Journal of Crystal Growth 311 (2008) 15–19

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Characterization of $MoSe_2$ thin film deposited at room temperature from solution phase

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ARTICLE INFO

Article history:
Received 21 April 2008
Accepted 25 September 2008
Communicated by K.W. Benz
Available online 11 October 2008

PACS:
71.20.Nr
73.61.Le
78.40.Fy
78.66.Li

Keywords:
A1. Crystal morphology
A1. X-ray diffraction
A2. Growth from solution
A3. Polycrystalline deposition
B1. Inorganic compound
B2. Semiconducting materials

ABSTRACT

A simple, low-temperature method has been developed to synthesis molybdenum diselenide semiconductor thin films, based on the chemical reaction of complexed ammonium molybdate, hydrazine hydrate and sodium selenosulphate in aqueous alkaline medium. The deposition parameter of the $MoSe_2$ thin film is interpreted in the present investigation. The films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), optical absorption and electrical measurements. The deposited film was found to be polycrystalline in hexagonal form. The direct band gap 'E_g' for the film was found to be 1.43 eV and electrical conductivity in the order of $10^{-2}\,(\Omega\,\mathrm{cm})^{-1}$ with n-type conduction mechanism.

1. Introduction

Transition metal dichalcogenides have attracted much attention because of their possible applications such as lubricants, switching devices and photo-electrochemical solar energy converters [1–4]. Molybdenum diselenide absorbs in the visible and near-IR region and exhibits an inherent resistive nature to photoconversion. It shows high absorption coefficient associated with energy band gap in the optimum range for solar conversion. It has a layered sandwich structure. The layer of Se–Mo–Se interacts with each other by van der waals forces, which allow adjacent layers to slide [5–9]. The chemical vapor deposition, electro deposition, spray pyrolysis and physical vapor deposition are some of the methods used for the deposition of $MoSe_2$ in thin film form [10–14]. But chemical bath deposition method is an alternative, low-cost method which can operate at low processing temperature and provides large-area deposition. The method consists of complexed metal ion of interest, source of chalcogen ions, the stability equilibrium of which provide a concentration of ions small enough for controlled homogenous precipitation of material in the thin film form on substrate [15–19].

This is probably the first manuscript that describes the synthesis of $MoSe_2$ by chemical bath deposition method at room temperature. This communication repeats the various preparative parameters such as growth kinetics, deposition temperature, etc. and the structural, morphological, optical, electrical properties have been studied.

2. Experimental details

2.1. Substrate cleaning

Substrate cleaning plays an important role in the deposition of thin films. Use of contaminated surface provides nucleation sites facilitating the growth, which results in non-uniform film growth. The deposition was done on glass slides of dimensions 26 mm × 76 mm × 2 mm. These substrates were cleaned by boiling in chromic acid for 1 h, followed by washing successively with

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doi:10.1016/j.jcrysgro.2008.09.188

detergent, alcohol and finally stored in double distilled water before use.

2.2. Reagents and preparation of solutions

All the chemicals used were analytical grade ammonium molybdate, citric acid, hydrazine hydrate, sodium sulfite and selenium. All the solutions were prepared in double distilled water. Sodium selenosulphate (~0.25 M) was used as a selenium source for the deposition of molybdenum diselenide thin films. The solution was prepared by refluxing 5 g selenium powder with 15 g sodium sulfite in 200 mL double distilled water for 9 h at 363 K. The solution was cooled, filtered to remove undissolved selenium and stored in an airtight bottle.

2.3. Syntheses of molybdenum diselenide thin film

For the deposition of molybdenum diselenide thin films, the bath solution was made by vigorous mixing of 10 mL (0.2 M) ammonium molybdate solution, 5 mL (1 M) citric acid, 14 mL (10%) hydrazine hydrate solution in 100 mL beaker. To this, 20 mL (0.25 N) sodium selenosulphate was added and the total volume of the reaction mixture was made up to 80 mL by adding double distilled water. Cleaned glass slides were positioned vertically on a specially designed substrate holder and rotated in the reaction mixture with a speed at 50 ± 2 rpm. The temperature of the bath was then allowed to increase up to 298 K slowly. After 9 h, the glass slides were retired from the bath. The films deposited on both the sides were rinsed several times with double distilled water, dried naturally and preserved in a dessicator over anhydrous calcium chloride.

3. Characterization of molybdenum diselenide thin films

The thickness of molybdenum diselenide thin film was measured by weight difference method. Crystallographic studies of molybdenum diselenide thin film were characterized by using a Phillips PW-1710 X-ray diffractometer with Cu Kα1 line ($\lambda = 1.54056$ Å) in 2θ range from 10° to 80°. The optical properties were studied by taking absorption spectra of films using a Hitachi-330 (Japan) double-beam spectrophotometer in the range from 400 to 1150 nm at room temperature. A substrate absorption correction was made by placing an identical uncoated glass slides in the reference beam. The study of spectrum was done by determining the values of absorption at every step of 2 nm. Film microstructure was studied by using 250 MK-III, Stereoscan, Cambridge (UK) scanning electron microscope (SEM). The electrical resistance measurements were carried out in the temperature range 300–500 K on a Zintek 502 BC milliohmmeter using the two-probe method. A quick drying silver paste was applied at the ends of the film for better ohmic contact. Maintaining a temperature gradient along the length of the film and measuring the potential difference across the terminals having a separation of 1 cm with the help of digital micro-voltmeter made thermoelectric power measurement. A calibrated thermocouple probe (chrome alumel) with a digital indicator was used to sense the working temperature.

4. Results and discussion

4.1. Kinetic studies and reaction mechanism

Molybdenum diselenide films have been deposited by decomposition of sodium selenosulphate in alkaline solution containing ammonium molybdate and citric acid as complexing agent. Citric acid controls the molybdenum ion concentration in the reaction vessel. Hydrazine hydrate acts as a reducing agent. The mixing of solutions was carried out at 278 K temperature, which lowers the kinetic energy of ions and avoids precipitation or film formation. A slow increase in temperature decomposes moderately stable sodium selenosulphate to yield Se^{2-}, while hydrazine hydrate reduces Mo^{6+} to Mo^{4+} in basic medium. The dissociation of Mo–CA complex at higher temperature liberates bear Mo^{4+} ions that react with Se^{2-} ion to get molybdenum diselenide thin film. The growth mechanism can be described from the following reactions:

$$Mo^{6+} + 3A^{2-} \rightarrow [Mo(A)_3]$$

$$[Mo(A)_3] + 2NH_2 - NH_2 + 2OH^- \leftrightarrow MO^{4+} + 3A + 2H_2O + 2N_2\uparrow$$

$$Na_2SeSO_3 + OH^- \rightarrow Na_2SO_4 + HSe^-$$

$$HSe^- + OH^- \rightarrow H_2O + Se^{2-}$$

$$MO^{4+} + 2Se^{2-} \rightarrow MoSe_2$$

The film deposition takes place by recombination of ions on the glass surface via nucleation followed by growth. The deposition of molybdenum diselenide film occurs when the ionic product of Mo^{4+} and Se^{2-} exceeds the solubility product. Initial higher bath temperature favors precipitation instead of film formation. This is because of the presence of large number of free ions in the

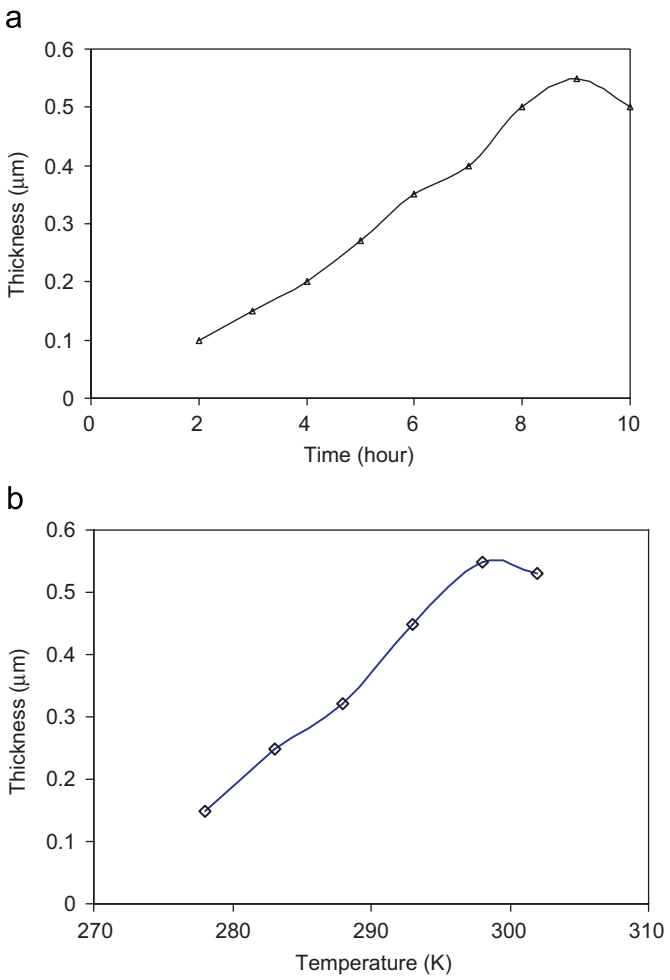

Fig. 1. (a) Variation of the film thickness with deposition time and (b) variation of the film thickness with deposition temperature.