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Improved structural properties, morphological and optical behaviors of sprayed Cu_2ZnSnS_4 thin films induced by high gamma radiations for solar cells

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A R T I C L E I N F O

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A B S T R A C T

Cu_2ZnSnS_4 (CZTS) thin films have been synthesized by spray pyrolysis technique, deposited on glass substrates and then irradiated by high gamma radiations. Six gamma radiation doses have been applied: 10, 20, 30, 40, 50 and 100 kGy. The main objective of this work was to study the physical properties behavior of CZTS thin films under high gamma irradiation. Structural, optical and morphological properties of CZTS thin films were explored by X-ray diffraction, spectrophotometer and Scanning Electron Microscope, respectively. Structural analysis has shown that no noticeable changes have been occurred in the preferred orientation (112) or diffraction angles after gamma irradiation. Nevertheless, a significant increase in crystallite size from 52 to 79 nm has been observed after irradiation with 100 kGy gamma dose, which indicates a clear enhancement in crystalline structure. Certain optical parameters such as absorption and extinction coefficients ($\alpha(\lambda)$,$K(\lambda)$) have been only slightly affected, which indicate a radiation hardness of the CZTS thin films within the ionizing radiation range studied in this paper. Band gap energy of the irradiated thin films have been increased with the irradiation and reached 1.6 eV at 100 kGy gamma dose. Other optical parameters such as refractive index $n(\lambda)$ and lattice dielectric constant (ε) have been determined and analyzed. All these experimental results clearly showed that structural properties of CZTS films have been improved by gamma irradiation while the optical properties have been slightly changed, which is favorable for optoelectronic applications working near nuclear environments or even for outer space solar cells and instrumentation for high-altitude flight, where gamma radiations are abundant.

1. Introduction

Cu_2ZnSnS_4 (CZTS) thin film is a quaternary chalcogenide semiconductor that has remarkable physical properties for many applications, essentially for solar cell devices [1,2] and recently in photoelectrochemical water splitting for hydrogen production [3,4]. The great potential of CZTS material is that its constituent elements such as Copper, Zinc, Tin and Sulfur are low cost, earth abundant and non-toxic, which facilitate its use for friendly environment applications. Compared to other materials of the same family, CZTS thin films are considered as excellent photovoltaic absorbers with a high absorption coefficient (i.e. higher than 10^4 cm^{-1}) and with an appropriate band gap energy near 1.5 eV [5]. CZTS thin films can be grown by different experimental techniques such as spray pyrolysis [6], sputtering [7], spin coating [8] and Pulsed Laser Deposition [9]. The physical properties of CZTS thin films have been extensively explored and studied by many researchers [10–17]. Many efforts have been deployed by the research community to optimize the physical properties of thin films materials by using doping, annealing at different temperatures, variation of synthesis conditions such as chemical precursors or solvent concentration or tuning experimental apparatus during nanomaterial growth, but there are only a few works that deal with irradiation by gamma rays, neutrons flux, electron and ion beams in order to optimize or modify the thin films physical properties. Gamma rays are considered as one of the most powerful electromagnetic waves and are emitted by radionucleide Cobalt 60 or Cesium 137 isotopes. They are widely used in many domains such as medicine, military, research and nuclear power production [18]. The literature shows many examples

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where the physical properties of thin films materials are improved by gamma irradiation [19–22] but there are also those where a degradation of thin films physical performances have been clearly observed depending on the applied gamma dose [22,24]. Previous works on gamma irradiated thin films materials show deep modifications of structural, optical and electrical properties after exposure to gamma energy. The irradiation- induced physical changes can lead to very interesting applications such as dosimetry measurements, if a physical property varies linearly or exponentially with the applied dose [18]. Irradiated thin films can also be used as sensors for biologic applications for the detection of microorganisms as reported in literature [18,25]. Our previous works on irradiated In_2O_3 [22] thin films have shown an enhancement in optical properties, which is also required for the photovoltaic applications.

In this paper, we have synthesized CZTS thin films on glass substrates and irradiated them at different high gamma doses 10, 20, 30, 40, 50 and 100 kGy. Structural, optical and morphological properties of thin films have been investigated before and after irradiation. Our purpose is to explore and analyze physical properties changes induced by the exposure of CZTS thin films to such higher gamma doses and understand the change in structural and optical properties of the thin films. Besides photovoltaic applications, these results could be useful for the researchers who used CZTS thin films in nuclear environments (particle accelerators, nuclear reactors, gamma rays facilities). Another application is found in solar cells for space applications where gamma radiations doses are considered very high and might affect the optoelectronic devices.

To the best of our knowledge, no previous study on the physical properties of gamma irradiated CZTS thin films has been performed before. These new data will provide new insights to the research community on gamma irradiated thin films.

2. Experimental details

Cu_2ZnSnS_4 thin films have been successfully grown in our laboratory using spray pyrolysis technique on glass substrates. The chemicals used as precursors were cupric chloride $CuCl_2$ for copper, zinc acetate $Zn(CO_2CH_3)_2$ for zinc, stannic chloride $SnCl_4$ for tin, and thiourea $SC(NH_2)_2$ for sulfur. All these precursors were dissolved in methanolic solution to be sprayed on the glass substrates that was placed on a heated plate. A detailed description of the synthesis of CZTS thin film was reported elsewhere [26].

Structural properties were determined by X-ray diffraction (XRD) using a monochromatic PANalytical diffractometer type X′pert PRO. Optical spectra of transmittance T(λ) and reflectance R(λ) spectra were recorded using UV–VIS–NIR spectra with Perkin–Elmer Lambda 950 spectrophotometer at normal incidence at room temperature in the wavelength range of [250–2500] nm. Surface morphology was explored using Scanning Electronic Microscope S–4100, Hitachi with resolution: 5 nm, magnification: 20–500,000, acceleration voltage: 0.5–30 kV and equipped with a digital image processing apparatus.

The irradiation with gamma rays was performed at the National Center for Nuclear Sciences and Technologies of Tunis **(CNSTN)** with an industrial (^{60}Co) source. More technical details about the gamma source used in this experiment can be found in these references [27,50–52]. Irradiation of thin films at CNSTN was performed in air at ambient temperature with a dose rate of 4 kGy/h. Many PMMA Harwell Dosimeters were used during the irradiation phase to measure the exact absorbed dose by each sample.

The gamma radiation source is managed by the national Center of Nuclear Sciences and Technologies by a specialized team that ensure its operations for all users from scientists (universities, institutions, laboratories) or industrials which use this source principally for medical sterilization or food treatment. Measurement of absorbed dose for each treatment is ensured and followed by this specialized team in collaboration with other laboratories in France and other foreign countries.

Fig. 1. Image of thin films samples installed around the Gamma radiation source.

The accuracy of measured absorbed dose is 10%. Before irradiation operations, the gamma source is maintained underground for radiation protection and when everything is ready to begin irradiation experience, the source is elevated using an hydraulic system. As we can see from the image in Fig. 1, after conditioning our films in small plastic bags, we paste them directly in the metallic cylinder in front of the gamma source to achieve the requested gamma dose.

3. Results and discussions

3.1. Structural analysis

XRD spectra of irradiated and non-irradiated CZTS thin layers are shown in Fig. 2. Firstly, the XRD spectrum of the as-deposited CZTS thin layer exhibits four main peaks (112), (200), (220) and (312) corresponding to the CZTS kesterite crystal structure(JCPDS 26-0575) [28,29]. The sharp and the intense peak (112) indicates preferential orientation and good crystallinity of the thin films. Regarding the irradiated CZTS thin films, the X-ray spectra presented in Fig. 1 shows that the crystal structure has been preserved with same peaks and angles but the full width at half maximum (FWHM) has been changed with the absorbed gamma dose, which indicates a modification in the grain size after applying gamma radiations. These results indicate that the CZTS films presents gamma radiation hardness compared to other irradiated nanomaterials [22,23], which have been deeply affected by gamma energy through many crystallographic aspects such as the appearance of new secondary phases, the shift in preferred orientation and diffraction angles, and significant changes in peak intensities. The observed increase in grain size of the thin films is related to the nature of gamma radiations that ionizes matter and gives velocity to atoms that will generate successively multiple electrons and ions through atomic collisions. Ionization affects directly the crystalline structure of CZTS thin films and depends on the gamma energy, the elements composing the crystal lattice and the thickness of the films. We can say