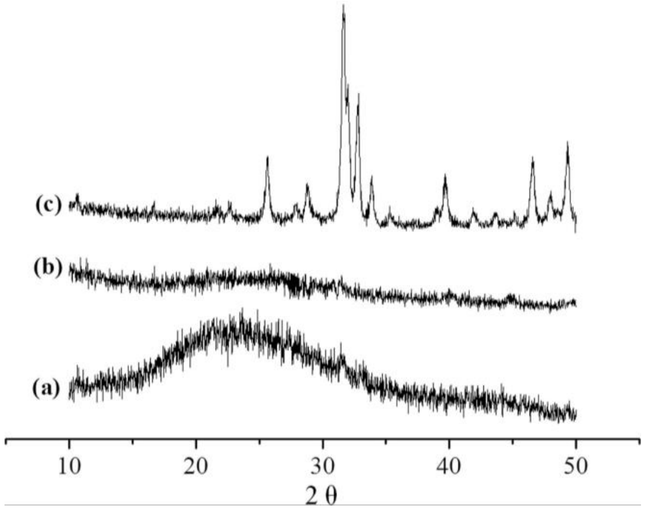

Fig. 2. XRD spectrum of Cadmium Oxide layers with various volumes (a: V1; b: V2; c: V3) of solution.

For more accurate investigation of structural properties, crystallite size (D), dislocation density (δ) and crystalline strains (ε) are calculated:[64–76]

$$D = 0.9\lambda / \beta \cos\theta \tag{1}$$

$$\delta = 1 / D^2 \tag{2}$$

$$\varepsilon = \lambda / D \sin\theta - \beta / \tan\theta \tag{3}$$

where, β is half width at full maximum, D is crystallite size, θ is Brug angle and λ is X–Ray wavelength. Results of these calculations are listed in Table (1).

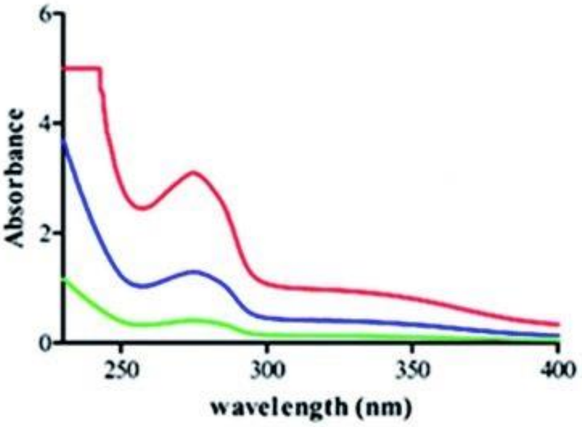

Fig. 3. Passing optical spectrum of Cadmium Oxide thin layers grew up in various volumes (V1: green spectrum; V2: blue spectrum; V3: red spectrum).

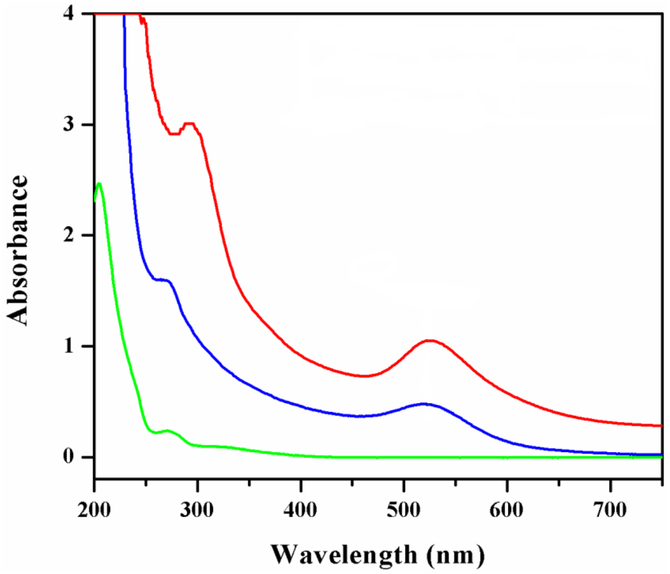

Fig. 4. Absorption spectrum of under studied samples in terms of wavelength (V1: green spectrum; V2: blue spectrum; V3: red spectrum).

5. Optical Properties

Fig. 3 shows optical passing spectrum of the under studied layers. It can be seen that in visible region of 400–700 (nm), V2 sample and V3 sample are of the lowest and highest passing, respectively. These variations may be largely due to relative electrical conductivity of layers (Section 4) which is effective is relative amount of metal–like and or insulator–like of layers.

According to the reported results, CdO layers are acted as a semiconductor with direct transition between bands so that during these transitions, absorption coefficient is a function of incident photon energy.[77–93] Fig. 4 shows the variations of absorption spectra of layers against wavelength.

Since Cadmium Oxide is a semiconductor with direct transitions between bands, to determine optical band gap of samples, $(ahv)^2$ is drawn against hv and data is extrapolated in linear region of high energy with horizontal axis as a=0. Fig. 5 shows this curve in order to determine direct optical band gap and the attached figure shows the results obtained from this analysis related to band gap amounts. The results indicate that the sample with largest crystallite size (V2) has the smallest band gap (1.74 eV) and the sample with smallest crystallite size (V3) has the largest band gap (2.01 eV) which can be a reason for happening a quantum limitation in these samples.

Because of their spontaneous nanostructure thin films behave differently from bulk materials of equivalent chemical composition. Depending both on material and deposition technique, optical thin films present structures, which when observed with an electronic microscope, may appear as columnar, polycrystalline, amorphous or lacunar. However, as these structures are in a nanometric scale they

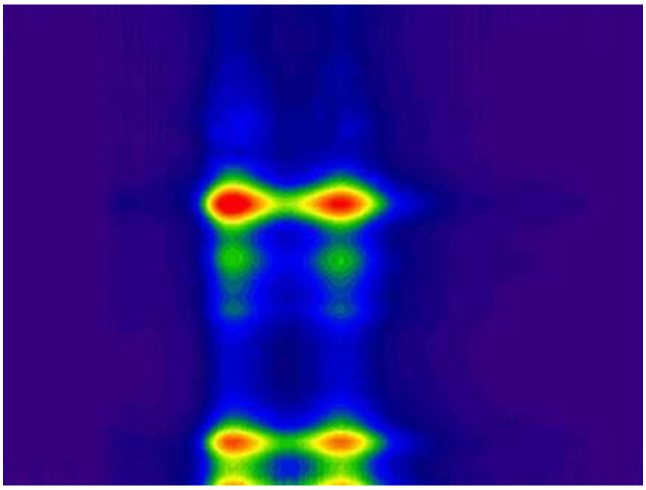

Fig. 5. Analysis of optical data as a function of photon energy. The attached figure shows band gap of layers.

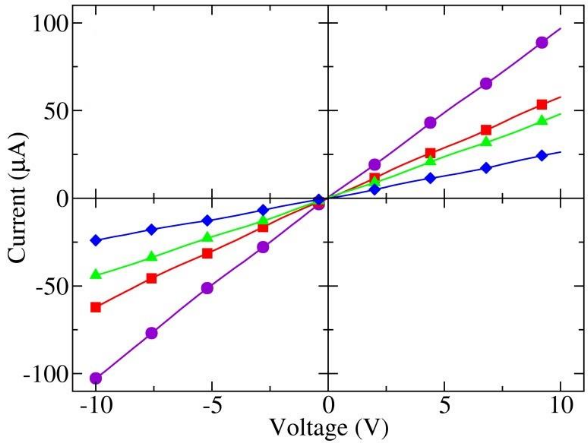

Fig. 7. Current–Voltage curve for samples subjected to visible light (V1: blue curve; V2: red curve; V3: purple curve; calibrated curve: green curve).

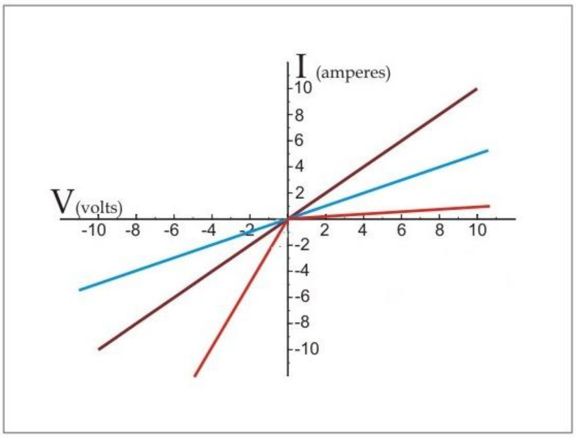

Fig. 6. Current–Voltage curve for samples grew up in darkness (V1: blue curve; V2: red curve; V3: purple curve).

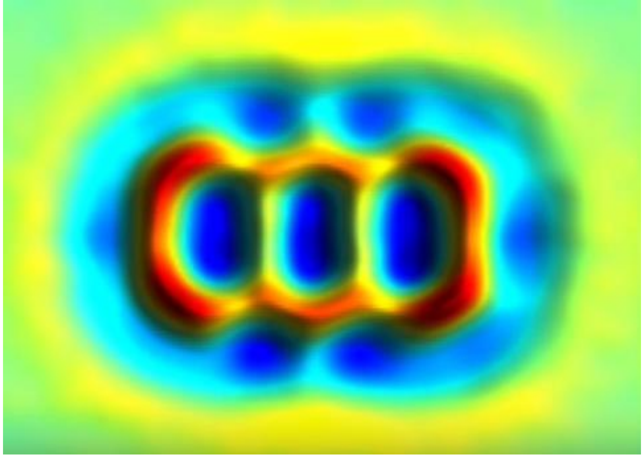

Fig. 8. Passed electrical current through investigated samples.

do not scatter light whereas they change the mean refractive index of the material. The lacunar structure also leads to water adsorption which induces shifts in the spectral properties of multilayer filters. A review of the work in this field is presented. Thanks to the progress in photolithography techniques, materials can now be artificially nano structured, and the mean refractive index can be controlled in this way. Thin films nano–structured in one dimension are anisotropic. A comparison between measured anisotropy and calculated anisotropy using homogenization models is given. Ion implantation is also shown to be a useful means of locally changing the refractive index and to control the mean refractive index. Calculation of polarizing multilayer filters made with such anisotropic layers is presented.

6. Electrical Properties

Fig. 6 shows current–voltage curve of these samples. The results indicate that sample V2 has the highest electrical conductivity (metal–like property) while sample V3 has the lowest one (isolator–like property). This is in good agreement with optical transition behavior of layers.

7. Photoconductivity Properties

To investigate photoconductivity of samples, the under studied samples were placed under visible light emission (halogen lamp). Fig. 7 shows current–voltage curve of samples under light. As can be observed, all three samples are reacted to the light and after emission, more electrical current passed through samples. This is an expected event due to producing electron – hole pairs in layers as a result of optical photon emission in $h\nu > E_g$. In order to compare optical sensitivity of these samples, the passed electrical current through samples in voltage of V3 in darkness and under visible light emission is shown in Fig. 8. As can be seen, sample V2 is of highest relative change of electrical current ($I_{Light}/I_{Dark} = 11$) and sample V3 is of lowest one (=3). These variations may be due to the effect of various factors such as optical absorption, band gap, crystallite size and crystalline obliquity in the investigated layer.

Photoconductivity is the incremental change in the electrical conductivity of a semiconductor or insulator upon illumination. The behavior of photoconductivity with photon energy, light intensity and temperature, and its time evolution and frequency dependence, can reveal a great deal about carrier generation, transport and recombination processes. Many of these processes now have a sound theoretical basis and so it is possible, with due caution, to use photoconductivity as a diagnostic tool in the study of new electronic materials and devices. This chapter describes the main steady–state and transient photoconductivity techniques applied in the investigation of semiconductors whose performance is limited by the presence of localized electronic states. These materials tend to be disordered, and possess low carrier mobilities and short free–carrier lifetimes in comparison with crystalline silicon. They are often prepared as thin films, and are of interest for large–area applications, for example in solar cells, display backplane transistors, photoemissive devices such as organic light–emitting diodes (OLEDs) and medical imagers. However, examples of where these techniques have been useful in the study of defective crystalline semiconductors are also given. The approach followed here is by way of an introduction to the techniques, the physics supporting them, and their applications, it being understood that readers requiring more detailed information will consult the references provided.

8. Conclusions

The thin layers of Cadmium Oxide nanostructures were deposited using spray pyrolysis technique with various volumes of spray solution over a glassy substrate. FESEM images indicate that surface morphology of samples are dependent on the variations of solution volume and XRD spectrum of layers indicate that polycrystalline structures are grew up in preferred direction of (002). Data analysis indicates that at solution volume of 50 ml, crystallite size and crystallite defect densities are optimum and photoconductivity properties are improved. In visible light region, layers are of low optical transition and of optical band gap between 1.74–2.01 (eV) so that sample V2 has the lowest band gap among all samples. The obtained results indicate that band gap variations in these samples are controlled by crystallite size and under the effect of happening a quantum limitation. Photoconductivity results indicate that sample V2 is of highest optical sensitivity to visible light.

Conflicts of Interest

The authors declare no conflict of interest.

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