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Optical and structural properties of zinc iodine thin films

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ABSTRACT

Zinc iodide (ZnI_2) crystalline thin film is produced with chemical bath deposition on substrates (commercial glass). The pH of chemical bath is scanned with controlled potassium hydroxide. Some properties of films changed with pH and changes of pH were analyzed. The pH values are scanned at 6.01–6.29. Transmittance, absorption, optical band gap and refractive index are investigated by UV/Vis. spectrum. The hexagonal and tetragonal form in structural properties in XRD at pH: 6.01 were seen. The pH of bath was up to 6.01, $KZnI_3{\cdot}2H_2O$ (orthorhombic), $KZnI_3{\cdot}(H_2O)_2$ (orthorhombic), ZnI_2 (tetragonal) and ZnI_2 (hexagonal) forms were observed in XRD patterns. The structural and optical properties of ZnI_2 thin films analyzed at different pH. SEM analysis studied for surface analysis in films. The SEM analyses were agreed with XRD patterns. The optical band gap increased with pH between 3.4 and 3.6 eV. The film thickness changed with pH at 108–345 nm. Also refractive index and transmission generally increased with pH.

1. Introduction

Many researchers produced metal halides and metal dihalides thin and thick films (AgI, Bi_2I_3, PbI_2, CdI_2). These halides are very useful in industry. For instance, AgI is used with photosensitivity and super ionic conductivity [1–5]; PbI_2: electroluminescence [6], photoluminescence [7]. They will continue to synthesize and produce their thin film in future because new technologies will appear in industry and they will contribute the science and technology. Also, zinc iodide (ZnI_2) and its' compounds may contribute to the technology like the other metal halides.

Zinc iodide solid was yellow but the anhydrous form was white. ZnI_2 was prepared by the direct reaction of zinc and iodine in refluxing in ether [8]. Also zinc salt with iodine in alcohol was synthesized. Different form of ZnI_2, it was observed in aqueous solution. In aqueous solution the following have been detected, octahedral $Zn(H_2O)_6^{2+}$, $ZnI(H_2O)_5^{+}$ and tetrahedral $ZnI_2(H_2O)_2$, $ZnI_3(H_2O)^{-}$, ZnI_4^{2-} [9]. So, the bath gradients and control were very important when ZnI_2 was produced with chemical bath deposition.

The aim of this paper is to produce compounds of zinc iodine thin film with chemical bath deposition and investigate its structural and optical properties. The crystal structure and optical properties of ZnI_2 could be controlled with pH of chemical bath. Nobody has studied ZnI_2 thin film with chemical bath deposition for the solar cell substrates, so we did not know anything about how the effect of pH of the bath changed the ZnI_2 film structure and optical properties. Producing ZnI_2 thin film was very difficult with chemical bath deposition. Zinc iodine compounds can be produced in aqueous solutions.

2. Experiment

The components of bath were 1% (w/v) potassium hydroxide, 0.005 M zinc sulfate and 0.010 M potassium iodide. Firstly, 10 ml 0.005 M zinc sulfate and 20 ml 0.005 M potassium iodide were added in glass beaker which was filled with 20 ml deionized water. Potassium hydroxide was used to adjust the pH of bath. In order to adjust the pH value of the solution to 6.01, 6.10, 6.18, 6.23 and 6.29, 1000 µl, 1100 µl, 1200 µl, 1300 µl and 1400 µl of potassium hydroxide (KOH), respectively, were added to the solutions. The amorphous glasses (76×26 cm) used to as substrate material and the films were coated on the amorphous glasses. The pH values of the chemical baths were determined by using a pH meter (Lenko mark 6230 N).

The crystalline structure of the ZnI_2 was confirmed by X-ray diffraction (XRD) with a Cu Kα_1 radiation source (Rikagu RadB model, $\lambda = 1.5406$ Å) over the range $10° < 2\theta < 90°$ at a speed of 3°/min with a step size of 0.02°. The surface properties of all films were investigated by using an EVO40-LEO computer controlled digital scanning electron microscope (SEM: Carl Zeiss AG, EVO40-LEO). The thicknesses of the films were preferred by atomic force microscopy (AFM). The optical measurements were determined by spectrometer (Hach Lange DR 5000 Spectrophotometer) at room temperature by placing an uncoated identical commercial glass substrate in the reference beam. The optical spectrum of thin

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films was recorded in the wavelength at range of 300–1100 nm. The film thicknesses of all films were measured using a Veeco multimod 8 atomic force microscope (AFM).

3. Results and discussion

Tables 1 and 2 and Fig. 1 show XRD values and XRD patterns of ZnI_2 thin films. The XRD patterns had polycrystalline structure. The (*a*)–(*e*) parameters, displayed at Fig. 1 were respectively as following: *a*: pH 6.01, *b*: pH 6.10, *c*: pH 6.18, *d*: pH 6.23, *e*: pH 6.29. The strongest peaks were shown in Table 1 and they were in the following directions: 25.018° (111) at pH: 6.01; 15.073° (003) at pH: 6.10; 10.061° (002) at pH: 6.18; 15.057° (200) at pH: 6.23; 15.033° (003) at pH: 6.29. Concentration of KOH affected the structure of films. $KZnI_3{\cdot}2H_2O$ (orthorhombic, *a* = 9.95, *b* = 13.72, *c* = 7.07) and $KZnI_3(H_2O)_2$ (orthorhombic, *a* = 9.95, *b* = 13.72, *c* = 7.07) structures begun to be dominant after the pH: 6.01. Before the pH: 6.01, the structure of films were ZnI_2 (body-centered tetragonal, *a* = *b* = 12.28, *c* = 23.58) and ZnI_2 (hexagonal, *a* = *b* = 4.25, *c* = 6.54) polycrystalline. XRD patterns of Fig. 1(c)–(e) clearly show the slipping of peaks.

$$Zn^{+2}_{aq} + 2I^{-}_{aq} \rightarrow ZnI_{2(s)} \tag{1}$$

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2 + \frac{l^2}{c^2}} \quad \text{(Tetragonal Structure)} \tag{2}$$

$$d^2 = \frac{1}{\frac{4(h^2+hk+l^2)}{3a^2} + \frac{l^2}{c^2}} \quad \text{(Hexagonal Structure)} \tag{3}$$

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad \text{(Orthorhombic)} \tag{4}$$

This result shows that equal (1) reaction doesn not only occur in bath. If KOH and KI were not used in this bath, the XRD patterns of $KZnI_3{\cdot}2H_2O$ (orthorhombic) and $KZnI_3(H_2O)_2$ (orthorhombic) structures would not be seen. The excess of potassium concentration caused these structures after the 1200 μl KOH added in bath. The change of structures of films can affect other properties. The structural properties were calculated with the Scherrer formula which were grain size (*D*), dislocation density (δ) , the number of crystallites per unit area (*N*), lattice parameters along the planes were calculated by using the formulas given below (according to Eqs. (5)–(7) [10–12]:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{5}$$

$$\delta = \frac{1}{D^2} \tag{6}$$

$$N = \frac{t}{D^3} \tag{7}$$

where t is the film thickness, λ is wavelength of X-ray used (1.5406 Å), β is full width at half maximum (FWHM) (preferred by EVA program) of the peak, θ is Bragg angle, δ is dislocation density which is defined as the length of dislocation lines per unit volume of the crystal. Higher δ values indicate lower crystallinity levels for the films and indicate the amount defects in the structure. The highest δ value was observed at pH: 6.29. Also the lowest average grain size (*D*) was calculated at pH: 6.29. The number of crystallites per unit area (*N*) changed with pH and the highest; the lowest values were observed at pH: 6.29 and 6.01, respectively. The changing of dislocation density, the number of crystallites per unit area and the grain size are presented in Fig. 2. The changing of dislocation density, the number of crystallites per unit area and the grain size

Table 1
XRD values of ZnI_2 thin films at different pH.

pH	(*hkl*)	2θ (observed)	2θ (ASTM values)	I/I_o	ASTM File	Compound/structure
6.01	100	15.738	15.015	15.7	070–1224	ZnI_2 (tetragonal)
	111	25.018	25.453	100.0	070–1224	ZnI_2 (tetragonal)
	102	27.583	27.475	19.2	070–1224	ZnI_2 (tetragonal)
	310	51.219	51.229	17.3	077–1342	ZnI_2 (hexagonal)
6.10	101	12.020	12.648	63.4	070–1224	ZnI_2 (tetragonal)
	003	15.073	15.015	100.0	070–1224	ZnI_2 (tetragonal)
	200	21.841	21.820	33.5	025–1068	$KZnI_3{\cdot}2H_2O$ (orthorhombic)
	005	25.237	25.453	71.4	070–1224	ZnI_2 (tetragonal)
6.18	002	10.061	10.982	100.0	025–1068	$KZnI_3{\cdot}2H_2O$ (orthorhombic)
	003	15.073	15.015	64.0	070–1224	ZnI_2 (tetragonal)
	100	25.194	25.453	29.9	070–1224	ZnI_2 (tetragonal)
6.23	200	15.057	15.015	100.0	070–1224	ZnI_2 (tetragonal)
	202	21.793	21.820	17.5	025–1068	$KZnI_3{\cdot}2H_2O$ (orthorhombic)
	311	25.180	25.165	53.5	073–0346	$KZnI_3{\cdot}(H_2O)_2$ (orthorhombic)
	415	51.561	51.229	11.7	077–1342	ZnI_2 (hexagonal)
6.29	002	10.060	10.982	60.3	025–1068	$KZnI_3{\cdot}2H_2O$ (orthorhombic)
	003	15.033	15.015	100.0	070–1224	ZnI_2 (tetragonal)
	100	25.150	25.453	50.3	070–1224	ZnI_2 (tetragonal)

Table 2
Lattice Parameters of ZnI_2 thin films at different pH (calculated by XRD-EVA program).

pH	2θ (Observed)	*d* (Å)	(*abc*)
6.01	25.018	3.553	*a* = *b* = 5.63, *c* = 7.88 (for tetragonal)
6.10	15.073	5.874	*a* = *b* = 8.12, *c* = 17.62 (for tetragonal)
6.18	10.061	5.877	*a* = *b* = 8.14, *c* = 21.85 (for tetragonal)
6.23	15.057	5.874	*a* = *b* = 3.53, *c* = 17.61 (for orthorhombic)
6.29	15.033	5.890	*a* = *b* = 3.53, *c* = 17.61 (for tetragonal)