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# Optoelectronic properties of the InSe/Ga<sub>2</sub>S<sub>3</sub> interfaces

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#### ABSTRACT

In this work, the nature of formation, the structural, optical and optoelectronic properties of the InSe/Ga<sub>2</sub>S<sub>3</sub> interfaces are explored by the Scanning electron microscopy, energy dispersive X-ray, X-ray diffraction, optical spectrophotometry and temperature dependent dark and photoconductivity. The InSe/Ga<sub>2</sub>S<sub>3</sub> interfaces that are prepared by the vapor deposition technique are observed to exhibit a physical nature of stacking with correct atomic stoichiometry of the layers. The deposition of the  $Ga_2S_3$  onto InSe substrate is induced to exhibit a polycrystalline nature. In addition, the optical characterizations have shown that the presence of  $Ga_2S_3$  onto the top surface of InSe enhances the absorbability significantly and causes valence and conductivity analysis in the range of 330–160 K, have shown that the conduction is dominated by the thermionic and variable range hopping transport mechanisms. The photoexcitation process tunes the current transport mechanisms. When the InSe/Ga<sub>2</sub>S<sub>3</sub> interface devices were exposed to laser light irradiations of wavelengths of 406 and 850 nm, promising photocurrent characteristics were observed. Namely, the linear growth of the photocurrent, responsivity, external and internal quantum efficiencies with increasing biasing voltage under these two laser lights nominates the InSe/Ga<sub>2</sub>S<sub>3</sub> interfaces for optoelectronic applications.

#### Introduction

Two dimensional layered InSe thin films which are regarded as one of the famous optoelectronic champions are recently reported to reveal high photoresponsivity of 27 A/W and short raise/decay photocurrent times that nominate it for photodetection [1]. Two dimensional layers are also used to design ambipolar field-effect transistors by using asymmetry contact metals [2]. The ambipolar field effect transistors are reported to be promising for use as photovoltaic devices, optical sensors and CMOS inverter circuits. As a two dimensional material it holds the properties of sizable band gap, high flexibility and exhibit an insignificant density of dangling bonds [3] which make them attractive for achieving practical device applications. It is also reported to exhibit features that allow it to be used as dual Terahertz/Gigahertz resonator [4].

The corporation of InSe in the design of heterojunction devices remarkably improved its optoelectronic properties. The GaSe/InSe two dimensional interfaced layers are reported to exhibit very fast response time of  $2 \,\mu$ s, they also exhibited self-driven photodetector characteristics with multicolor photoresponse that operate in a wide range of spectrum that extends from the ultraviolet to the near-infrared [5]. In addition, highly mismatched InAs/InSe heterojunctions with lattice mismatch of  $\sim 34\%$  are observed to exhibit rectifying properties with rectification ratio of 10<sup>4</sup> broadband photoresponse in the near infrared and visible spectral ranges [6]. Moreover, in our previous investigation, we have shown that the ZnS/InSe heterojunctions could be used as plasmon resonators, photodetectors and Microwave Cavities at the same time [7]. A wide plasmon resonating range that extends from 0.31 to 5.26 GHz associated with free particle mobility of  $212 \text{ cm}^2/\text{V}$  s was observed. Since the use of InSe as component of heterojunction device is shown to reveal smart features, we are motivated to report and show the applications of an interface made of InSe and Ga<sub>2</sub>S<sub>3</sub>. The InSe/Ga<sub>2</sub>S<sub>3</sub> two dimensional multilayers will be studied by means of X-ray diffraction, scanning electron microscopy and optical spectroscopy techniques. The temperature dependent photocurrent and dark and illuminated conductivity of the device will also be studied to fix the recombination centers and current transport mechanisms in the interface. The work that can be regarded as complement to the existing archives of InSe based heterojunctions will report the effect of the InSe on the crystalline nature of  $Ga_2S_3$  and on its optoelectronic performance.

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**Fig. 1.** (a) The SEM images for (a) the InSe/ $Ga_2S_3$  interfaces (b) 60,000 magnifications for InSe and for  $Ga_2S_3$ , (c) the 60,000 magnified image for the InSe/ $Ga_2S_3$  interfaces and (d) The X-ray diffraction patterns for the InSe,  $Ga_2S_3$  and or InSe/ $Ga_2S_3$  heterojunctions. The inset of (a) show the real photograph of the prepared sample.

#### **Experimental details**

As the picture which is presented in the inset of Fig. 1(a) shows, both of the InSe (dark brown) and Ga<sub>2</sub>S<sub>3</sub> (blue violet) thin films are deposited onto glass substrates in a VCM 600 thermal evaporator under pressure of  $5 \times 10^{-5}$  mbar. The high purity (99.99%) source materials were  $\alpha - \text{In}_2\text{Se}_3$  crystal lumps and Ga<sub>2</sub>S<sub>3</sub> powders. Some of the resulting InSe thin films were used as substrate to grow the Ga<sub>2</sub>S<sub>3</sub> thin films. Both of the single layers and interfaced layers were characterized using a Miniflex 600 X-ray diffraction unit, Joel scanning electron microscope connected to an energy disperse X-ray (EDS) analyzer, Evolution 300 spectrophotometer (300–1100 nm) and ARS (Model CS202AE-DMX-3AL cryostat) closed cycle He cryostat. The cryostat is attached to an automated system that record the current-voltage characteristics concurrently with the continuous illumination of the light. The illumination was actualized with the help of Thorlab laser source that generates light of the wavelength of 406 and 850 nm.

#### **Results and discussion**

Early published works about the InSe and Ga<sub>2</sub>S<sub>3</sub> have shown that, both materials exhibit an amorphous nature with correct stoichiometry when deposited onto glass substrates at room temperature [7,8]. Fig. 1(a) show an electron photograph of an  $\sim 80 \,\mu m$  width region that show the interface region between the InSe and Ga<sub>2</sub>S<sub>3</sub> films. The energy dispersive X-ray (EDS) analysis of the heterojunction device has shown that the InSe region is composed of 49 at.% In and 51 at.% Se. The EDS spectrum from the Ga<sub>2</sub>S<sub>3</sub> region displays atomic contents of 41 at.% Ga and 59 at.% S. The correct stoichiometry distribution at the junction region of the interface make the heterojunction of physical formation nature. On the other hand, the scanning electron microscopy images for InSe and  $Ga_2S_3$  which are shown in Fig. 1(b) assured the amorphous nature of InSe with undetectable grain size. The image of the Ga<sub>2</sub>S<sub>3</sub> thin film which refers to a 60,000 times magnification displayed larger grains of average size of  $\sim 38$  nm. The image of Ga<sub>2</sub>S<sub>3</sub> which is deposited onto glass exhibits short ranges of ordered regions, which makes the decision about its crystalline nature hardly possible. The same type of image is also observed for the InSe/Ga<sub>2</sub>S<sub>3</sub> interface. The average grain size for the interface region which appears in Fig. 1(c)

is ~45 nm. To reveal more clearer idea about the crystalline nature of the films and the interface, the X-ray diffraction for the InSe, Ga<sub>2</sub>S<sub>3</sub> and InSe/Ga<sub>2</sub>S<sub>3</sub> which are deposited onto glass substrates are recorded and shown in Fig. 1(d). It is clear from the figure that while both of the InSe and Ga<sub>2</sub>S<sub>3</sub> films exhibit amorphous nature of structure, the double layer exhibited diffraction patterns that when analyzed with "TREOR 92" and "Crystdiff" software packages appeared to related to the  $\alpha$  – phase of Ga<sub>2</sub>S<sub>3</sub>. The crystal structure is of monoclinic type with lattice parameters of a = 11.094, b = 9.578, c = 6.395 Å and  $\beta = 141^{\circ}$ . All the diffraction peaks are related to the Ga<sub>2</sub>S<sub>3</sub> and are consistent with literature data [9]. In its as grown form, due to the existence of the monoclinic, cubic and hexagonal phases in the same films, the Ga<sub>2</sub>S<sub>3</sub> hardly exhibit polycrystalline nature when deposited onto glass substrates. It clear that the presence of the InSe is the main reason for the structural improvements. The crystalline phase of InSe is known [8] to exhibit hexagonal structure with lattice parameters of a = 4.005 and c = 16.640 Å. No lattice match can be formed between these two layers. As the first layer is amorphous and grains are very randomly distributed, the crystallization process of the Ga<sub>2</sub>S<sub>3</sub> over this amorphous layer should have resulted from the critical nucleation energy. The process of crystallization consists of nucleation and growth of crystals. During the slow nucleation process, small nuclei containing the newly formed crystallites are established. Thereafter in the second stage of growth which is faster than the nuclei formation process, the crystal growth spreads outwards from the nucleating sites. This process is fast due to the presence of dislocations and defects that behaves as growth points, which provide the necessary catalyst for structural transformation and long-range order formation [10].

On the other hand, the probable formation of Ga<sub>2</sub>Se<sub>3</sub> and or In<sub>2</sub>S<sub>3</sub> bonds should depend on the ability of the atomic substitutions of the ions in vacant sites of each other. Since the  $\alpha$  – phase of Ga<sub>2</sub>S<sub>3</sub> with this structure type is known for its ordered vacancy, and because the ionic radiuses of Ga<sup>+3</sup>, In<sup>+3</sup>, S<sup>-2</sup>, Se<sup>-2</sup> are 76, 94, 170 and 184 pm [11], respectively, the substitution of In in sites of Ga and substitution of Se in sites of S is impossible. For this reason, the probable presence of the Ga<sub>2</sub>Se<sub>3</sub> and In<sub>2</sub>S<sub>3</sub> as minor phases in the heterojunction structure could be excluded. This tenet is also confirmed from the X-ray patterns that contain no peak that refers to these phases and the correct readable stoichiometry.

The optical properties of the InSe/Ga<sub>2</sub>S<sub>3</sub> heterojunction device are

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