

PREPARATION AND CHARACTERIZATION OF CHEMICAL BATH DEPOSITED NiSe THIN FILMS

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Abstract: Nickel selenide thin films were deposited on microscope glass substrates using the chemical bath deposition method. The deposition was carried out using nickel sulphate as a Ni^{2+} ion source and sodium selenite as a Se^{2-} ion source in the presence of Na_2EDTA as a complexing agent. The structural and morphological properties of NiSe films obtained were investigated using X-ray diffraction and atomic force microscopy. X-ray diffraction patterns indicated that the films were polycrystalline NiSe with hexagonal structure. Based on the atomic force microscopy analysis, all the samples showed complete coverage of the substrate surface with the thickness of the films about 156-664 nm. When the bath temperature was increased from 55 to 75 °C, the grain size was increased but the band gap was decreased from 1.89 to 1.80 eV.

Keywords: nickel selenide, chemical bath deposition, thin films, complexing agent

INTRODUCTION

The thin films technology becomes more and more attractive for the researchers. The interest for chalcogenide semiconductor materials is based on their potential applications such as solar cells, sensor and laser materials. Thin films can be prepared by various methods such as spray pyrolysis (Badera et al., 2008), pulsed laser deposition (Shen et al., 2008), vacuum evaporation (Murali et al., 2004), electrodeposition method (Anuar et al., 2009), electron beam evaporation (Ahamed et al., 2010) and chemical bath deposition (Ezema et al., 2007). The preparation of thin films by the chemical bath deposition (Joshi et al., 2004; Chaudhari et al., 2008; Song et al., 2009; Anuar et al., 2011; Gopakumar et al., 2010; Raniero et al., 2010; Ubale 2010; Babu et al., 2011) is currently attracting a great deal of attention due to simple, no requirement of sophisticated instruments, minimum material wastage and easy coating of large surfaces. This method is based on the controlled release of the metal ions and chalcogenide ions in an aqueous bath into which the substrates are immersed.

In this paper, we prepare NiSe thin films by chemical bath deposition method and study the effects of bath temperature on the properties of these materials. So far, we have not seen any literature review for the deposition of NiSe films in the presence of Na_2EDTA as a complexing agent in acidic medium.

EXPERIMENTAL

Microscope glass slides were used as the substrate during the deposition process. The substrates were first cleaned in ethanol solution and subsequently ultrasonically washed with distilled water. Substrates were then dried in an oven at 90 °C. Nickel sulphate, sodium selenite, disodium ethylenediaminetetraacetate and hydrochloric acid of analytical reagent grade were used as received. Aqueous solutions of nickel sulphate, sodium selenite and disodium ethylenediaminetetraacetate were separately prepared before experiment. 25 mL of nickel sulphate (0.2 M) and 25 mL of disodium ethylenediaminetetraacetate (0.2 M) were mixed in a beaker. Then, 25 mL of sodium selenite (0.2 M) was added and the pH of the solution was adjusted to 2.5 by addition of hydrochloric acid. Substrates were immersed vertically in the beaker. Then, the beaker was placed in water bath at desired temperature (55, 65 and 75 °C). The beaker was not stirred during the thin films deposition. After completion of films deposition (150 min), the deposited films were then washed with distilled water and dried in air at room temperature.

X-ray diffraction (XRD) analysis was carried out using a Philips PM 11730 diffractometer for the 2θ ranging from 25° to 60° with $\text{CuK}\alpha$ ($\lambda=1.5418 \text{ \AA}$) radiation. The surface morphology and thickness were examined by recording atomic force microscopy (AFM) images with a Q-Scope 250 in contact mode with a commercial Si_3N_4 cantilever. The elemental composition of the films was studied by scanning the electron microscope (JEOL JSM 6400) attached with energy dispersive analysis of the X-ray (EDAX) analyzer. Photoelectrochemical experiments were performed in $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox system, by running linear sweep voltammetry between -400 to -900 mV versus Ag/AgCl (silver-silver chloride). The halogen lamp (100 W) was used for illuminating the electrode. The film-coated microscope glass slide was placed across the sample radiation pathway while the uncoated microscope glass slide was put across the reference path. Thus, the absorbance measurement included only the contribution from NiSe thin films. From the analysis of absorption spectrum, the band gap energy was determined.

RESULTS AND DISCUSSION

X-ray diffraction patterns recorded for the chemical bath deposited NiSe films on microscope glass slide at various bath temperatures (55, 65 and 75 °C) are shown in Fig. 1. The studies showed that the films of NiSe are polycrystalline in nature with hexagonal structure with lattice constant ($a=3.66\text{\AA}$, $b=3.66\text{\AA}$, $c=5.33\text{\AA}$). For the films deposited at lower bath temperature, the presence of two peaks at $2\theta=28.3^\circ$ and 32.6° corresponds to the (100) and (101) planes, respectively can be seen in Fig. 1a. The different peaks in the XRD patterns were indexed and the corresponding values of d -spacing values were compared with the standard d -spacing values (JCPDS reference No.: 01-075-0610). It is observed that the height of prominent peaks (100) of NiSe increases and some new peaks of NiSe start to appear while increasing bath temperature from 55 to 75 °C. As the bath temperature was increased to 65 and 75 °C, the NiSe peaks increased to three and finally four, respectively. Overall we can conclude that the XRD patterns confirm the presence of NiSe in the films, the only other peaks such as (112), (103), (121), (211) and (220) planes being those of the SiO_2 (JCPDS reference No.: 01-074-0201) (Weiss and Weiss, 1954) substrate.

Atomic force microscopy (AFM) images of NiSe thin films deposited under various bath temperatures are shown in Fig. 2. Based on the atomic force microscopy images, all the samples show a distribution of grain which covers the surface of the substrate completely. The films deposited at lower bath temperature (55 °C), show less particles compared to the other films. These films are consisting of smaller grain with the size of 0.8-1 μm . For the films deposited at 65 °C, the samples appear more homogeneous which have a grain size of 1.5 μm . As the bath temperature is increased up to 75 °C, the grain size increased compared to the films deposited at lower bath temperature. The irregular shape of the grains can be seen as shown in Fig. 2c. Several crystallites grouped together to form larger grains. The average size of grains is in the range between 2 and 3 μm . The thickness of thin films was investigated using AFM images. The thickness values obtained are 156, 322 and 664 nm for the films deposited at 55, 65 and 75 °C, respectively. These results conclude that an increase in bath temperature allow more materials to be deposited onto the substrate and thicker films to be formed.

Band gap energy and transition type can be derived from mathematical treatment of data obtained from optical absorbance versus wavelength with Stern relationship of near-edge absorption:

$$A = \frac{[k(h\nu - E_g)]^{n/2}}{h\nu} \dots(1)$$

where ν is the frequency, h is the Planck's constant, k equals a constant while n carries the value of either 1 or 4. The value of n is 1 and 4 for the direct transition and indirect transition, respectively. According to equation (1), $(Ah\nu)^2$ linearly depends upon the photon energy (eV). This fact is confirmed by the curves presented in Fig. 3. The values of band gap were determined by extrapolating the linear portions of the respective curves to $(Ah\nu)^2=0$. A direct band gap of 1.80, 1.86 and 1.89 eV was found for the films deposited at 75, 65 and 55 °C, respectively. These band gap values are in good agreement with the values reported earlier (Hankare et al., 2010; Moloto et al., 2009).

The composition of the films has been studied from energy dispersive analysis of X-rays (EDAX). The typical EDAX result (Fig. 4) revealed that the following composition in atomic percentage (%): Ni(51.36 %) and Se (48.64 %) for a films deposited at 65 °C. The atomic ratio of Ni:Se is 1:1. This result is consistent with XRD analysis of the sample with phase corresponding to NiSe.

Fig. 5 indicates the photoresponse of the deposited films (which prepared at 65 °C) in contact with Fe^{2+}/Fe^{3+} redox couple. The figure shows the resulted changes in the current as the films have been illuminated intermittently. We observed that the photocurrent occur on the negative potential shows that the films prepared are p-type. The same behavior has been reported for the NiSe films deposited by electrodeposition method (Zainal et al., 2005 and chemical vapour deposition technique (Panneerselvam et al., 2008).

CONCLUSIONS

NiSe thin films were deposited on microscope glass substrate by chemical bath deposition method. Deposition was carried at different bath temperatures from 55 to 75 °C in the presence of Na_2EDTA as a complexing agent. The XRD patterns showed polycrystalline films of hexagonal phase with (100) preferential orientation. According to the atomic force microscopy analysis, all the films showed complete coverage of the substrate surface with the thickness of the films about 156-664 nm. As the bath temperature was increased from 55 to 75 °C, the grain size was increased but band gap was decreased from 1.89 to 1.80 eV.

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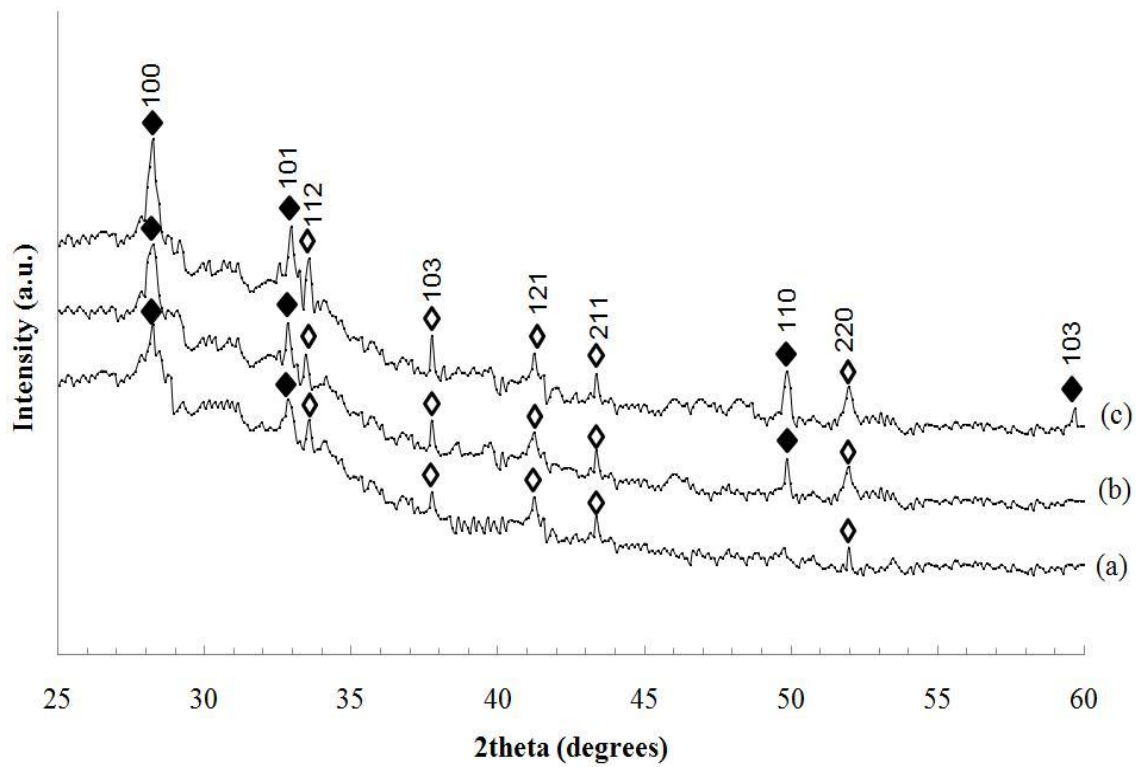
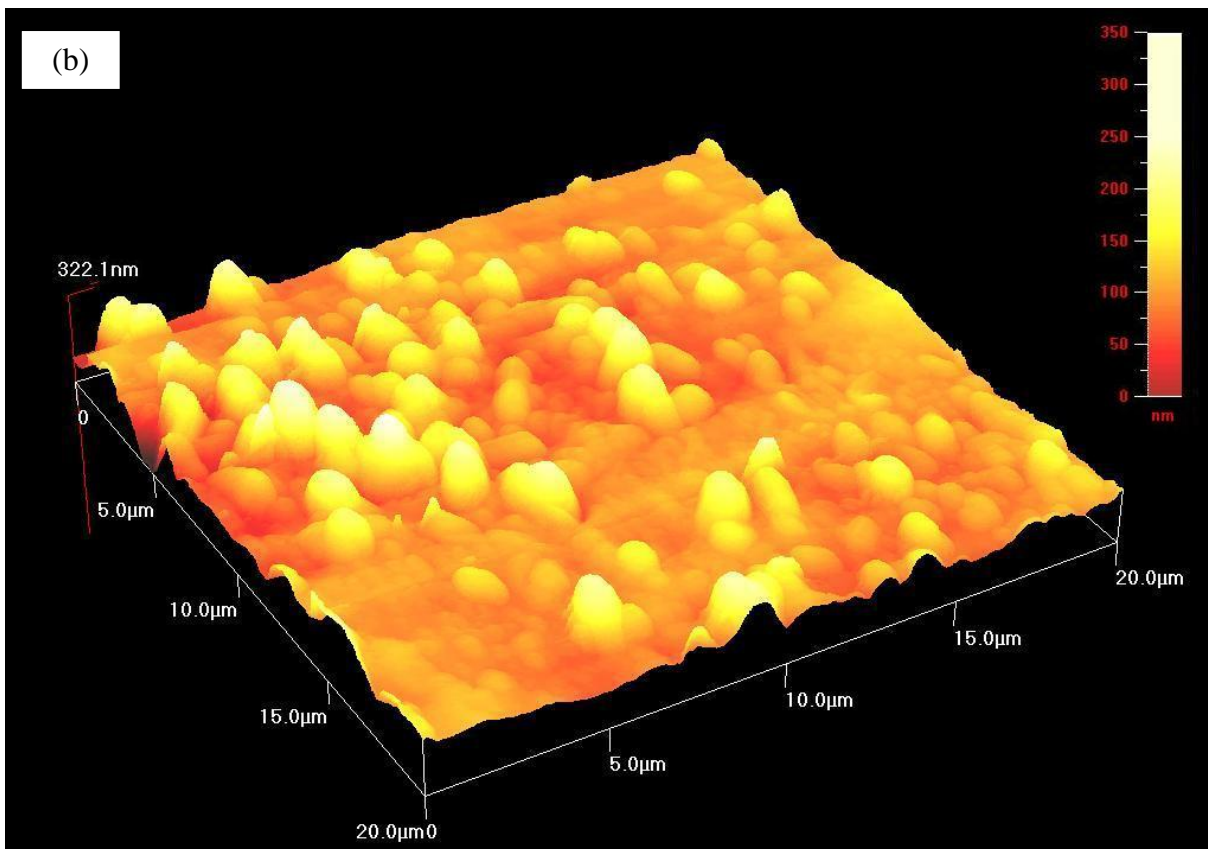
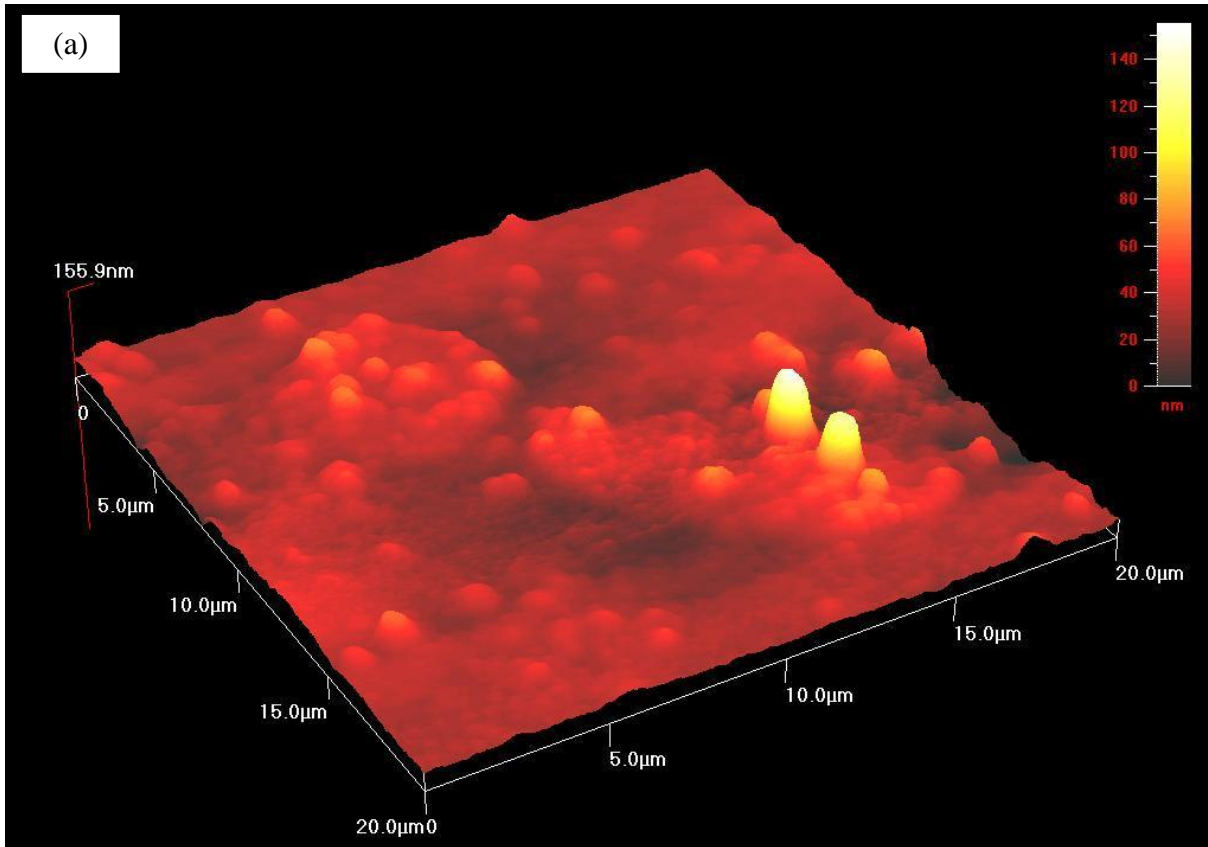


Figure 1: X-ray diffraction patterns of NiSe thin films deposited at different bath temperatures (a) 55 °C (b) 65 °C (c) 75°C (◆ NiSe; ◇ SiO₂)



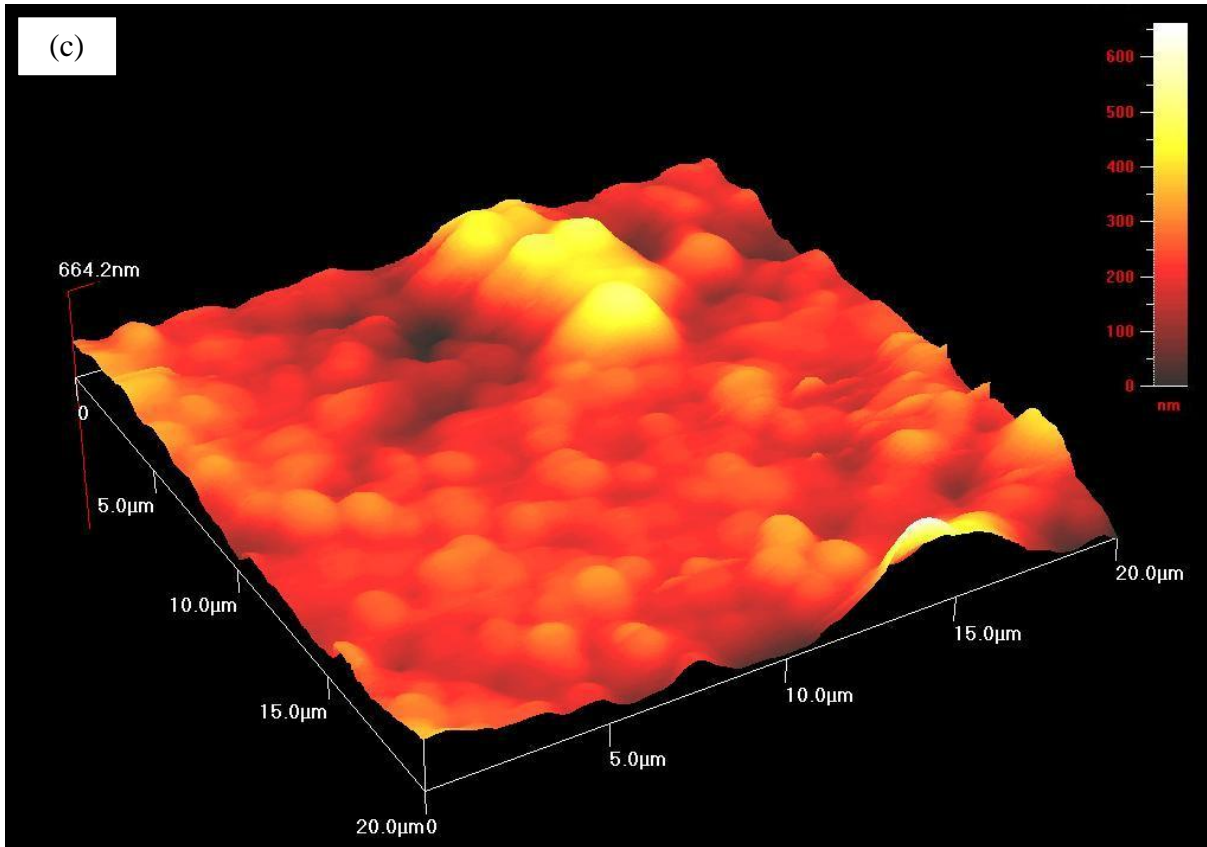
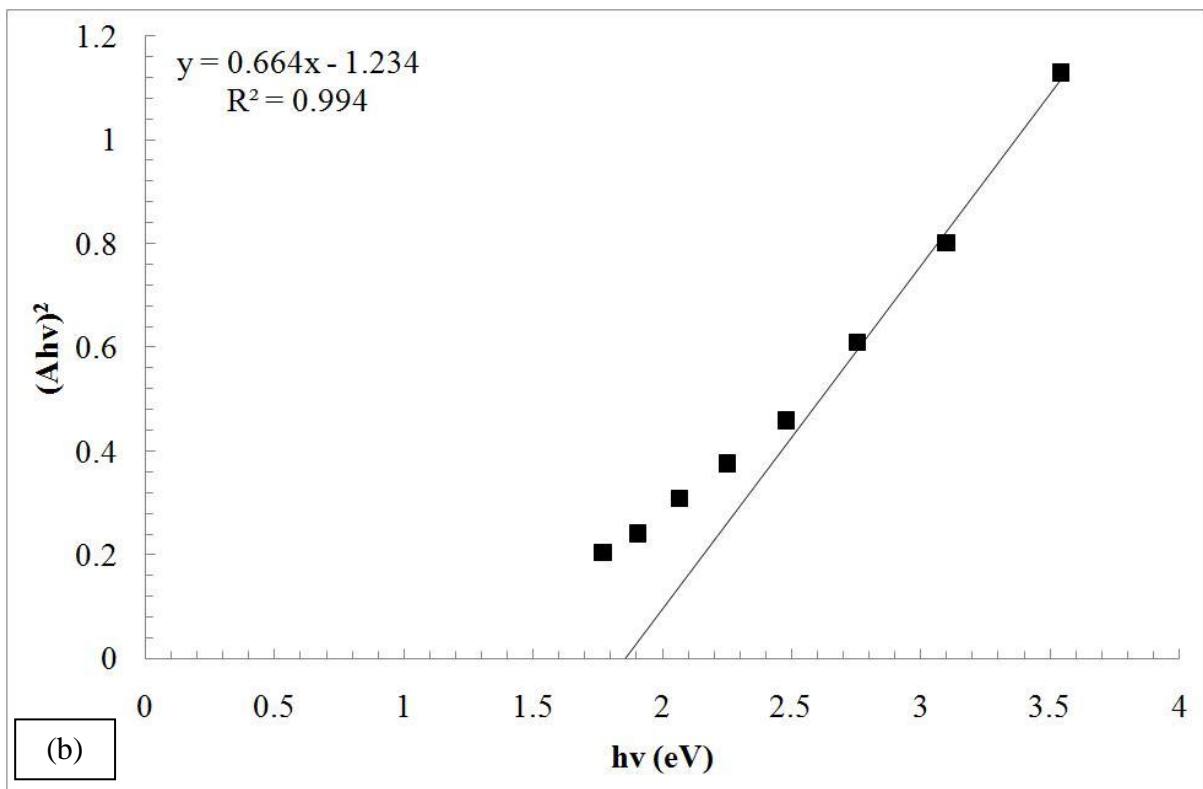
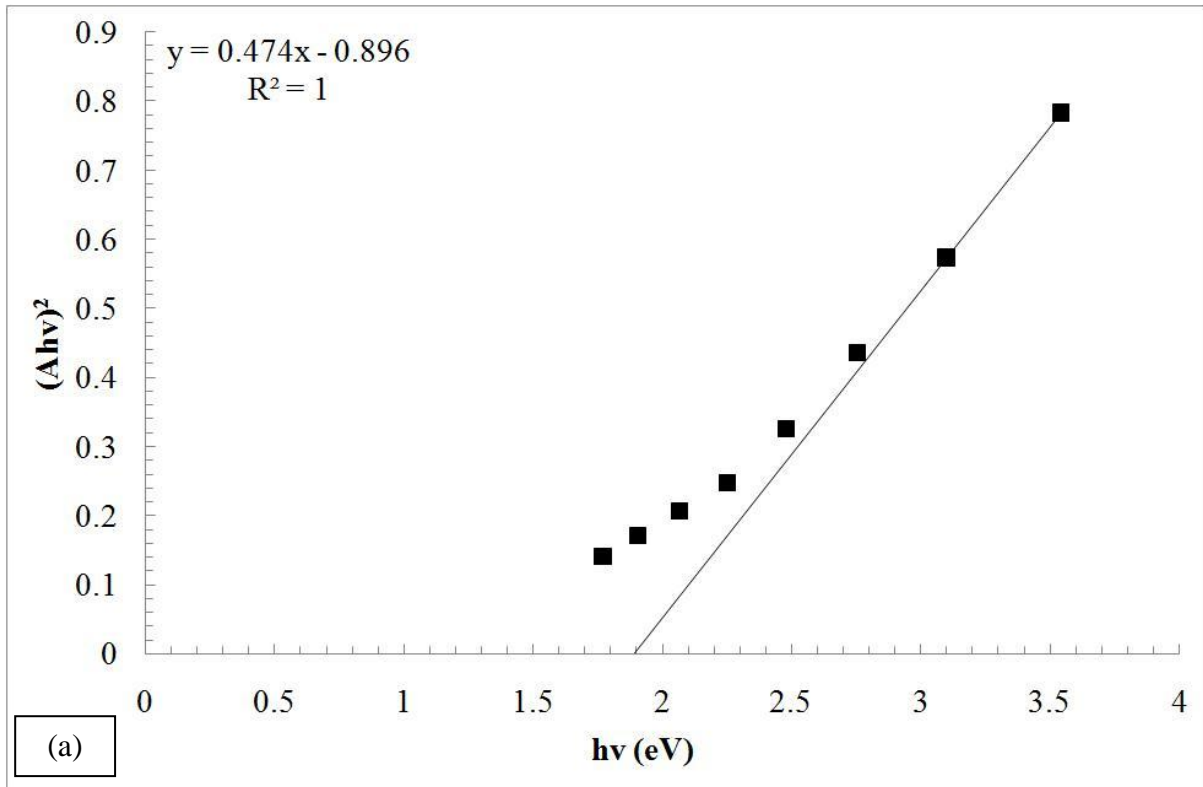


Figure 2: Atomic force microscopy images of NiSe thin films deposited at different bath temperatures (a) 55 °C (b) 65 °C (c) 75°C



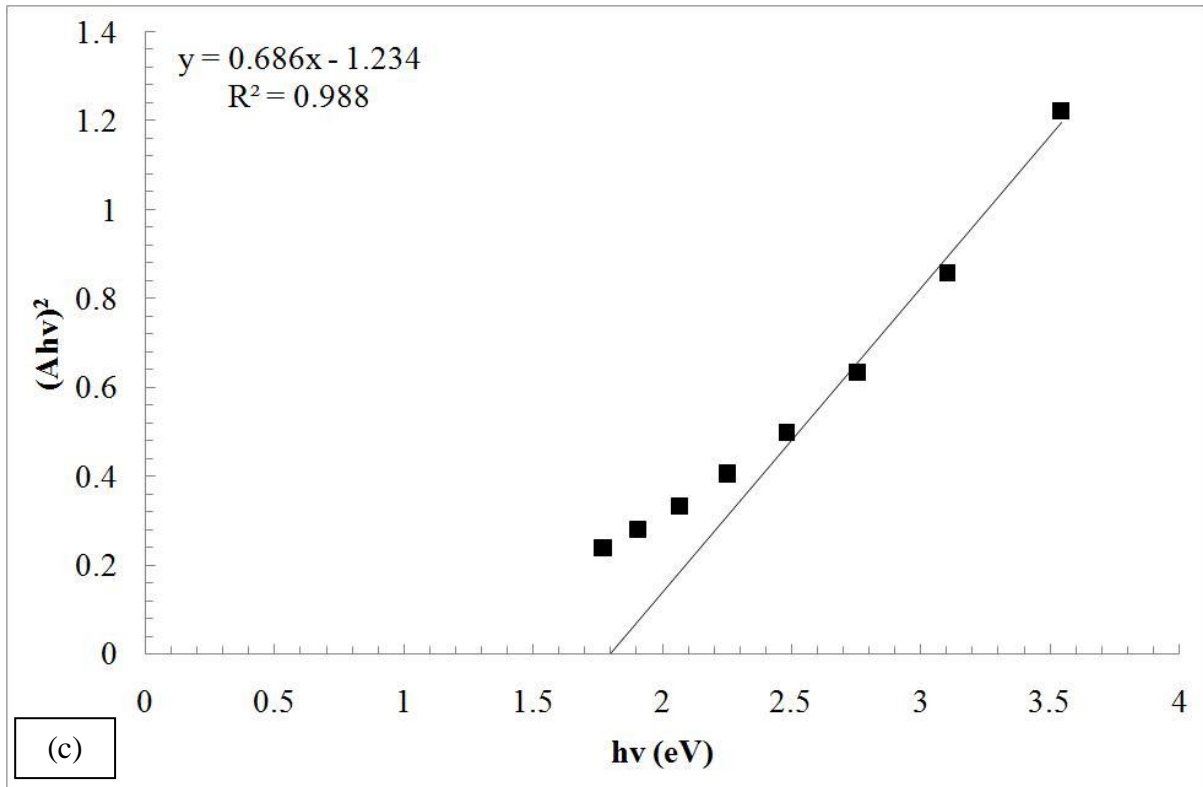


Figure 3: Plots of $(Ahv)^2$ versus hv of NiSe thin films deposited at different bath temperatures (a) 55 °C (b) 65 °C (c) 75°C

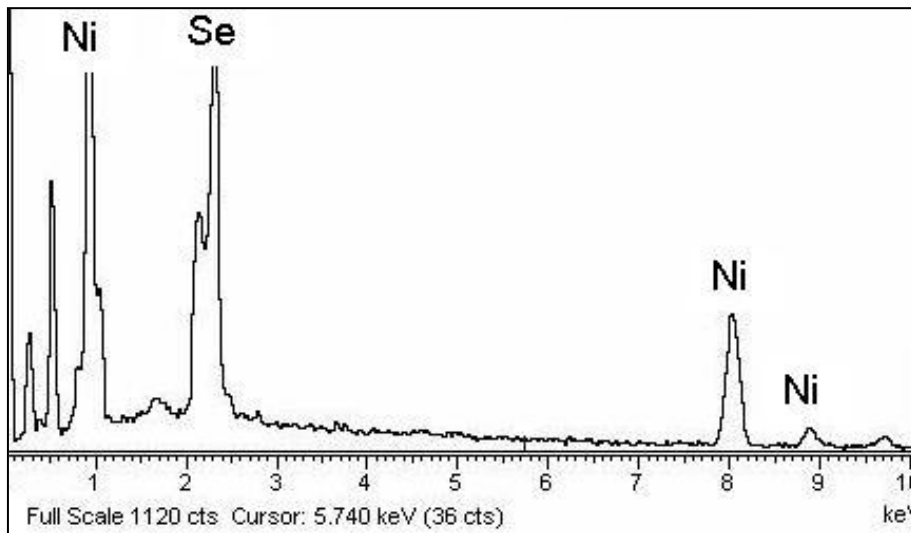


Figure 4: Typical EDAX spectrum of NiSe thin films deposited at 65 °C

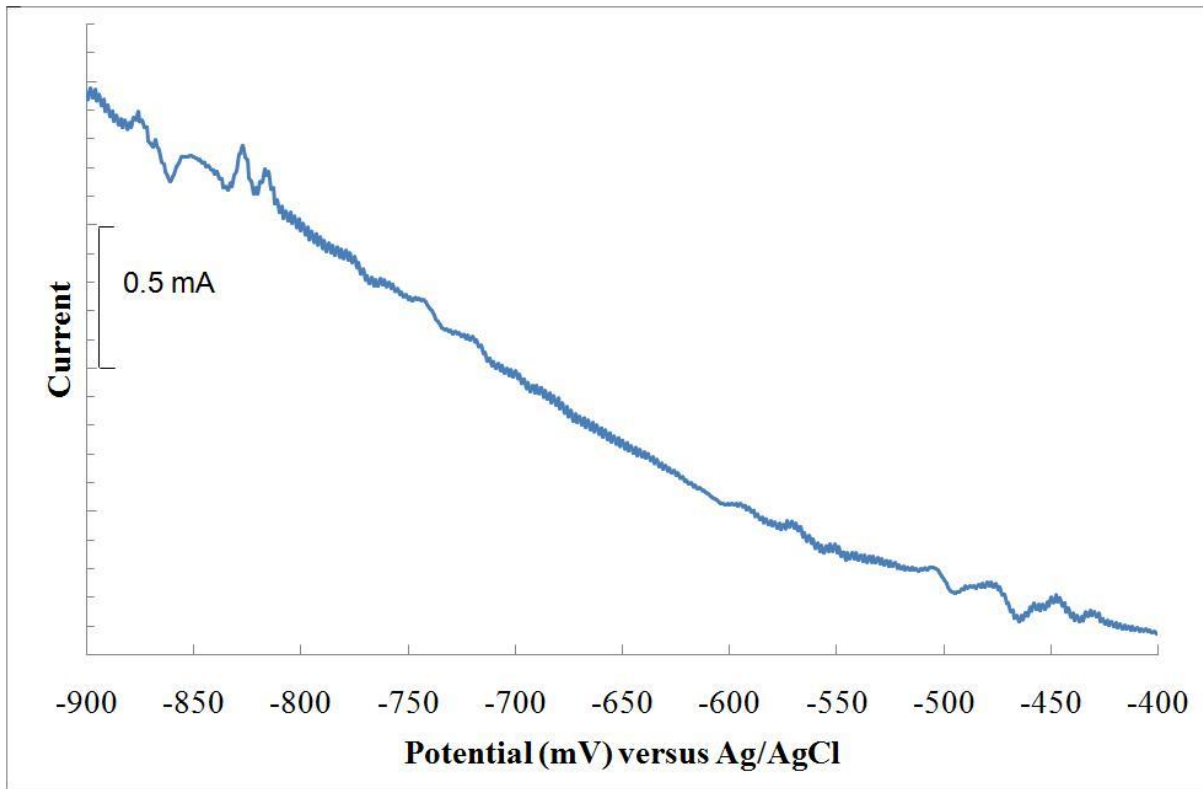


Figure 5: Typical photosensitivity of NiSe thin films deposited at 65 °C