



Spray pyrolysis synthesis of $\text{Cu}_x\text{Fe}_{1-x}\text{S}_2$ and their structural, electronic and optical properties: Experimental and first-principles study

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ABSTRACT

Iron pyrite, FeS_2 (FS) and the chalcopyrite copper iron sulphide $\text{Cu}_x\text{Fe}_{1-x}\text{S}_2$ (CFS) thin films were synthesized using chemical spray pyrolysis (CSP) deposition technique. The effect of different Cu concentration (1, 3, 5 and 7 at.%) on growth of these films was investigated. The as-synthesized CFS thin films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and ultraviolet–visible (UV–Vis) spectroscopy. The XRD pattern of FS show a structured cubic phase with preferential orientation along (2 0 0) plane, and CFS crystallized in chalcopyrite (tetragonal) with preferential orientations along (1 1 2) plane with crystallite size 142–91 Å. Optical absorption data show that the band gap of spray deposited FS and CFS films is 0.920–0.558 eV and the absorption coefficients significantly modified with the increase of Cu concentration from $3.619 \times 10^5 \text{ cm}^{-1}$ to $4.231 \times 10^5 \text{ cm}^{-1}$. Furthermore, these results have been adopted in accordance with the first principles calculations of electronic structure.

1. Introduction

Chalcogenide semiconductors have been of much interest and studied actively in the last decades because of their important physical and chemical properties and their great potential applications [1–7]. Iron pyrite, FeS_2 , as a member of them, has been exhibited a simple cubic (sc) structure with space group $\text{Pa}\bar{3}(T_h^6)$ and lattice constant $a = 5.416 \text{ Å}$ [8]. In particular, FeS_2 has a band gap of (0.95 eV), high optical absorption coefficient ($\alpha > 4 \times 10^5 \text{ cm}^{-1}$ for $h\nu > 1.4 \text{ eV}$), adequate minority carrier diffusion length (100–1000 nm) as well as comprises solely of earth abundant elements, low-cost and non-toxic [9,10]. It exhibits also interesting semiconducting properties (optical, electrical and magnetic) [11,12], pyrite devices show low efficiency (2.8%) and small photovoltages (typically $< 200 \text{ mV}$). The low photovoltage is the main obstacle for the low efficiency [10,13]. It has a potential application for cathodes in high-energy-density batteries [14], solar energy applications [15], depolarizer anode for H_2 production [16] and optoelectronic applications [17]. Considering the different technological applications of FeS_2 , this compound has been prepared via different deposition techniques such as sol–gel process [18], chemical vapor transport [13], solvothermal method [19], sulfurization of

iron films [20], microwave irradiation [21], electrochemical deposition (ECD) [22] and spray pyrolysis [23]. In order to improve its physical properties (optical and electrical properties), many eminent researchers have been alloyed iron pyrite with various elements keeping different views. For example, Alam Khan et al. [24] have studied the physical characteristics of FeS_2 , and showed that the band gap energy increased by tuning the crystal sizes. Hu et al. [25] have also reported that the optical band-gap increased depending on oxygen content by DFT calculation. Besides that, Sun et al. have investigated the properties of this compound alloying with some metallic elements (Zn, Os, Ru, Mg, Ba, etc.) in view of possible applications in photovoltaics [26]. Lehner et al. [27] have explained the important differences in the behavior of pyrite doped with As, Co or Ni. A number of studies have shown that metal (Cu, Al, Ni) doped FeS_2 materials and exhibited n-type behavior [28]. On the other hand, the ternary CuFeS_2 with its inherent properties (optical, electrical and magnetic) [29], has widened its applications in the fields of photovoltaics, thermoelectric and spintronic devices [30–32]. In 2012, a DFT calculation has been used to investigate the reconstruction of the chalcopyrite surfaces [33]. Kumar et al. also have reported precursor driven solution based synthesis of Wurtzite and chalcopyrite CuFeS_2 nanocrystals [34]. Wang et al. used a modified

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solvothermal method utilizing the metal halides and ammonium sulfide in a solution of ethylenediamine for the synthesis of CFS nanowires [35]. More Recently, Tanka Raj Rana et al. [36] have also analyzed the fabrication of $\text{Cu}_x\text{Fe}_{1-x}\text{S}_2$ (CFS) thin films using electrostatic field assisted chemical spray pyrolysis (CSP) accompanied with post-sulfurization, and showed that CFS thin films has a chalcopyrite structure with single annealed and the band gaps of sulfur deficient CH-CFS films were estimated to be 0.885–0.949 eV.

The purpose of the present study is to investigate the growth of the deposited ($\text{Cu}_x\text{Fe}_{1-x}\text{S}_2$ (CFS)) films using chemical spray pyrolysis (CSP) deposition technique with optimizing the spray deposition parameters like precursor concentration (both host and dopants), solution flow rate, substrate–nozzle distance, carrier gas, carrier gas pressure, substrate temperature, spray time and solvents as well as a comparison of experimental results with calculated ones obtained by Korringa-Kohn-Rostoker method (KKR) combined with the coherent potential approximation (CPA). This sort of research is not treated in most existing studies on ($\text{Cu}_x\text{Fe}_{1-x}\text{S}_2$ (CFS)) thin films [24–36]. This work stipulates that CFS film as a semiconductor with good optical properties in the visible region could be used for photovoltaic, thermoelectric and spintronic devices.

2. Experimental and first-principles calculations details

2.1. Preparation of CFS thin films

For the present deposited thin films, aqueous solution containing copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), iron chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and thiourea ($\text{CS}(\text{NH}_2)_2$) were used as the precursors for Cu, Fe and S. $\text{Cu}_x\text{Fe}_{1-x}\text{S}_2$ ($x = 0, 1, 3, 5, 7$ at.%) thin films were deposited on glass substrates kept at 500°C by using the chemical spray pyrolysis (CSP) technique like to our previous research works [37–40]. The concentration of FeCl_2 and $\text{CS}(\text{NH}_2)_2$ in the solution was 0.01 M and 0.08 M, respectively with changing the amount of CuCl_2 from (1 at.% to 7 at.%) and was dissolved in distilled water (100 ml), followed by addition of 5 ml ethanol as solvent. Then, the solution was stirred at $40^\circ\text{C} > 35$ min. It noticed that the mixture including the solvent was more stable than that prepared with only distilled water and exhibited high-quality films. Before the deposition process, the cleaned glass substrates is a very important step: it is necessary to remove all traces of grease and dust and to check, even to the eye, that the surface of the substrate does not have any scratches or defects in flatness. The glass substrates are cut by a diamond and are cleaned with ethanol and then rinsed with distilled water and finally dried with a hair dryer. Fig. 1 shows the schematic diagram of a chemical spray pyrolysis system. This consists of (1) Extractor, (2)

Hotplate, (3) Temperature controller, (4) Substrates, (5) Thermocouple, (6) spray nozzle, (7) Dosing pump, (8) Solution, (9) Air pump, (10) Drive motor. The mixture solution was sprayed through a spray nozzle onto glass substrates with the spray rate of 1.5 ml/min with the fine droplets of $40\ \mu\text{m}$ in diameter was estimated from data of Master flex apparatus, the diameter depend on flow rate of the solution. To spray the solution, we have used the dry air as carrier gas. After sprayed deposition, the samples were annealed at 500°C for 60 min.

2.2. Characterization of the thin films

The crystalline structure of the samples were characterized by XRD, using a Bruker D8 Discover Advanced Diffractometer $\text{Cu K}\alpha$ ($\lambda = 0.154056\ \text{nm}$). The state of the surface and the composition elements of the thin film were observed using a Scanning Electron Microscopy (SEM, JEOL-JSM) and Energy Dispersive X-ray spectroscopy (EDX) respectively. The optical properties of the FS and CFS thin films were measured with a UV-Vis spectrophotometer (Lambda 900 UV/VIS/NIR Spectrophotometer) from 300 nm to 800 nm.

First-principles calculations were executed using the Korringa-Kohn-Rostoker method (KKR) combined with the coherent potential approximation (CPA) within a framework of density functional theory (DFT).

3. Results and discussion

3.1. Structural properties

The crystalline structures of the sprayed FS and CFS thin films were characterized by X-ray diffraction as shown in Fig. 2. The (XRD) pattern of the film FS ($x = 0$ at.%) shows that the film is crystallized in the cubic phase and presents a preferential orientation along (2 0 0) and matched with the standard JCPDS card database (Pyrite, N° 1-079-0617) and characteristic peaks assigned to 28.21° , 32.81° , 36.91° , 40.51° , 47.31° , 56.21° and 59.08° corresponding respectively to (1 1 1), (2 0 0), (2 1 0), (2 1 1), (2 2 0), (3 1 1) and (2 2 2) planes of FeS_2 phase are recorded for $x = 0$. The values of lattice parameters are $a = b = c = 5.412\ \text{\AA}$ are in good agreement with the cubic type FeS_2 structure [8]. XRD patterns of $\text{Cu}_x\text{Fe}_{1-x}\text{S}_2$ ($x = 1, 3, 5, 7$ at.%) shows that the films were polycrystalline in nature with preferential orientation along (1 1 2) plane. The diffraction peaks of the CuFeS_2 compound at $2\theta = 18.827^\circ$, 29.399° , 33.949° , 34.328° , 48.771° , 49.053° , 58.475° and 59.018° can be attributed to the (1 0 1), (1 1 2), (2 0 0), (0 0 4), (2 2 0), (2 0 4), (1 1 6) and (2 1 5) plans respectively. All diffraction peaks can be indexed to the chalcopyrite structured CuFeS_2 (ICSD card,

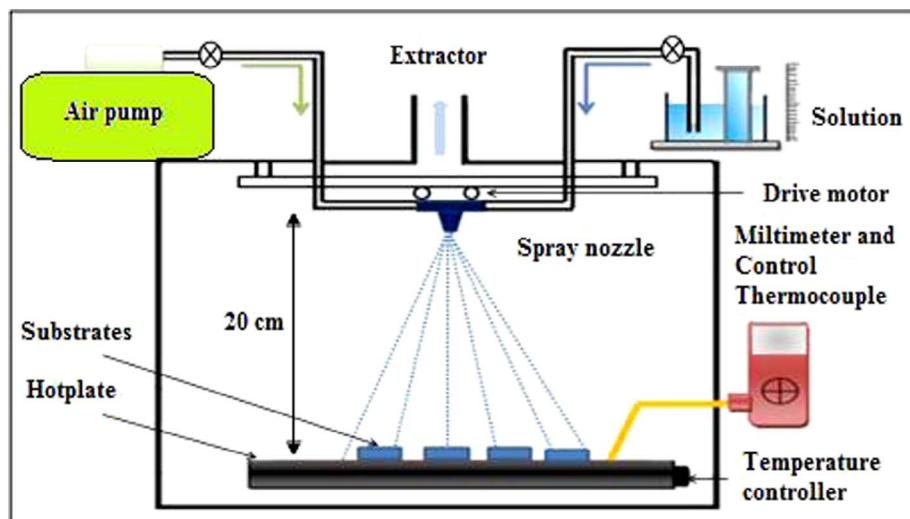


Fig. 1. Schematic of spray pyrolysis technique.

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