Detection of crystal structure of chemically-deposited copper selenide thin films

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Received 20 August 2003, accepted 6 November 2003

Abstract: A low cost Chemical Bath Deposition (CBD) system has been developed in our laboratory for the preparation of copper selenide thin films. Good quality thin films of smooth surface of copper selenide thin films of compositions (Cu<sub>1</sub>S<sub>e</sub> x = 0.1-0.5) and Cu<sub>S</sub>Se<sub>2</sub> were deposited using sodium selenolate as a source of selenolic ions. Crystal structure of copper selenide (Cu<sub>1</sub>S<sub>e</sub> x and Cu<sub>S</sub>Se<sub>2</sub>) thin films has been identified by X-ray diffraction (XRD) method. When the film is annealed at 250°C in air, the phases of Cu<sub>1</sub>S<sub>e</sub> x and Cu<sub>S</sub>Se<sub>2</sub> become crystalline, with structures of cubic (berzelianite) and tetragonal, respectively, whereas the as-deposited film was found to be disorder. The crystallinity is very low in as-deposited samples, which improves on annealing in air at 250°C. The grain size of the as-deposited samples was very small, which was increased about 30% owing to annealing in air at 250°C.

Keywords: Chemical bath deposition, copper selenide, X-ray diffraction

PACS Nos.: 61.10.Nz, 68.55.Hk, 81.15.Gp

The thin films include a variety of concepts, which describe on various scales, the arrangement of the building blocks of materials. On an atomic scale, one deals with the crystal structure, which is defined by the crystallographic data of the unit cell. These data contain the shape and dimension of the unit cell and the atomic position within its lattice structure. They are obtained by diffraction experiments. On a coarser scale, one deals with the microstructural observations of the microstructure, which characterizes the sizes, shapes and mutual arrangements of individual crystal grains. It also includes the microstructure and surface morphology of the materials. Suitable techniques are surface replication and scanning electron microscopy [1-4].

Frequently, one has to determine whether a given deposit is a single crystal or polycrystalline either with a random distribution of orientation with respect to the coating plane. For a single crystal coating, it is important to know its orientation relationship with respect to the substrate [5]. X-ray diffraction is a suitable tool to determine the crystal structure of any unknown materials, whether the sample is a single crystal or polycrystals [6]. Cu<sub>1</sub>S<sub>e</sub> x is a kind of photovoltaic semiconductor, which can be used as a good absorber. In our previous study, we have reported that Cu<sub>1</sub>S<sub>e</sub> x thin film has been successfully grown onto glass slide using CBD technique [7]. The resistivity is observed in the range (2-25)×10<sup>4</sup> Ω cm from as-deposited to annealed Cu<sub>1</sub>S<sub>e</sub> x film. The transmittance and reflectance is obtained to be about 87.5% and 4-20% in the wavelength range 400-1100 nm from as-deposited to annealed samples. In the present Note, we report the detection and structural study of Cu<sub>1</sub>S<sub>e</sub> x and Cu<sub>S</sub>Se<sub>2</sub> thin films using X-ray diffraction method.

The chemicals, used for the preparation of thin films, were LR grade (Merck) capric chloride di-hydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O), selenium powder of 99.95% purity, sodium sulfite (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>), tri-ethanol amine (TEA) and ammonium hydroxide (NH<sub>4</sub>OH). At first, selenium was used for the preparation of sodium selenosulfate. Secondly, CuCl<sub>2</sub>·2H<sub>2</sub>O solution was mixed with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> at constant stirring. Then TEA was added to this solution. NH<sub>4</sub>OH was used to adjust the pH of the reaction bath. Microscope glass slides were used as substrates. The substrates were cleaned well with detergent and distilled water, and were kept in H<sub>2</sub>S<sub>2</sub>O<sub>3</sub> for about 1h. Then they were rinsed with distilled water and were dried in air prior to film deposition. The substrates were then immersed vertically into the deposition bath against the wall of the beaker containing the reaction mixture. After deposition at room temperature, the glass slides were taken.

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out from the bath and then rinsed with distilled water and were
dried in blowing air.

A Philips X-Pert X-ray diffractometer (XRD) was used to
obtain X-ray data of the samples at the Bangladesh Council for
Scientific and Industrial Research (BCSIR), where the powder
diffraction technique was used with a primary beam power of 40
kV and 30 mA for Cu radiation. A nickel filter was placed before
the sample to reduce CuKα radiation and finally CuKα radiation
was only used as the primary beam. Here, sample-1 represents
the as-deposited Cu1.8Se film followed by annealing at 250°C
for one hour in air and sample-2 represents the as-deposited
Cu1.8Se film followed by annealing at same condition.

All the X-ray diffraction data of the samples were analyzed
using computer to get d values and peak intensities. The spacing
d was calculated using Bragg relation

\[ 2d \sin \theta = \lambda \]

where \( \lambda \) is the wavelength of the incident radiation and for
Cu(Kα), \( \lambda = 1.54178 \text{ Å} \). The XRD pattern was then analyzed
using the d-values of their main fundamental peaks. The d-values
and their intensity ratios were compared to the data available in
the analytical library of the computer software, which contains
JCPDS International Centre for Diffraction Data [8]. The unknown
compounds and elements were identified from the observed
data.

The XRD pattern of as-deposited Cu1.8Se film is shown in
Figure 1. Loss of noise observed in the XRD pattern may be due
to the growth of disorder film. The result has been presented
here after slight removal of noise. From this pattern, it shows
that no well-defined peak was found and no well-defined plane
was obtained in the case of as-deposited films, which suggests
that the as-deposited films were disorder. A little tendency of
growing peak is found at angle 2θ = 27.30°, 45.35° and 62.78°.
The intensity of the observed peaks is very low, which become
stronger due to annealing at 250°C.

![Figure 1. XRD pattern of as-deposited Cu1.8Se thin film.](image1)

The XRD pattern of sample-1 is shown in Figure 2. The XRD
pattern shows well-defined peaks suggesting the formation of

![Fig. 2. XRD pattern of sample-1.](image2)

crystalline film due to annealing. A comparison of the observed
pattern with the standard JCPDS (Joint Committee on Powder
Diffraction Standards) cards shows that the annealed samples
with above condition possess a structure, matching the cubic

![Fig. 3. XRD pattern of sample-2.](image3)

(berzelianite) (JCPDS 26-512) Cu1.8Se with \( x = 0.2 \), which belongs
to the cubic system with lattice parameter \( a = 5.697 \text{ Å} \) [9]. The
crystallinity of the films was observed to improve owing to
annealing at 250°C. The observed peak positions are in good
agreement with those due to reflections from (111), (200) and
(311) planes of the reported structure observed for as-deposited
Cu1.8Se thin film prepared by CuSO4 and tri-sodium citrate [10]
and for as-deposited Cu1.8Se thin film of 0.13 μm thickness
[11,12]. The XRD pattern of sample-2 is shown in Figure 3. It
shows well-defined peaks matching to Cu1.8Se (JCPDS 25-263),
which belongs to the tetragonal phase with \( a = 5.63 \text{ Å} \) and
c = 11.23Å. The observed peak positions are also in good
agreement with those due to reflections from (112), (204) and
(312) planes of the reported structure [13]. It can be concluded
that the crystallinity found is very low for as-deposited samples,
which improves due to annealing in air at 250°C.

The crystalline grain size in the films was calculated using
the Scherrer formula. The full width at half maxima (FWHM) of
the largest peak for as-deposited sample was found to be 11.29 and that for the samples (1 and 2) were found to be 0.38 and 0.40, respectively. The average grain diameter for as-deposited sample was found to be 0.025 mm that increases to 0.724 and 0.688 mm in case of the samples 1 and 2, respectively. Very low grain size is observed for as-deposited samples, which was observed to increase about 30% owing to annealing. The X-ray diffraction parameters for samples-1 and 2 are summarized in Tables 1 and 2, respectively.

<table>
<thead>
<tr>
<th>Table 1. X-ray diffraction parameters of sample-1.</th>
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<tr>
<td>d (Å)</td>
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<tr>
<td>------</td>
</tr>
<tr>
<td>3.324</td>
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<td>1.996</td>
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<td>1.734</td>
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<table>
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<tr>
<th>Table 2. X-ray diffraction parameters of sample-2.</th>
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<tr>
<td>d (Å)</td>
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<tr>
<td>------</td>
</tr>
<tr>
<td>3.245</td>
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<tr>
<td>2.005</td>
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<tr>
<td>1.744</td>
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</table>

- Our interest was to identify the newly formed compound on the glass slide and to determine its structure. Therefore, X-ray diffraction (XRD) is used for identification of Cu₃₆Se₂ and Cu₃₆Se₂ phases. When the film annealed at 250°C in air, the phases Cu₃₆Se₂ and Cu₃₆Se₂ become crystalline, with structures of cubic (berzelianite) and tetragonal, respectively, whereas the as-deposited film was found to be disorder. The observed peak positions are those due to reflections from (111), (220) and (311) planes for Cu₃₆Se₃ phase and (112), (204) and (312) planes for Cu₃₆Se₂ phase. The crystallinity is very low in as-deposited sample that improves on annealing in air at 250°C. The grain size of the as-deposited samples was very small, which was increased about 30% owing to annealing in air at 250°C.

Acknowledgments

The authors are grateful to the Director of Institute of Glass and Ceramic Research and Testing, BCSIR for allowing the XRD facilities. They acknowledge the financial support given from Bose Center for Advanced Study and Research in Natural Sciences, Dhaka University.

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