Journal of Alloys and Compounds 685 (2016) 129–134

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Effect of double substitutions of Cd and Cu on optical band gap and electrical properties of non-colloidal PbS thin films

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ARTICLE INFO

Article history:
Received 17 December 2015
Received in revised form
14 May 2016
Accepted 19 May 2016
Available online 21 May 2016

Keywords:
Chalcogenides
PbS
CdS
Chemical bath deposition
Band gap
Electrical property

ABSTRACT

Controllable band gap has been pursued to absorb a proper range of light by p-type absorber semiconductors for better performance photovoltaic devices. Here we introduce double substitutions with Cd and Cu for non-colloidal p-type PbS thin films to cover a broader range of optical band gap from 1.22 to 1.78 eV. Thin films of $(Pb_{1-x}Cd_x)_{1-y}Cu_yS$ ($x = 0–0.3$ and $y = 0–0.3$) were grown by a single step chemical bath deposition process at a low temperature of 70 °C. The incorporation of Cd resulted in a wider band gap but changed the type of semiconductor into n-type above $x = 0.2$. Only the proper substitutions with both Cd and Cu induced an optimal band gap of 1.63 eV, which means a substantial improvement compared to 1.22 eV for pure PbS thin film, while maintaining p-type conductivity. Interestingly, excessive Cu substitutions beyond $y = 0.2$ inhibited crystallization significantly and generated an undesirably high carrier concentration.

1. Introduction

Lead sulfide (PbS) as one of the rare p-type absorbers has been in great interest for photovoltaic applications because of its high absorption coefficient of ~10^5 cm^{-1}, excellent photosensitivity and high carrier mobility [1–4]. However, the intrinsic band gap of PbS has a small value of ~0.4 eV, which is not suitable as an absorber [5]. It is well known that colloidal PbS quantum dots can be designed to exhibit desirable optical band gaps by controlling their size for better photo-conversion efficiency due to the quantum confinement effect [6]. The tunable optical band gap ranges from ~0.7 eV to 1.3 eV in this quantum approach [2]. On the other hand, there have been also studies on non-colloidal PbS thin films, which are usually processed by chemical bath deposition (CBD), for the purpose of increasing band gap of the films for better photovoltaic properties. Processing parameters, such as bath temperature, different type of chemicals, concentration of precursor, etc., have been studied in the CBD process for optimization of the optical properties [5,7,8]. The origin of the band gap tuning in these non-colloidal cases is believed to come from the size-dependency of crystallites in the films although the reason for the dependency is not clear since the crystallite sizes are beyond the quantum confinement range [8,9].

Recently, several research groups demonstrated the successful chemical modifications for the purpose of tuning the band gap particularly by substituting Pb site in PbS films with metal elements including Sb, Fe, Cd, Cu and Hg [10–14]. Only the incorporations of Fe and Sb were reported to decrease the band gap of thin films while the other elements to increase the band gap substantially [10,11]. Since the reference band gap differs from the each research group, it is difficult to compare directly all the band gap data in a consistent way. A very broad range of band gap from 0.5 to 1.61 eV has been reported in the case of PbS-based thin films depending on the film quality and processing conditions [7–9]. There are some examples of higher conversion efficiency (>3.0%) for the PbS solar cells when the band gap is close ideally to 1.6 eV [9,15]. Recently, double absorber approach of combining small and large band gaps in non-colloidal PbS thin films was also reported to have an increased conversion efficiency of ~4.03% [16].

Here, we demonstrate a successful example of manipulating the band gap of non-colloidal PbS thin films by co-incorporating Cd and Cu into the chalcogenide structure to achieve the most suitable range (~1.6 eV) of band gap for photovoltaic devices. There is no report so far on effects of such double substitutions in PbS thin films, which deals with a larger band gap while keeping p-type

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http://dx.doi.org/10.1016/j.jallcom.2016.05.203
0925-8388/

conductivity. The co-existence of proper Cd and Cu contents is utilized to control band gap effectively in the state of p-type conductivity. CdS is known to have a band gap of ~2.4 eV with n-type conductivity while CuS has a band gap of ~2.5 eV with p-type conductivity [17]. The either choice of Cd or Cu may induce the increased band gap but the maintenance of p-type conductivity is assumed to be achievable with the existence of Cu. The sole use of Cu may be not desirable to avoid too high carrier concentration which causes the degeneracy state. There have been several studies on Cd-substituted PbS thin films [12,18]. Depending on the content of Cd, different crystal structure and optical properties were reported since CdS has a hexagonal wurtzite structure compared to the cubic structure of PbS [12]. Cu is considered as a promising doping element because d-orbitals of Cu provide deep acceptor states in metal sulfides [19]. Considering the electronic configuration of Cu $3d^{10}4s^1$ and Pb $5d^{10}6s^26p^2$, Cu has less outer electrons than Pb, probably resulting in a stronger p-type conductivity if a proper content of Cu is used.

In this work, $(Pb_{1-x}Cd_x)_{1-y}Cu_yS$ films are prepared by a single step chemical bath deposition process. A systematic investigation on structure, optical and electrical properties of the resultant films is carried out to conclude the effects of the double substitutions. Compositional limitation in enhancing band gap while maintaining p-type conductivity is proposed with the changed degree of crystallinity that depends on the relative content of Cd and Cu.

2. Experiments

$(Pb_{1-x}Cd_x)_{1-y}Cu_yS$ (x = 0, 0.1, 0.2 and 0.3; y = 0, 0.1, 0.2 and 0.3) thin films were deposited onto a soda lime silicate (SLS) glass substrate by a single step chemical bath deposition (CBD) process at a fixed temperature of 70 °C for 30 min. First, a Pb-precursor aqueous solution containing 0.05 M lead nitrate ($Pb(NO_3)_2$, Kanto Chemical, 99.3%), 0.08 M triethanolamine ($C_6H_{15}NO_3$, Aldrich, 98%), and 0.2 M sodium hydroxide (NaOH, Duksan, 93%) was prepared. An aqueous Cd-precursor solution containing 0.05 M cadmium nitrate ($Cd(NO_3)_2\cdot 4H_2O$, Kanto Chemical, 98%), 0.15 M sodium citrate ($Na_3C_6H_5O_7$, Duksan, 99%), and 0.3 M ammonia (NH_4OH, Duksan, 30%) was dissolved into the Pb-precursor solution. 0.06 M thiourea was injected into the mixed solution at 70 °C to initiate the chemical reaction for $(Pb_{1-x}Cd_x)S$. An ultrasonically cleaned glass substrate was vertically immersed into the chemical bath solution for 30 min for the film deposition.

To incorporate copper into the lead cadmium sulfides, Cu-precursor solution containing 0.05 M copper nitrate ($Cu(NO_3)_2\cdot 3H_2O$, Aldrich, 98%), 0.08M triethanolamine and 0.2 M sodium hydroxide were added into the Pb/Cd precursor solution to prepare a complete Pb/Cd/Cu precursor solution. Only the Pb/Cd precursor solution corresponding to $(Pb_{0.8}Cd_{0.2})S$ composition was used for the study of Cu substitutions. After deposition of the films on a vertically inserted glass substrate at the identical temperature of 70 °C, all the specimens were rinsed with distilled water and dried with N_2 gas.

Surface microstructures were observed by field emission scanning electron microscopy (FESEM: JSM-7001F, JEOL). The existence of Cd or Cd/Cu in the films was confirmed by observing corresponding elemental peaks using the SEM-EDS analysis (not shown here). Phase evolution of the films was analyzed using an X-ray diffractometer (XRD: Max-2500, Rigaku) in Cu-kα radiation with λ = 1.5405 Å. Optical transmission and reflection of the films were analyzed at room temperature in the spectral range of 300–1800 nm using a UV–visible spectrophotometer (JASCOV530, Jasco). Electrical properties including dark resistivity, Hall mobility and carrier concentration were measured at room temperature using a standard Hall measurement system (Model HMS-3000, Ecopia Co.) in the van der Pauw configuration. The valence states of selected elements were characterized by X-ray photoelectron spectroscopy (XPS: K-alpha, Thermo VG) using an Al kα radiation source (1486.6 eV).

3. Results and discussion

3.1. Characteristics of $Pb_{1-x}Cd_xS$ thin films

Fig. 1 shows XRD patterns of the $Pb_{1-x}Cd_xS$ thin films deposited at 70 °C with different Cd contents. The pattern of pure PbS thin film was included. All the patterns correspond to chalcogenide phase having fcc cubic structure, which corresponds to the JCPDS 05-0592. There is no secondary phase even with the x = 0.3 film. Distinguishable differences with increasing Cd content are the broadening and shift of the peaks as represented in the (200) peak at 2θ ≈ 30° in the inset of Fig. 1. The average crystallite size was estimated using the known Scherrer equation from the full width half maximum (FWHM) of the main (111) and (200) peaks. As a result, average crystallite size was calculated to be 42.2, 37.6, 33.7 and 30.1 nm for the x = 0, 0.1, 0.2 and 0.3 films, respectively. The substitution of Cd into the Pb site is expected to shift the peak position to higher 2θ values since the ionic radius of Cd^{2+} (0.97 Å) is smaller than that of Pb^{2+} (1.19 Å) [20]. In addition, lattice parameter of the $Pb_{1-x}Cd_xS$ films decreased gradually from 5.986 Å to 5.964 Å with increasing x from 0 to 0.3, respectively, due to the difference in ionic size.

Fig. 2 shows the surface microstructures of Cd-substituted PbS thin films grown by CBD at 70 °C. For the comparison, surface microstructures of pure CdS and PbS films are also included. The substitution of Cd induced the morphology changes on surface depending on the content of Cd. Large grain size tended to be diminished with increasing Cd content by accompanying less faceted grains. It is evident that the grain morphology follows the surface characteristics of pure CdS films as the content of Cd increases. The tendency of decreasing grain size matches well with the result of XRD where the degree of crystallinity was reduced with increasing the content of Cd. Some clusters on film surface in x = 0.3 sample were observed. Generally, smooth surface is desired for better photovoltaic performance. Thus the presence of the macro-particles on the film surface may lead potential degradation of the device performance by inducing poor interfacial junction and

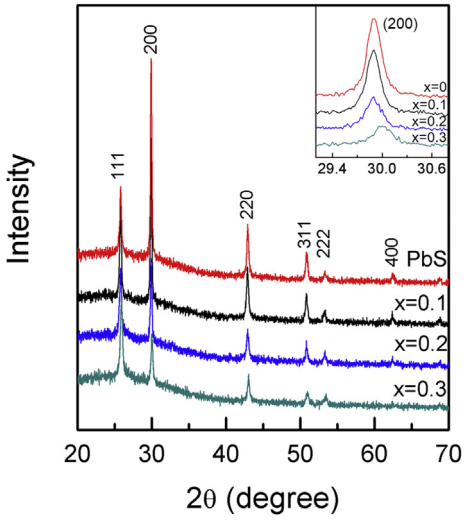

Fig. 1. XRD patterns of $Pb_{1-x}Cd_xS$ thin films with different Cd content. The (200) peak in the 2θ range of 29.2–30.8° is highlighted as an enclosed plot.