JOURNAL OF MATERIALS SCIENCE **40** (2005) 3803–3807 LETTERS

Properties of CdS:Ni films prepared by chemical bath deposition method

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Cadmium sulphide (CdS) is one of the well known II–VI compounds, which has gained considerable attention as a promising candidate for photodetector application. It has a wide range of applications in the technology of optical detectors, field-effect transistors and optoelectronic devices [1–3]. CdS thin films are also widely used as n-type window layers in thin film solar cells. There are many methods to fabricate CdS thin films, such as vaccum evaporation (VE), hot-wall vacuum evaporation (HWVE), close-spaced vapor transport (CSVT), spray pyrolysis (SP), chemical vapor deposition (CVD), screen printing (ScP), electrodeposition (ED), sputtering (ST) and chemical bath deposition (CBD) [4]. Among them, the chemical bath deposition (CBD) was the most suitable method to produce CdS thin films for n-CdS/p-CdTe solar cells applications because it has 15.8% cell efficiency, is cost-effective and a large-scale method [4, 5]. In the CBD, CdS films were formed by precipitation from solution containing cadmium ions and thiourea molecules in ammonia. In order to improve the efficiency of the CdS films, many attempts have been made to mix or dope other materials into the films. For example, Atay *et al.* [6] prepared CdS:NiS films by spray pyrolysis, as nickel sulphide (NiS) is an interesting compound. It has a good electronic conductivity and an energy band gap of 0.35 eV [7].

In this work, we have synthesized thin films of CdS:NiS by CBD method. Various quantities of Ni were used for mixing. Surface characterization, structure, microstructure and morphology of the films after heat treatment as well as their resistivities have been studied.

The CdS and CdS:Ni films, for Ni mole percentages of 10 to 40, were deposited by the chemical bath deposition method on 2.5×7 cm^2 commercial glass substrates. The starting solutions containing 0.05 M $CdCl_2$ (cadmium chloride), 0.01 $SC(NH_2)_2$ (thiourea), ammonia solution (NH_4OH 25%) were added to maintain the pH value of the solution at 11. The $CdCl_2$, $NiCl_2$ solutions were mixed together at room temperature with continuous stirring. Then the NH_4OH solution was added until a colorless solution was obtained. Then the $SC(NH_2)_2$ solution was added. The mixed solution was maintained at 80 °C. The clean glass substrates were immersed vertically into the bath. The solution was continuously stirred for 30 min for film deposition to keep a homogeneous distribution of chemical components. Finally, after deposition, the glass substrates were removed from the chemical bath and cleaned several times with de-ionized water, then dried in air atmoshere. The experimental setup is shown in Fig. 1.

The structural properties of the films were studied by an X-ray diffractometer with Cu K_α radiation (Jeol model JDX-8030). Microstructure and surface characterization of the films were investigated using scanning electron microscopy (Jeol SEM 6335 F) and atomic force microscopy (Seiko model SPI 3800 N), respectively. The compositions of the films were determined by energy dispersive X-ray spectroscopy (EDS) and the resistivity of films (both dark and light conditions) were determined by the two-probe technique, using a

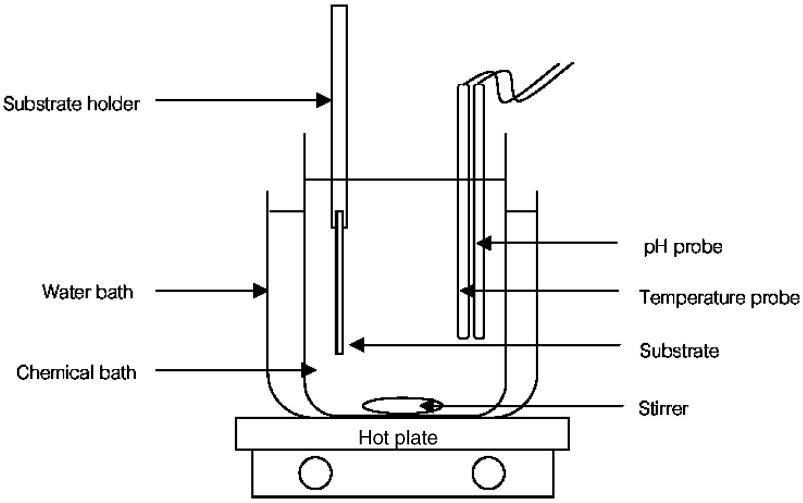

Figure 1 Experimental setup for preparation of chemical bath deposited CdS and CdS:Ni.

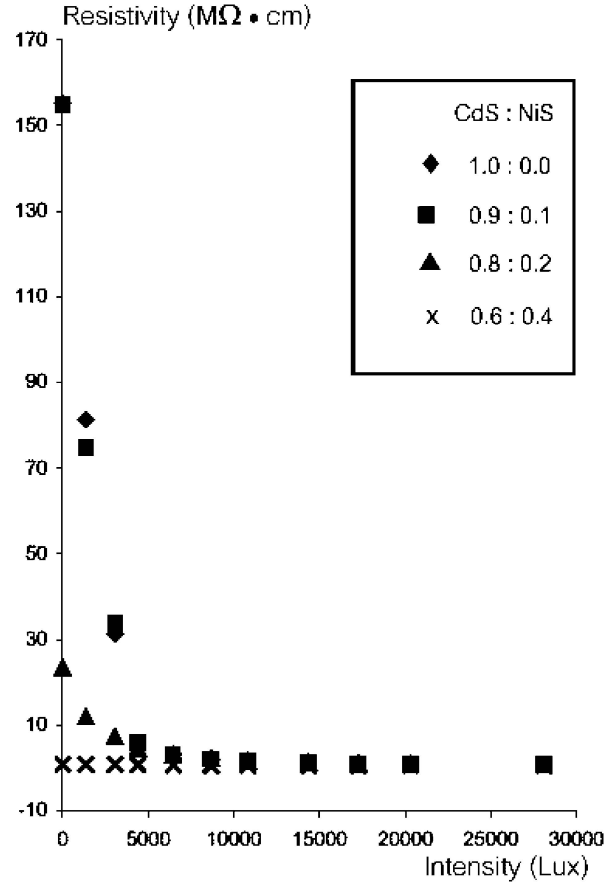

Figure 2 The relationship between the intensity of light source and the resistivity of CdS:Ni films.

Fluke digital multimeter model 111. Various intensities of light were used for the light conditions employing a 40 W Phiplip superlux lamp. Intensities of light were detected using a Foot Candle/Lux meter (EXTECH INSTRUMENTS:model 407000).

The plots of resistivities against the light intensities of CdS and CdS:Ni films at various ratios of Ni are presented in Fig. 2. The plot of CdS:Ni, 7:3 was omitted since it is almost identical to the plot for ratio 6:4. It was seen that the resistivity of the films decreased markedly with increasing light intensity until at about 5000 lux and became constant at 10 830 lux (40% of light source). This may be due to the fact that the light intensity with enough energy activated the electrons in the valence band to jump across the energy gap of the CdS:Ni films. The higher the light intensity the more electrons jump across the gap. Subsequently their mobility increases and hence reduces their resistivity until it reached the saturation point. The dark and light resistivity values of CdS and CdS:Ni films are tabulated in Table I. It can be seen that all the films are photoconductive materials and that the resistivity of the film decreases as the Ni concentration increases for both dark and light conditions. The values obtained in our work are of the same order as that obtained by Atay *et al.* [6], though they employed spray pyrolysis for preparation. Eventually at Ni concentration of 40%, both dark and light resistivities are equal.

Fig. 3 shows the X-ray diffractograms of the CdS and CdS:Ni films. It can be seen that the as-deposited CdS films appear to be in cubic form (Fig. 3(a)), which is in agreement with that obtained by Oliva *et al.* [8] who used the same method for preparation. This is in contrast to the films prepared by Atay *et al.* [6], which were hexagonal phase. This may be due to the occurrence of heating during the spraying process. In this work, the cubic CdS phase transformed into hexagonal one when the as-deposited cubic CdS film was subjected to heat treatment schedule at 300, 400 and 500 °C. From Fig. 3b the XRD patterns of the CdS:Ni films with 10–40. wt.% Ni concentrations, the cubic CdS phase was found in all concentrations together with the unknown phase which related to the peak at about 29° of 2θ. It can be noticed that the CdS patterns of the films remain unchanged until the concentration of Ni increases up to 30 wt.% then the CdS peaks become broader at 40 wt.% Ni. This may be due to the decrease in particle

TABLE I The resistivity values of CdS and CdS:Ni films

Sample	The resistivity in dark (Ω cm) (0 Lux)	The resistivity in light (Ω cm) (28100 Lux)
CdS	1.55×10^8	1.82×10^6
CdS:Ni (at 10%)	1.54×10^8	8.56×10^5
CdS:Ni (at 20%)	2.34×10^7	6.84×10^5
CdS:Ni (at 30%)	7.90×10^5	6.02×10^5
CdS:Ni (at 40%)	0.54×10^3	0.54×10^3

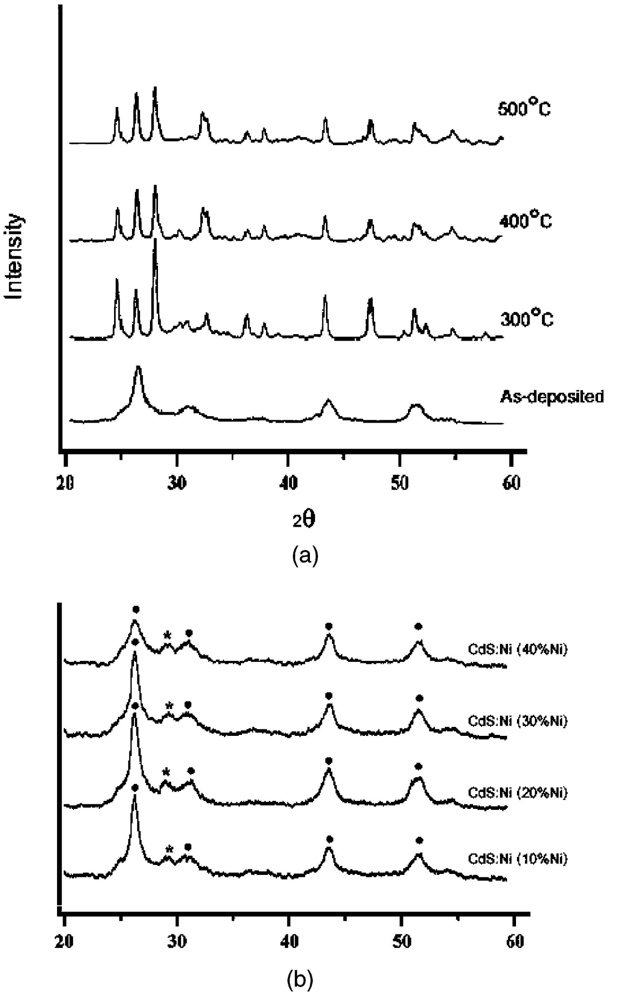

Figure 3 X-ray diffractograms of CdS and CdS:Ni films: (a) Undoped CdS films at, 300, 400 and 500 °C; (b) CdS and CdS:Ni films at 28 °C. (• represents the CdS phase with JCDPS No.75-1546 and ∗ represents the unknown phase).

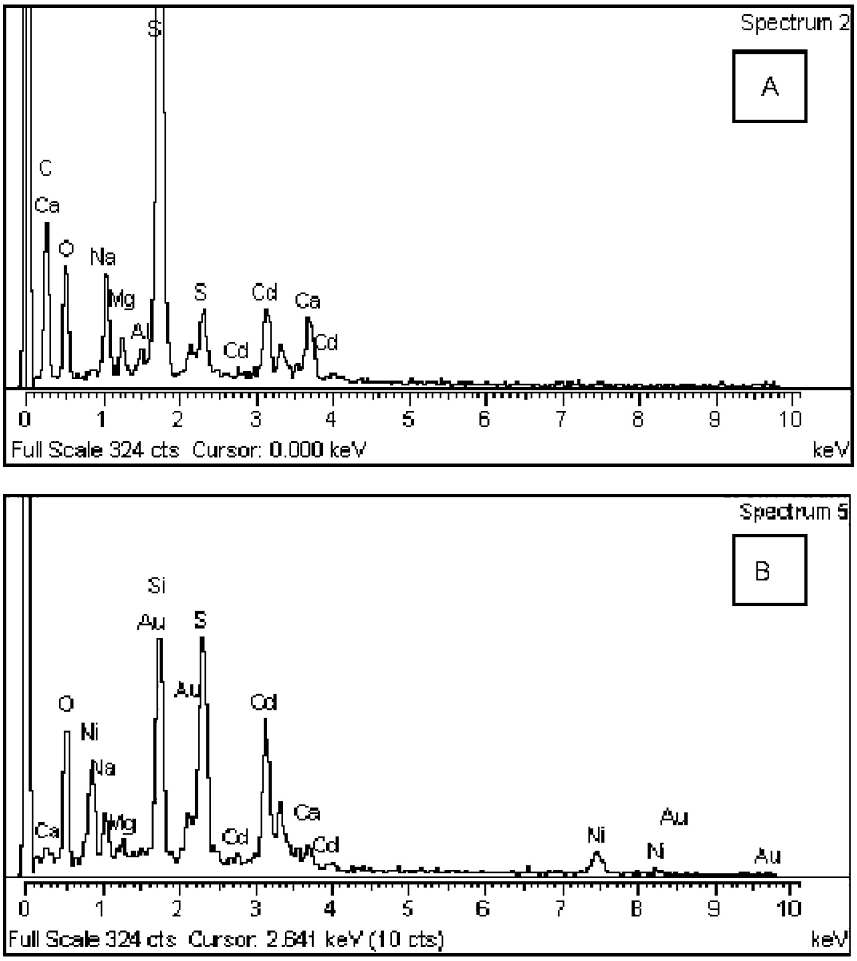

Figure 4 EDS spectra of CdS and CdS:NiS films: (A) CdS film and (B) CdS:Ni film.

size of CdS phase. The same trend was also obtained by Atay *et al.* [6]. Analysis of the XRD peaks was carried out based on the Joint Committee Powder Diffraction Standard (JCPDS) file no. 75-1546 [9] and no. 50-1791 [10], respectively.

From the AFM observation of the CdS films, it was found that the Ni concentration affects the thickness and rounghness of CdS films. These values are tabulated in Table II. The thickness and roughness of the films were found to vary with the Ni concentration. This may be due to the fact that the ionic radius of Ni (0.720 Å) is smaller compared to that of Cd (0.976 Å). Therefore, the roughness increases as the Ni concentration increases. The reason for thickness increasing can be attributed to the strong ionic bonding between Ni and S which may reduce the rate of evaporation of S, which, in turn, increase the thickness of the films with increasing Ni concentration. Our results on thickness agree well with that obtained by Atay *et al.* [6].

TABLE II The surface charaterization of CdS and CdS:Ni films observed from AFM

Sample	Rounghness (nm)	Thickness (nm)
CdS	246	69
CdS:Ni(10%Ni)	389	143
CdS:Ni(20%Ni)	432	144
CdS:Ni(30%Ni)	560	168
CdS:Ni(40%Ni)	647	164

The elements on the films were analyzed by energy dispersive X-ray spectroscopy (EDS). The results are shown in Fig. 4. EDS analysis results show that the films contain O, Na, Mg, Al, Si, S, Ca, Ni, Cd and Au elements. The Cd, Ni and S elements were found as expected. The other elements such as O, Na, Mg, Al, Si and Ca are from the glass substrates, and the Au resulted from the Au coating for SEM observation.

The surface morphology of the films was investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). SEM micrographs of the films are shown in Fig. 5. and AFM micrographs of the films are shown in Fig. 6. It can be seen that the CdS films have spherical particles with different sizes ranging from 200 to 400 nm, covering on the glass substrate. The voids of about 50–60 nm in size were also observed, indicating the low of packing density of the film. In the CdS:Ni films of all concentrations of Ni atom, hard agglomerate of spherical particles appeared.

In conclusion, CdS and CdS:Ni films were prepared by chemical bath deposition technique (CBD). Effects of the Ni concentration on the structural and morphological properties as well as the resistivities for both dark and light conditions were investigated. The as-depositied CdS films were found to be in cubic form which transform to hexagonal after annealing at temperature above 300 °C. Incorporation of Ni concentration causes some damage regarding the crystallinity of CdS films. The hexagonal NiS appeared to mix with the CdS

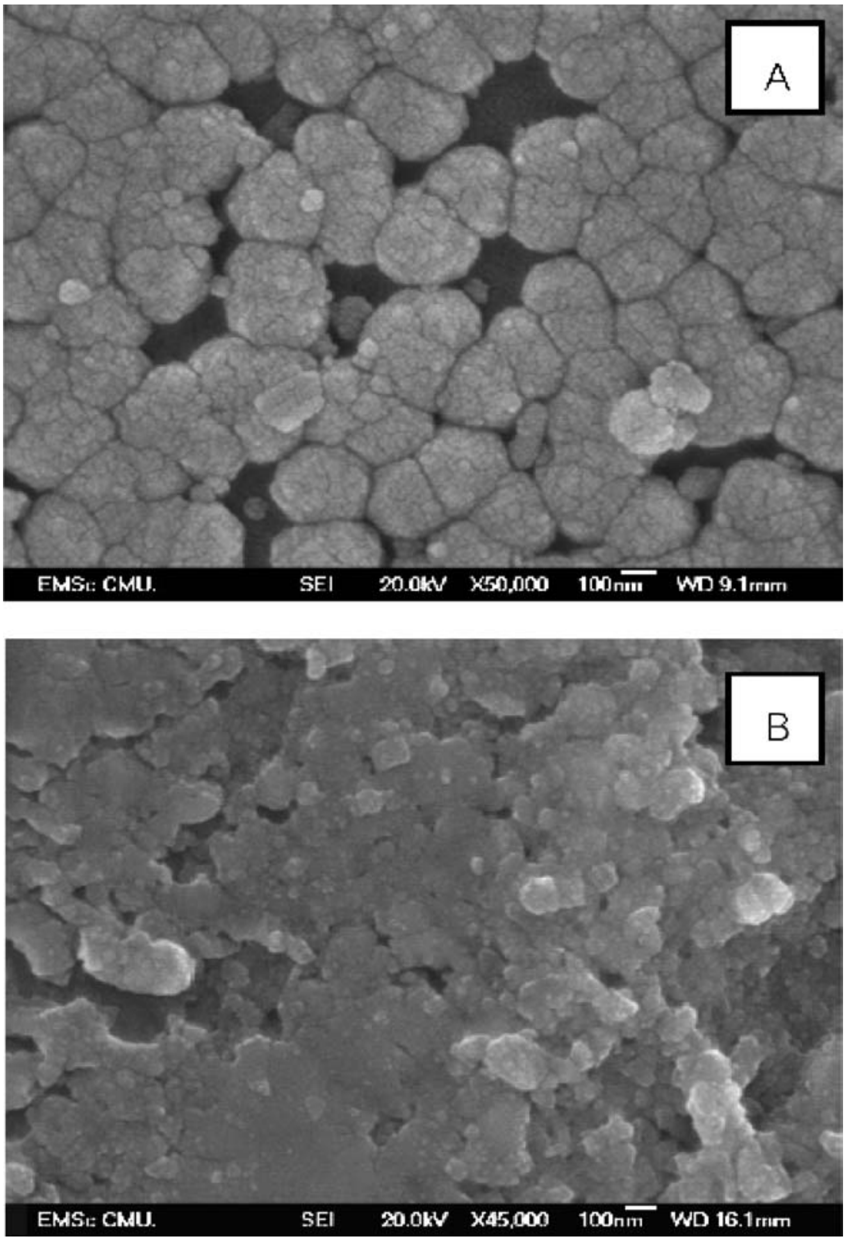

Figure 5 The surface morphologies of CdS and CdS:Ni from SEM (A) CdS, (B) CdS:Ni.

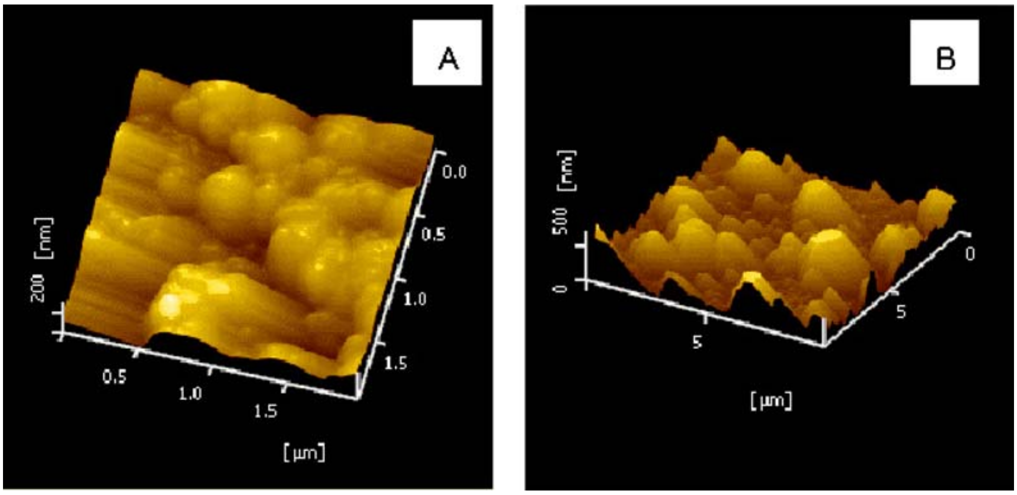

Figure 6 The surface morphologies of CdS and CdS:Ni from AFM (A) CdS, (B) CdS:Ni.

in the CdS:Ni films. Roughness and thickness increased with increasing Ni concentration. Spherical particles of 200–400 nm in diameter were found to pack into thin CdS sheets with high porosity while hard agglomerates of the spherical particles appeared on CdS:Ni films. Resistivities of CdS and CdS:Ni films decreased with increasing light intensity and decreased with Ni concentration.

Acknowledgments

The authors thank the Thailand Research Fund, Graduate School, Chiang Mai University, Faculty of Science Chiang Mai University and Ministry of University Affairs for financial support throughout the project.

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Received 20 April 2004
and accepted 4 January 2005