



Rapid Communication

CdS thin films on LiNbO₃ (1 0 4) and silicon (1 1 1) substrates prepared through an atom substitution methodHaiming Qin^a, Yue Zhao^a, Hong Liu^{a,*}, Zheng Gao^a, Jiyang Wang^{a,*}, Duo Liu^a, Yuanhua Sang^a, Bin Yao^a, Robert I. Boughton^b^a State Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, PR China^b Center for Material Science, Bowling Green State University, Bowling Green, OH 43403, USA

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ABSTRACT

CdS thin films on LiNbO₃ (1 0 4) and silicon (1 1 1) substrates were prepared through an atom substitution technique using cadmium nitrate as a reactant in an H₂S atmosphere at 230 °C. X-ray diffraction, scanning electron microscopy and transmission microscopy results indicate that the CdS film grows on LiNbO₃ oriented along the [0 0 1] axis in form of crystallized nanoplates, while that deposited on silicon forms randomly oriented nanoparticles. Investigation of the precursor thin film suggests that CdS forms from the O in the CdO precursor thin film being substituted by S from H₂S in the surrounding environment, which is designated as an atom substitution process. This novel method involving an atom substitution reaction between the CdO precursor thin film and its environment can provide a new low cost approach to the preparation of chalcogenide or other compound thin films. A schematic illustration and corresponding mechanism describing the details of this method are proposed.

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1. Introduction

Cadmium sulfide is a semiconductor with formula CdS. Thin CdS films have distinctive physical and chemical properties that differ from the corresponding bulk materials due to the quantum confinement effect [1,2]. Therefore, much work has been focused on the deposition of CdS thin films to exploit this feature in energy conversion and storage [3], light emitting diodes [4] and photoelectric devices [5,6]. In recent years, a variety of methods have been developed to prepare CdS thin films such as physical vapor deposition (PVD) [7], chemical vapor deposition (CVD) [8], metalorganic chemical vapor deposition (MOCVD) [9], chemical bath deposition (CBD) [10,11], molecular beam epitaxy (MBE) [12], etc. These methods always involve expensive equipments and rigorous operational conditions. Besides various other techniques, the Langmuir–Blodgett (LB) [13] and successive ionic layer adsorption and reaction (SILAR) [14] methods have emerged as potential accessible techniques for producing nanoparticle thin films. In the LB method, CdS nano-films are grown by the slow infusion of H₂S gas through a monolayer of arachidic acid (AA) floating over an aqueous solution of cadmium chloride. The reactants for producing the CdS film are separated into two phases by the AA monolayer that the as-prepared film attaches

to. But the CdS film cannot grow on just any substrate using this method. In the SILAR method, the substrate is successively immersed in solutions of cadmium salt and sodium sulfide. The growth of CdS films is based on the absorption of ions onto the substrate and formation of CdS particles in an aqueous environment, making the CdS particles that are formed susceptible to degradation. In the present work, we propose a novel method for the synthesis of CdS thin films based on a conventional spin coating method for the preparation of the precursor film. This process is usually applied to the preparation of oxide films involving calcining or the preparation of organic thin films that result from solvent evaporation [15,16]. The synthesis process of the present method involves the exchange of elements between the CdO precursor film and H₂S in the reaction environment. A well oriented CdS film with a high degree of crystallinity formed on a LiNbO₃ single crystal substrate has been obtained through this new and simple method. Beside CdS thin films, this simple low cost method should have application to the preparation of other chalcogenide thin films, because the apparatus and raw materials are low priced and readily accessible.

2. Experimental section

CdS thin films were fabricated on LiNbO₃ (1 0 4) and silicon (1 1 1) substrates using the following method. First, the substrates were sequentially cleaned with acetone, ethanol and

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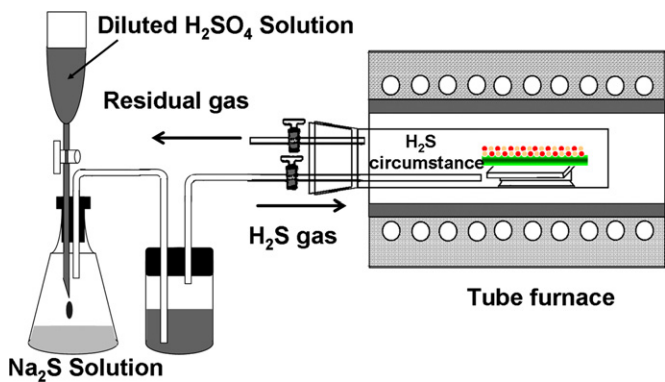


Fig. 1. Apparatus for atomic substitution reaction.

deionized water. A quantity of 0.5 g of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.7%, analytical grade, Sinopharm Chemical Reagent) was dissolved in 10 ml of ethylene glycol under vigorous stirring to obtain a transparent precursor solution. Then, the precursor solution was spin-coated on LiNbO_3 (1 0 4) and Si (1 1 1) substrates at a rotation speed of about 3500 rpm. After the spin coating process, the substrates were dried at 350 °C on a hot plate for 20 min to remove the residual solvent. The dried precursor film was then put into a heating apparatus (see Fig. 1) and heated at 230 °C for 4 h in an H_2S atmosphere. H_2S was generated by the reaction between $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (99.7%, analytical grade, Sinopharm Chemical Reagent) and diluted H_2SO_4 solution. The residual H_2S was then combined with an aqueous alkali solution to avoid pollution after the reaction was completed.

The CdS films products were characterized using an X-ray diffractometer (Cu $K\alpha$, Bruker model D8), and a field-emission scanning electron microscope (FE-SEM, Hitachi model S-4800). Fragments scraped from the as-prepared films were examined with a transmission electron microscope (JOEL model JEM-100CXII).

3. Results and discussion

Fig. 2 shows the XRD patterns of CdS films on LiNbO_3 (1 0 4) and silicon (1 1 1) substrates. In Fig. 2a, only the (0 0 2) diffraction peak of CdS can be found in the pattern of the film on the LiNbO_3 substrate apart from the diffraction peak of (1 0 4) LiNbO_3 itself, which gives evidence that the grains of the film grow along a preferred crystal plane (0 0 1) in CdS on the (1 0 4) surface of LiNbO_3 substrate. By contrast, in Fig. 2b, in addition to the strong (1 1 1) diffraction peak of Si, there are some broad short peaks, that can be indexed as hexagonal CdS (JCPDS no. 41–1049). Most typical diffraction peaks of hexagonal CdS, such as the (1 0 0), (0 0 2), (1 1 0), (1 0 3), and (1 1 2) peaks can be found in this pattern, which indicates there is no preferred grain orientation in the thin film. All four measurable peaks were calculated to analyze the particle size of the film according to the Scherrer formula— $D_c = 0.89\lambda / (B \cos \theta)$, where 0.89 is the shape factor, λ is the X-ray wavelength, B is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle. The calculated size of the particle is around 20 nm.

SEM and TEM images of the prepared films are shown in Fig. 3. In Fig. 3a, we see that the CdS film surface prepared on the (1 0 4) LiNbO_3 substrate is smooth and flat. The surface of the film is split into segmented flakes like a completed tangram puzzle. Most of the flakes are about 150–250 nm in size. The flakes are predominantly oriented along the CdS (0 0 1) plane according to the aforementioned XRD analysis. To confirm the orientation of the film, some fragments of the film scraped from the as-prepared

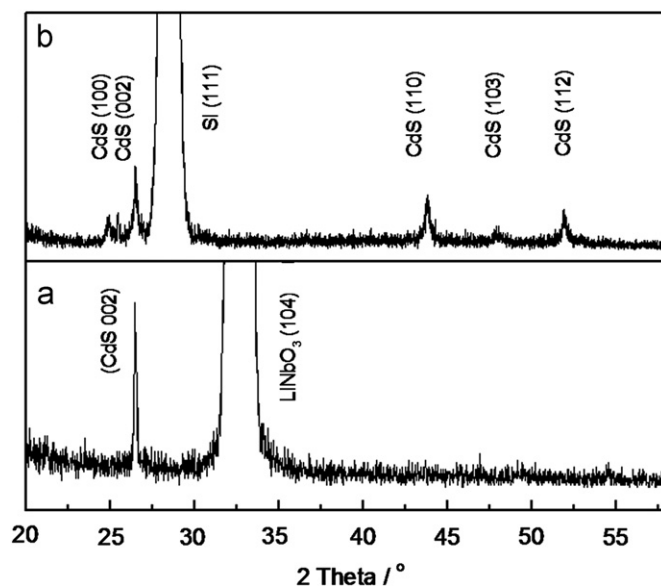


Fig. 2. XRD patterns of the CdS films on different substrates. (a) XRD pattern of (0 0 2) CdS prepared on LiNbO_3 and (b) XRD pattern of CdS prepared on silicon.

film were used for TEM observation. Fig. 3b shows a fragment and its electron diffraction pattern. The fragment of the film is about 250 nm in width with uniform thickness. The diffraction pattern exhibits typical hexagonal symmetry, and can be indexed as lying along the [0 0 1] axis of CdS. This result is consistent with the XRD analysis that indicates the film grows along the (0 0 1) plane. The morphology of the films prepared on different substrates is quite distinct. Although the film on silicon substrate appears to be very flat when observed at a low resolution, it is actually composed of tiny particles of about 10–20 nm in diameter (Fig. 3c). The particle size is confirmed to be 10–20 nm by TEM observation (Fig. 3d) of the nanoparticles scraped from the film. The very weak and random diffraction dots in the electron diffraction pattern (inset in Fig. 3d) of these particles indicate that the film is poorly crystallized with no direction preference, which is consistent with the XRD results. A nanoparticle film, rather than a film consisting of flakes, was obtained on the silicon substrate probably because of the oxide layer exist on the substrate surface. The non-crystalline SiO_2 layer on the surface of the silicon substrate makes it difficult for CdS particles to join together as they do on the LiNbO_3 substrate.

To investigate the chemical mechanism of CdS film synthesis using this method, a relatively thick film was prepared on silicon by dipping the substrate into a precursor solution with a high concentration of $\text{Cd}(\text{NO}_3)_2$ and then applying heat treatment at 350 °C for 20 min to produce a reaction that CdO should be prepared [17]. XRD patterns of the precursor film and final product powder on the silicon substrate are shown in Fig. 4. The diffraction pattern of the precursor film shown in Fig. 4a displays diffraction peaks at approximately 33.07°, 38.34°, and 55.34°. These peaks match the (1 1 1), (2 0 0), and (2 2 0) diffraction peaks of the cubic CdO structure (JCPDS no. 5-640), respectively. The diffraction pattern of the final prepared film can be related to the hexagonal CdS structure (JCPDS no. 41-1049), since the diffraction peaks of the CdS (1 0 0), (0 0 2), (1 0 1), (1 1 0), (1 0 3), and (1 1 2) lattice planes are observed.

Based on the above experimental results, a mechanism of spin coating-atom substitution process for the synthesis of CdS thin films is proposed and schematically shown in Fig. 5.

The $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution is spin-coated on the substrate, and a wet $\text{Cd}(\text{NO}_3)_2$ precursor film is obtained. After the heat

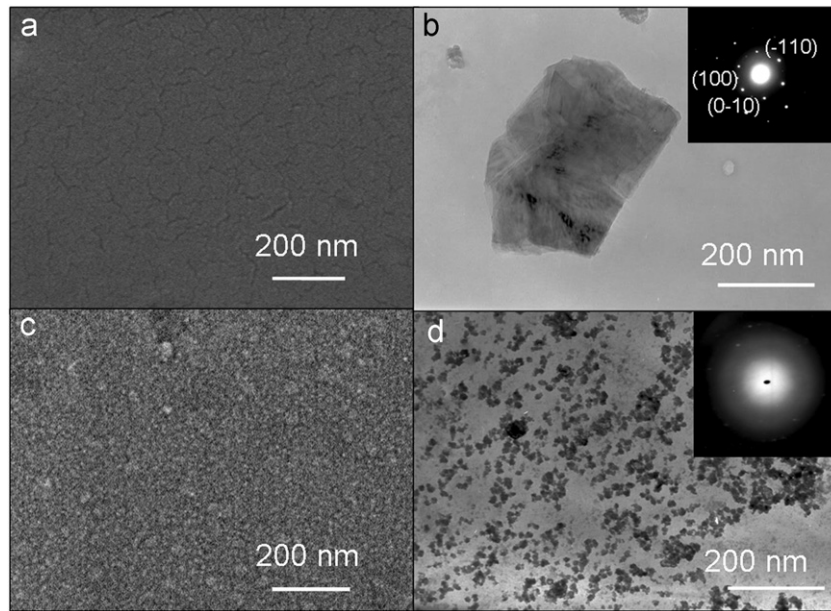


Fig. 3. SEM and TEM micrographs of the CdS films prepared on different substrates. (a) SEM pattern of CdS film prepared on (1 0 4) LiNbO₃, (b) TEM pattern of CdS fragment scraped from (1 0 4) LiNbO₃, (c) SEM pattern of CdS film prepared on (1 1 1) Si, and (d) TEM pattern of CdS fragments scraped from (1 1 1) Si.

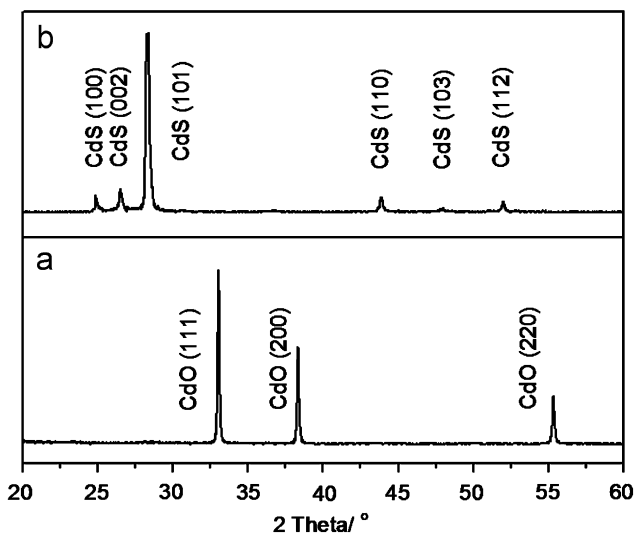


Fig. 4. XRD pattern of the precursor film (a) and final film (b).

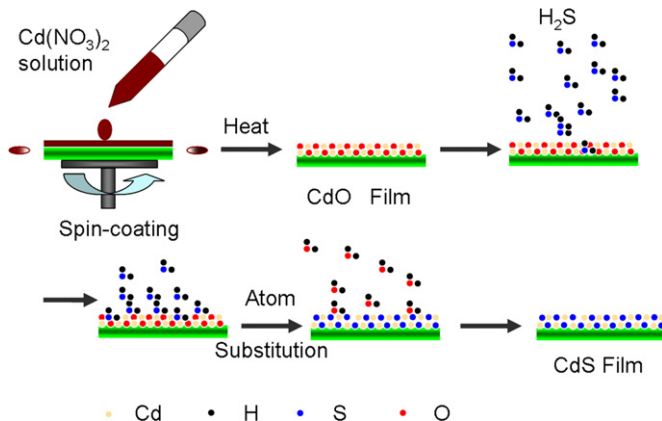
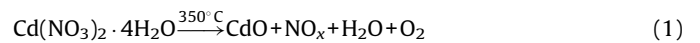


Fig. 5. Schematic demonstration of atomic exchange methodology.

treatment at 350 °C, Cd(NO₃)₂ · 4H₂O is decomposed, and a CdO precursor film is obtained [17].



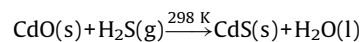
The CdO film is put into the sealed apparatus shown in Fig. 1, which is filled with H₂S gas produced by the reaction of H₂SO₄ and Na₂S.



The CdO molecules react with the H₂S obtained from the above reaction, and form CdS molecules, as shown in the reaction below.



The elemental exchange between the precursor film and the H₂S atmosphere plays a key role during the process of CdS synthesis. Elemental O in CdO is substituted by elemental S from the atmosphere in the apparatus. The Gibbs free energy change for this process under normal temperature–pressure (NTP) is –119.69 kJ/mol, which makes the reaction possible [18].



$$\Delta_r G_m^\ominus = -119.69 \text{ kJ/mol} \quad (4)$$

A substitution reaction between a solid phase and a gas environment can occur in many different compound systems, such as, sulfides, selenides, phosphides, arsenides and their solid solution compounds. All of the above are important functional materials. Because spin coating is a common and mature technique that has a wide range of application in many industrial film manufacturing processes, and the atom substitution reaction apparatus is simple, this reliable and low cost film preparation method should have wide application in the electronics industry.

4. Conclusions

CdS thin films were prepared on silicon and LiNbO₃ substrates using a simple spin coating-atom substitution approach. The CdS

thin film on the LiNbO_3 substrate is well-crystallized with *c*-axis orientation. The film on the silicon substrate is composed of tightly contacting nanoparticles of about 10–20 nm in diameter. Further investigation of the formation mechanism suggests that CdS forms from a substitution reaction of oxygen in the CdO precursor film by S reduced from the H_2S in the surrounding atmosphere in the apparatus, which is designated as the atom substitution method. This novel method has the potential to be widely applied in the fabrication of many kinds of thin films in the electronics industry because of its low cost and high reliability.

Acknowledgments

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