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Kesterite Cu_2ZnSnS_4 thin films by drop-on-demand inkjet printing from molecular ink

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ABSTRACT

Inkjet printing of kesterite Cu_2ZnSnS_4 (CZTS) thin films on glass from molecular ink is described. CZTS ink consists of copper acetate, zinc acetate, tin chloride and thiourea dissolved in a mixture of ethylene glycol and isopropyl alcohol. The printed precursor films are vacuum dried and thermolysed at 200 °C in air to obtain CZTS films. X-ray diffraction and Raman spectroscopy of films confirm the formation of kesterite CZTS without any secondary phases. The band gap of the films is 1.48 eV as deduced from transmission spectrum using Tauc plot. The films are p-type with hole density and mobility of 2.65×10^{19} cm^{-3} and 0.3 $cm^2V^{-1}s^{-1}$, respectively. Measurement of electrical conductivity of films in the temperature range from 77 to 300 K show that dominant mechanisms of conduction are Mott-Variable Range Hopping, Nearest Neighbour Hopping and Thermally Activated Band Conduction in the temperature ranges of 77–155 K, 180–240 K and 250–300 K, respectively.

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1. Introduction

Inkjet printing (IJP) is a direct-write, non-contact, non-vacuum and atmospheric method for deposition of solid thin films [1]. In this technique, picolitre drops of a liquid ink are impelled onto a substrate to precisely deposit films in pre-defined pattern. The ejected drops fall until they come in contact with the substrate. The drops spread because of momentum and surface tension and eventually coalesce on the substrate to form a film. Printed solid film is then formed by solvent evaporation. IJP has high material utilization factor. Printing of films can be sequential or layer-by-layer and can form any pattern without masks. Printed films are likely to be contamination free because of non-contact deposition. Further, IJP is amenable to large scale roll-to-roll deposition of films. Printing of films on a substrate depends on inkjet ink, jetting voltage and dots per inch (DPI). IJP has been utilized for fabrication of variety of devices and films, such as, flexible electronics [2–4], organic electronics [2,3,5], metal electrical contacts [3,4,6], photo-detectors [5,7,8], sensors [9–11], optoelectronic devices [7], thermoelectric devices [12], supercapacitors [13], micro-batteries [14], smart windows [15], ceramics [16], organic solar cells [17–19] and perovskite solar cells [18].

The special attributes of IJP have not been fully exploited for inorganic solar cells and only few investigations [20–26] have been reported so far. There are some recent studies on inkjet-printed $Cu_2ZnSn(S,Se)_4$ (CZTSSe) solar cells [20,25,26], Cu_2ZnSnS_4 (CZTS) films [21] In_2S_3 non-toxic buffer layers [22], $Cu(In,Ga)(S,Se)_2$ (CIGSSe) solar cells [23] and NiO dye-sensitized solar cells [24]. Lin et al. [20] were first to demonstrate inkjet-printing of solar cells. Solar cells with Mo/CZTSSe/CdS/i-ZnO/ZnO:Al/Ni:Al grids were fabricated based on the inkjet-printed CZTSSe absorbers. CZTS precursor layers were IJP on Mo/glass substrates from CZTS ink. Molecular solution ink was prepared by dissolving copper (II) chloride, zinc acetate dihydrate, tin (II) chloride dihydrate, thiourea and sodium fluoride in dimethyl sulfoxide (DMSO) with the help of overnight stirring. The printed precursor layers were preheated at 300 °C in air for 2 min to remove solvent. Later, the films were finally annealed in Se vapour at 560 °C for 20 min to obtain large-grained CZTSSe films. CZTSSe solar cell with an active area of 0.5 cm^2 yielded power conversion efficiency of 6.4% with an open circuit voltage (V_{OC}) of 431 mV, short current density (J_{SC}) of 34.6 mA/cm^2 and fill factor (FF) of 42.8%, respectively.

Colina et al. [25] optimized the inkjet-printed precursor films for CZTSSe solar cells. Light-yellow coloured CZTS molecular ink was made by stirring overnight DMSO containing copper (II) acetate monohydrate, tin (II) chloride dehydrate and anhydrous zinc (II)

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chloride. The precursor films were printed layer-by-layer on Mo-coated glass and dried at different temperatures (180°, 220° and 280° C) in air. The dried precursor films were then converted to CZTSSe absorbers by annealing in Se vapour at 550 °C for 45 min. Higher drying temperatures of precursor helped in grain growth and recrystallization of CZTSSe films. Solar cells with architecture of Mo/$MoSe_2$/CZTSSe/CdS/i-ZnO/ITO were fabricated and performances were optimized with respect to drying temperature and number of printed precursor layers. The best solar cell was obtained for drying temperature of 280 °C and 5 layer printing (1.9 μm). The solar cell (without any antireflection coating) showed photo-conversion efficiency was 6.55% with V_{OC}, J_{SC} and FF as 366 mV, 33 mA/cm^2 and 54%, respectively.

In continuation of their earlier work [20] on IJP CZTSSe solar cells, Lin et al. [26] also studied the effect of sodium (Na) in inkjet-printed CZTSSe absorber on solar cell performance. Sodium is known to have a positive effect on the morphology as well as electronic properties of CZTSSe absorbers. Incorporation of sodium in CZTSSe results in improved grain growth, increase of charge carrier concentration and/or mobility, passivation of deep defects, increase of open-circuit voltage (V_{OC}) and fill factor and conversion efficiency. For Na doping in printed CZTSSe films, different concentrations of NaF were added in the CZTS molecular ink. It was found that 0.144 M NaF produced the best CZTSSe solar cell with conversion efficiency of 6.4%.

Both Lin et al. [20] and Colina et al. [26] have printed CZTS films from molecular solution inks. In a different approach, Martini et al. [25] have inkjet-printed CZTS films from nanoparticle ink. CZTS nanoparticles of 3–5 nm sizes were continuously synthesized from an aqueous solution of tin (IV) chloride, copper acetate monohydrate, zinc acetate dihydrate, 3-mercapto acetic acid and sodium sulphide in a microwave reactor. Nanoparticles were washed, centrifuged and then redispersed in methyl-ethyl-ketone with 10% (v/v) of 1-dodecan-thiol to form inkjet ink. The ink was then used for printing of CZTS films with an inkjet material printer. The as-printed films were dried for 1 h under vacuum at 190 °C and then at 300 °C. The ultimate CZTS films with large grains were obtained by annealing in sulphur vapours at 540 °C for 3 h.

IJP was utilized for developing In_2S_3 films [22] as non-toxic Cd-free buffer layer for CIGSSe thin film solar cells. Precursor ink consisted of indium nitrate and thiourea dissolved in ethanol with 10% (v/v) ethylene glycol. The performances of CIGSSe solar cells with conventional CdS and In_2S_3 buffer layers were at par with efficiencies above 12%. Lin et al. [23] reported inkjet-printed CIGSSe solar cells with 12.3% conversion efficiency. Precursor Cu–In–Ga molecular ink was prepared from by mixing the metal nitrate precursors in a solvent mixture of 2-propanol and ethylene glycol. The printed precursor layers on Mo-coated glass were dried at 250 °C for 2 min in air. The dry precursor films were then selenized and sulfurized at 400° to 580 °C to obtain the desired CIGSSe films. Inkjet-printed solar cell of 0.5 cm^2 area achieved an efficiency of 11.3% with V_{OC}, J_{SC} and FF of 541 mV, 31.1 mA/cm^2 and 67.0%, respectively. Preliminary assessment on utilization of inkjet-printed p-type NiO films for dye-sensitized solar cells was carried out by Brisse et al. [24] and concluded that IJP is promising.

In this paper we report inkjet printing of CZTS films on glass from a simple molecular solution ink. The ink consists of a solution of (Cu^+-Zn^{+2}-Sn^{+2})-thiourea (CZTTU) complex dissolved in a blend of ethylene glycol and isopropanol which can be easily prepared in 10 min. The printed precursor films were first dried at 70 °C in vacuum followed by heating in air at 200 °C. Films thus obtained are kesterite CZTS as confirmed by X-ray diffraction and Raman spectroscopy. Electrical properties of such films have been also investigated in the wide temperature range of 77–300 K.

2. Experimental

2.1. Formulation of ink

Molecular solution ink basically consists of a precursor dissolved in an appropriate solvent. Chaudhuri and Tiwari [27] showed that precursor of (Cu^+-Zn^{+2}-Sn^{+2})-thiourea (CZTTU) complex yields kesterite CZTS on heating at 200 °C in air. Precursor solution ink was prepared by dissolving copper (II) acetate monohydrate (0.1 M), zinc acetate dihydrate (0.05 M), tin (II) chloride (0.05 M) and thiourea (TU, 0.5 M) in methanol. CZTS films were deposited on glass by dip-coating and subsequently heating the precursor films at 200 °C in air. Later, Ghediya et al. [28] also reported doctor-blade coating of CZTS films from a solution of CZTTU complex in ethylene glycol (EG). Hence, CZTTU complex was chosen as the precursor for CZTS films.

Next step was to select appropriate solvent suitable for inkjet printing. The solvent had to satisfy the following criteria: (i) It should dissolve readily all the precursor chemicals mentioned above, (ii) Viscosity should be between 10 and 12 cPs, (iii) Surface tension should be between 28 and 33 dyn/cm and (iv) Boiling point should be as low as possible. As mentioned above, the precursor chemicals readily dissolved in both methanol [27] and EG Ref. [28]. Hence, a mixture of EG and isopropanol (IP) was used as the solvent. EG-IP mixtures with different proportions were prepared and viscosity and surface tension were measured to tune the fluid properties to the desired values. It was found that a blend of 40% by volume of EG with 60% by volume of IP has viscosity and surface tension of 10 cPs and 35 dyn/cm, respectively which was close to the targeted values. Thus, for preparing inkjet printing ink, solvent with 40% EG and 60% IP was used. Inkjet ink was prepared by dissolving copper (II) acetate monohydrate (0.2 M), zinc acetate dihydrate (0.1 M), tin (II) chloride (0.1 M) and thiourea (0.8 M) in EG-IP at room temperature (~300 K). At first, 50 mL of EG-IP was taken in a beaker and stirred continuously by a magnetic stirrer. Copper (II) acetate powder was slowly added to EG. A dark blue suspension was formed which turns into dark blue clear solution on adding a few drops of concentrated hydrochloric acid. Then zinc acetate powder was slowly put into the solution which gradually changes into light green colour. Further addition of tin (II) chloride turns the solution into light yellow. Finally, thiourea (TU) powder was slowly introduced into the solution which first becomes curdy and then turns colourless as shown in Fig. 1. TU reduces Cu(II) to Cu(I) under acidic condition to form colourless $[Cu(TU)3]^+$ complex [29]. TU also forms complexes with Zn^{++} and Sn^{++} as $[Zn(TU)_2]_{++}$ and $[Sn(TU)]^{++}$, respectively. Finally, a colourless complex $[CuZnSn(TU)_n]^{m+}$ is formed in the EG-IP solvent which is the desired CZTS molecular solution ink. Total time taken for preparing CZTS ink is about 10 min. The ink has been found to be very stable

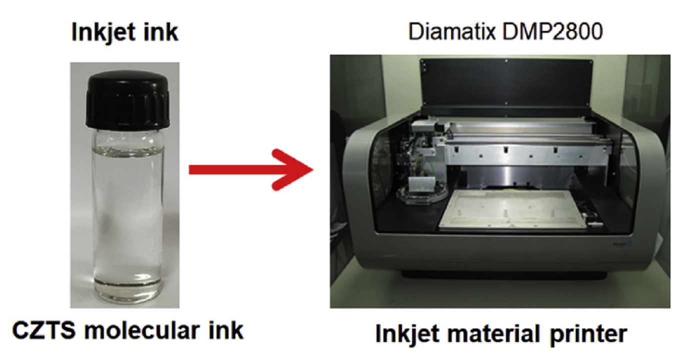

Fig. 1. Colourless CZTS molecular ink prepared for inkjet material printing.

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