Electrical and Optical Characterisation of CZTS Thin-Film for Sensing Applications

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Abstract— **The low-cost, earth abundant kesterite copper-zinc-tin-sulfide (CZTS) is the most desirable material for the upcoming sustainable energy, sensors and energy storage as well as generation. However, the research on the material was hindered due to the instability of the zinc and copper in the quaternary phase, thus, resulting in secondary complex phase with defects. This led to the structural inhomogeneity, challenges in the repeatability of the synthesis procedure and degradation (especially) in the efficiency of the solar cell. Therefore, synthesis of CZTS in right phase and purity (without any stoichiometric imbalance as well as secondary phases and defects) is a challenge to overcome. Moreover, due to the presence of copper and zinc, it is an interesting material for the scientific community as gas sensor. In this report we have synthesized CZTS through chemical synthesis and examined a spin coated CZTS thin film for probable sensing application at room temperature. We utilized the CZTS thin-film for room temperature gas sensing of the volatile organic compound (ethanol) at 68 PPM. In addition, the Phase purity of the film was confirmed by the X-ray diffraction. While, the optical characterization of the film was investigated by the UV-Spectrometer. Thickness of the film was confirmed by atomic force microscopy and the electrical characterization of the film was done by Kiethley 2420.**

Keywords— Transition Metal Dichalcogenides, CZTS, Gas Sensing, Volatile Organic Compounds, Ethanol sensing

I. INTRODUCTION

CZTS is reportedly have multifunctional application as: (i) main absorber in inorganic [1] and hybrid [2] solar cells, (ii) counter electrode material in DSSC [3] and batteries [4], (iii) as a photo catalyst [5], and (iv) for gas sensing [6] applications. CZTS have optimal bandgap, conductivity, and thigh throughput fabrication. The elements in CZTS are Copper Zinc Tin and sulphur which are all nontoxic and highly abundant in earth crust CZTS have advantageous optical and electronic properties optimal bandgap, conductivity, and thigh throughput fabrication. CZTS has been prepared by a variety of vacuum and non-vacuum techniques. Methods can be broadly categorized as vacuum deposition vs. non-vacuum and single step vs. sulfurization/selenization reaction methods. Nonvacuum methods are cost-effective and more suitable for mass production than vacuum methods. These fabrication methods are appealing because of their low complexity, low-cost, and scalability, leading to low-cost and large-scale film fabrication. Being made up on naturally abundant and relatively nontoxic ingredient elements, it is a suitable material for energy applications such as solar cell given its versatility. However, application n batteries and gas sensing are also widely reported for CZTS. Gas sensor device generates an electrical/optical signal in response to chemical interaction with environment/gases. The important point here is the detection level and concentrations of various gases into electrical/optical signals. The specificity to identify a particular gases and sensitivity in term of lowest concentration for detection are important. The advancement of gas sensors, could be of prime interest for their application in safely requirements in homes, institution, industries, offices. The working principle of gas sensor is that gas molecules are adsorbed on the surface of the film. The interaction of the gas molecule and the substrate film result into changes the resistivity of the substrate film. By monitoring the resistivity of the film detection of gas can be made. [6] P-type CZTS with n-type material like (ZnO [7], PANI [8-9]) are reported for the sensing application of LPG. The hetero-junction sensing is shown and documented in literature. We performed experiments and studied the response of single layer CZTS film on glass (sodium borosilicate) substrate for detection of volatile organic compounds, the result are being discussed in next section.

II. EXPERIMENTAL PROCEDURE

Metal precursors such as $CuCl_2.2H_2O$, $ZnCl_2$, $SnCl_4.5H_2O$, and sulphur source thiourea are taken in ratio of 1:0.75:0.5:3. Copper, Zinc and Tin chlorides are dissolved in isopropanol under magnetic stirring to obtain a greenish solution. [10] A second solution is prepared by dissolving thiourea in polyethylene glycol. Under constant stirring the isopropanol solution is added to the polyethylene glycol solution to form a transparent molecular precursor. The colour of solution changed from green to brown to finally transparent. The final transparent solution is then spin coated at 3000rpm followed by annealing in sulphur environment at 500°C to get CZTS films as shown in Figure 1(a). The sulfurization steps are linearly increasing the temperature from 0 to 500°C in 30 minutes and hold at there for 60 minutes followed by the cooling to room temperature as schematically depicted in figure 1(b). X-ray diffraction (XRD) of films is done to match phase purity using Rigaku TTRX-III XRD employing Cu Kα radiation. The optical absorption study is performed using Perkin Elmer UV visible spectroscopy in wavelength range of 350nm to 1000nm. IV measurement is done using Keithley 2420 controlled by LabView program. The gas sensing is performed in the custom designed setup. Thickness of the film is estimated by atomic force microscopy by using Agilent 5500 S at the edge of film and substrate.

III. RESULTS AND DISCUSSION

STRUCTURAL CHARACTERIZATION

X-ray diffraction pattern of CZTS thin film on sodium silicate are represented in Figure 2. The sulphurised film shows kesterite CZTS phase having polycrystalline nature and matched with [ICDD No.01-075-4122]. Obtained peak of sulphurised CZTS film are indexed (112), (200), (220) and (312). These peaks matched with theoretical ICDS pattern to ascertain the film is need have correct CZTS phase. Theoretically, it's been predicted that CZTS has a tetragonal crystal structure with space group such as kesterite, Stannite and primitive-mixed CuAu structure. While, kesterite was obtained by replacing Indium (In) atom in $CuInS_2$ (CIS) by zinc (Zn) and tin (Sn), Stannite and PMCA are obtained from the CuAu liked structures. The only parameter which differentiates between the kesterite and stannite is the distribution of the copper and zinc atoms with the unit cell. It should be noted that the tin (Sn) atom remains in the same occupancy in the kesterite and stannite structure. In addition, the kesterite structure has found to be the most stable structure than stannite by the energy difference of ~3 meV/atom. The tetragonal unit cell of stable kesterite phase (I4) of CZTS is shown in Fig 2 (b) depicting the arrangement of Cu-Zn plane and Cu-Sn plane along with S location within the unit cell. The Wycoff positions of Cu is 2a and 2c, Wycoff positions of Zn atoms 2d, Wycoff positions of Sn atoms is 2b, and eight anions (S) atoms on the 8g position. Inset of figure 1(a) contains UV spectroscopy of CZTS film showing absorption in wavelength range of 350-1000 micrometre.

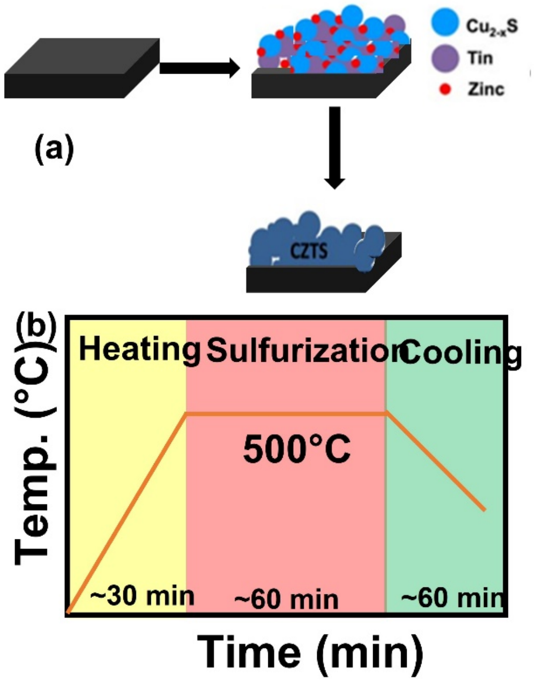

Fig. 1(a) The schematic showing the spin coating synthesis of CZTS film. (b) The schematic showing the temperature treatment profile for sulphurisation of the CZTS sample.

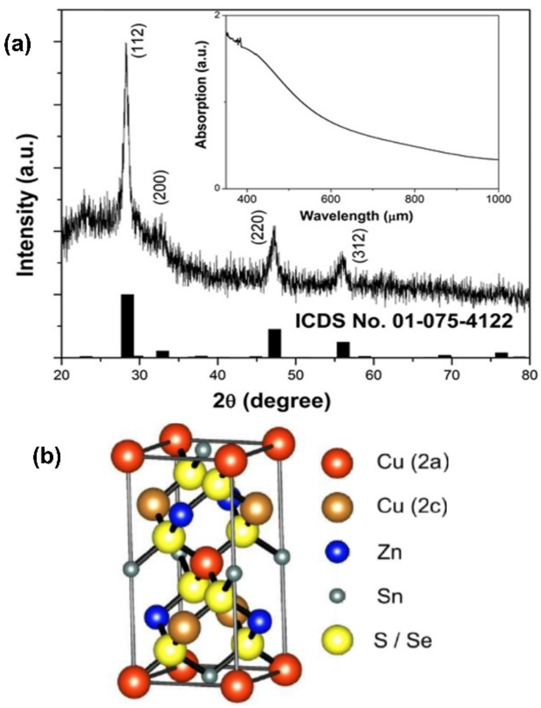

Fig. 2(a) The XRD of the CZTS sample. The bar corresponds to the ICDD No.01-075-4122 for CZTS, showing close match. Inset plot shows the absorption spectra of CZTS in visible region. (b) Shows the lattice structure of CZTS unit cell.

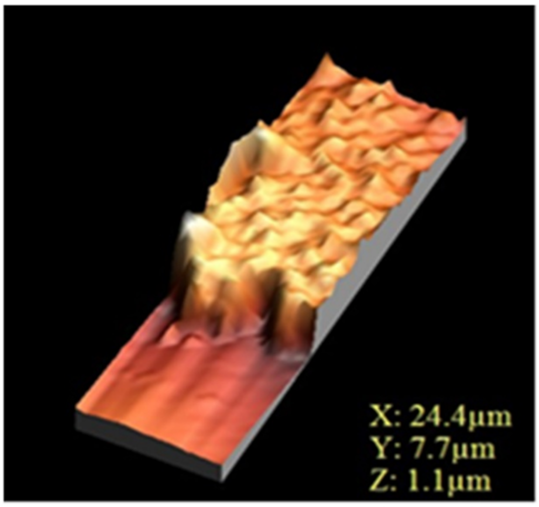

Fig. 3 AFM image of the CZTS film.

AFM image of the spin coated and sulphurised CZTS film on the glass substrate which shows thickness of 1.1μm and 24.4*7.7 micron sq. area. The AFM is performed in non-contact mode with raster scanning over an square area of 50*50μm area. The Fig. 3 shows 3D portion of the film refined using WSxM software. The AFM image show the smooth glass sheet, and CZTS film with roughness. The CZTS film cross section is marked by razor sharp line which is mapped by AFM to gauze the thickness of CZTS film. The prepared film by spin coating is further used to make electrical contacts and to do electrical characterization, and gas sensing.

IV. DEVICE TESTING

The p-type CZTS film was fabricated and tested for ethanol detection. Figure 4(a) shows I-V characteristics of film which was taken at room temperature in presence and absence of ethanol. We observed the detection property of the film in presence of 68 ppm of ethanol. The electrical characterization of the film was taken in vacuum and in ethanol for comparison. Instead of heating the film to detach gases molecules from the dangling bonds we tried vacuum desiccating and eventually succeeded in our strategy. This can be confirmed as the film regain its resistance (see figure 4(b)) value after exposure of the volatile gases. We observe change in resistance of film from 165KΩ to 215KΩ. The change of 50KΩ resistance in the film is unique signature for detection of ethanol. Further we tried for different concentration of ethanol to detect but found that the film starts degrading as time exceeds. The response time and recovery time of the film was found to be 2sec and 2.5sec respectively for a concentration of 68ppm. The gas detection mechanism for CZTS/ZnO is proposed by K.V. Gurav et al. [6]. The presence of humidity at room temperature will led to acquire top surface of the film by hydroxyl group (either chemisorbed or physiosorbed). [11-14] In our case the resistance increases upon ethanol exposure as shown in figure 4(a-b). When ethanol is being injected the reaction of the alcohol group with the hydroxyl group could lead to surface complex responsible for decrease in current. The probable sensing mechanism is schematically depicted in Figure 5.

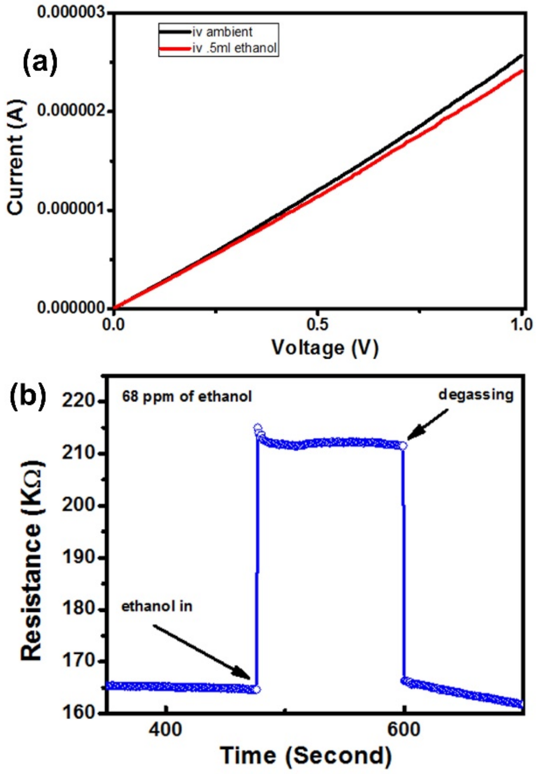

Fig. 4 (a) The IV of CZTS film under ambient and under ethanol environment. (b) The resistance-time of the CZTS film under ethanol gassing and degassing.

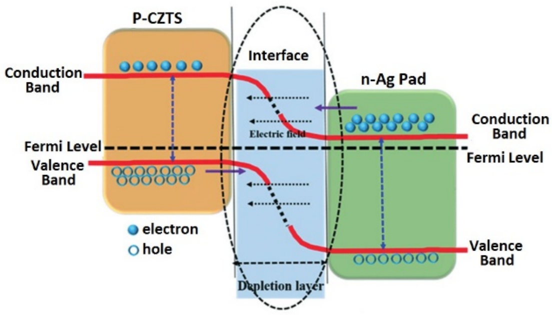

Fig. 5 The band diagram of p-CZTS interface with Ag metal contact and charge flow during sensing process of ethanol analyte

CONCLUSION

CZTS films are synthesised by wet chemical and spin coating techniques. Prepared films are uniform with thickness of around 1.1μm as shown by AFM. Prepared films show kesterite phase as confirmed by XRD and have good absorption property in visible region. Initial investigation of gas sensing property of CZTS based upon electrical property (resistance) shows a detectable change, under degassing and ethanol environment. Seeing the versatility of CZTS, it could be suitable and potential volatile/hazardous gas sensing alternative. This property of film needs meticulous optimization for probable sensing application.

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