Materials Science in Semiconductor Processing 87 (2018) 174–180

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Characterization of $TlInS_{1.8}Se_{0.2}$ as advanced functional crystals

A.F. Qasrawi[a,b,*], Areen A.M. Atatreh[a], N.M. Gasanly[c]

[a] Department of Physics, Arab American University, Jenin, Palestine
[b] Group of Physics, Faculty of Engineering, Atilim University, 06836, Ankara, Turkey
[c] Physics Department, Middle East Technical University, 06800 Ankara, Turkey

ARTICLE INFO

Keywords:
$TlInS_{1.8}Se_{0.2}$
X-ray
EDS
Gigahertz
Terahertz
Photosensor
Communications

ABSTRACT

In this work, selenium doped $TlInS_{1.8}Se_{0.2}$ crystals are used to fabricate multifunctional devices that can handle more than one duty at a time. After revealing the morphological, compositional, structural and optical properties of the doped crystal, it is sandwiched between Ag and carbon metals. The crystals are characterized by means of ultraviolet-visible light spectrophotometry, impedance spectroscopy and illumination dependent current-voltage characteristics techniques. While the optical spectroscopy allowed determining the energy band gap of the crystals as well as the optical conductivity in the terahertz frequency domain, the impedance spectroscopy allowed identifying the conductance and reflectance spectra in the gigahertz frequency domain. The two techniques reveal promising characteristics presented by optical switching at 2.20 eV and band pass filtering properties in mega/gigahertz frequency domains. On the other hand, the analysis of the current (*I*)- voltage (*V*) characteristics which are recorded in the dark and under photoexcitation of unfiltered tungsten light in the light power range of 25–130 mW, revealed light intensity dependent rectifying properties. Particularly, the modeling of the experimental *I-V* curves in accordance with the Richardson Schottky and Chueng's theoretical approaches have shown that the Schottky diode ideality factor, series resistance and barrier height decreases with increasing light power. Such behavior indicates wide tunability of the device when used as photosensors. With the features presented by small size, photosensitivity, gigahertz/terahertz spectral responses, the device can be promising element for use in visible light and microwave communications.

1. Introduction

$TlInS_2$ is a compound that is known for its layer nature of crystallization. It is a low dimensional material which can be employed in nanotechnology [1–4]. Recent reports on this compound indicated information about its interesting properties. Examples of these features are the acousto-optic anisotropy [5], Faraday effect [6] and polarization dependent ferroelectric property [7]. However, practical applications of this crystal in optoelectronic technology and nanotechnology are rarely found. Most of the available reports focus on its physical nature and characterization. Several studies which attempt to alter its physical characteristics may be found [8,9]. It is reported that the doping of the crystals with B and Ag impurity do not alter the intrinsic photoluminescence emission in the crystal while Er atoms participation enhances it significantly [8].

Pure $TlInS_2$ single crystals are known to exhibit conductivity types conversion from *p*- to *n*- type near 315 K [9]. This property makes the usability of the crystals in electronic applications hardly possible. For this reason, here in this work, we attempt to force the material exhibit one type of conduction by reducing the content of sulfur and replacing it by Se. The selenium with the electronic configuration $3d^{10}4s^24p^4$ can cause more energy level overlapping than sulfur whose electronic configuration is $3s^23p^4$. The *4p* orbitals of Se forms stronger bonding and the overlapping of the energy levels make it easier for the electrons to move freely in the material, thus, the resistivity to the electronic motion is reduced [10]. The Se doped crystals which we report here, is fundamentally characterized by scanning electron microscopy, X-ray diffraction, the ultraviolet-visible light spectrophotometry, impedance spectroscopy and dark and illuminated current-voltage characteristic techniques. The study reflects the basic properties of the crystals and also reports the practical applicability of this material in optoelectronic technology.

2. Experimental details

$TlInS_{1.8}S_{0.2}$ single crystals are prepared by the modified Bridgman method from the high purity elements (99.999%) taken into stoichiometric proportions. As illustrated in Fig. 1(d), the crystal growth is

* Corresponding author at: Department of Physics, Arab American University, Jenin, Palestine.
E-mail addresses: atef.qasrawi@atilim.edu.tr, atef.qasrawi@aauj.edu (A.F. Qasrawi).

https://doi.org/10.1016/j.mssp.2018.07.022
Received 11 May 2018; Received in revised form 10 July 2018; Accepted 11 July 2018
Available online 23 July 2018
1369-8001/

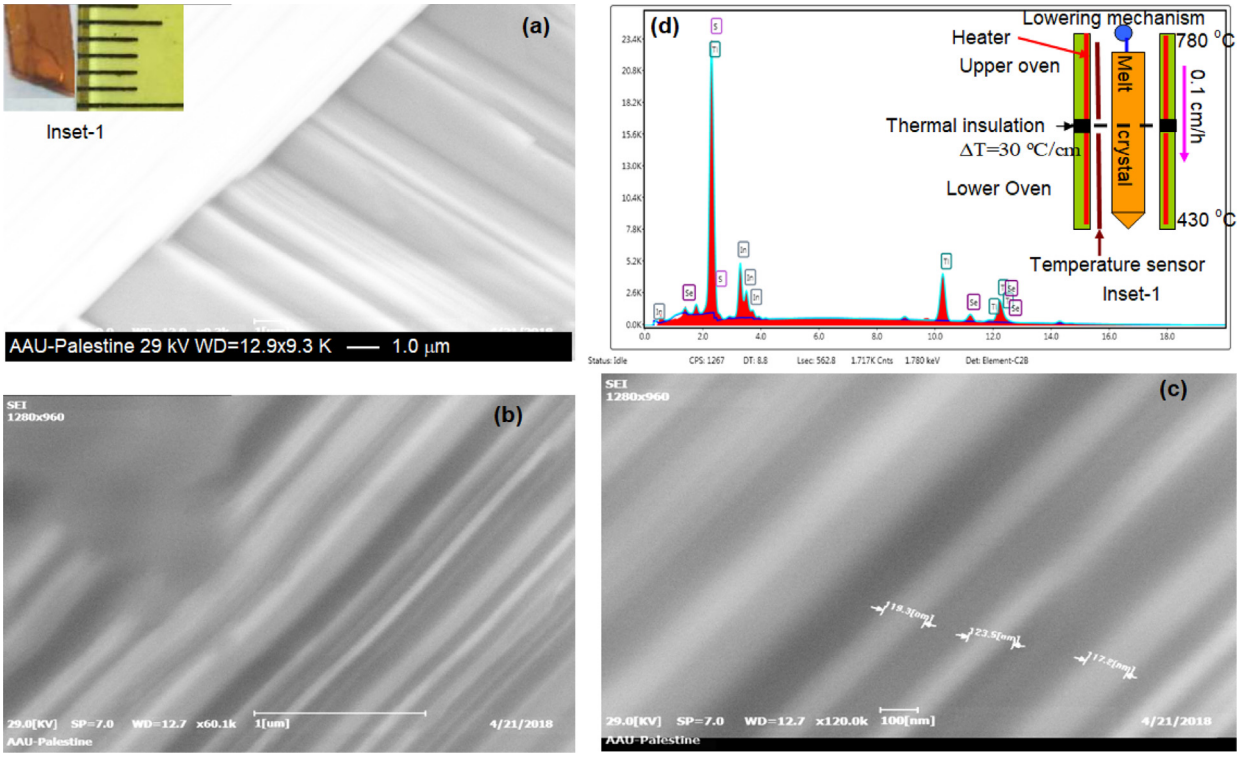

Fig. 1. The scanning electron microscopy images for the $TlInS_2$ crystals being magnified for (a) 9300, (b) 60,000 and (c) 120,000 times. (d) The energy dispersive X-ray spectra for the $TlInS_{1.8}Se_{0.2}$ crystals. The inset of (a) show the optical image of the sample and inset of (d) show the crystal preparation procedure.

actualized in an evacuated silica tubes with a tip at the bottom. The ampoule is moved with thermal gradient of 30°/cm in a vertical furnace in a temperature range of 780–430 °C at rate of 0.1 cm/h. The resulting crystals (inset-1 of Fig. 1(a)) are dark orange in color and display good optical quality. The crystals are morphologically and structurally characterized by means of COXEM-200 scanning electron microscope equipped with EDS energy dispersive x-ray analyzer and Miniflex-600 X-ray diffraction units, respectively. The optical transmittance and reflectance are measured by Evolution-300 spectrophotometer. The electronic sensors are prepared by evaporating Ag metal onto the surface of the crystal using Norm-600 physical vapor deposition system under vacuum pressure of 10^{-5} mbar. The thickness of the Ag film is 1.0 μm. The top contacts are made of high purity (99.999%) carbon paste. The area of the circular shaped device is 7.3×10^{-3} cm^2. The Ag/$TlInS_{1.8}Se_{0.2}$/C device is electrically characterized by Keithley 235 voltage source and Keithley 6485 picoammeter. The impedance spectroscopy is recorded in the frequency domain using Agilent 4291B 10–1800 MHz impedance analyzer. Light irradiation to the samples is carried out by using tungsten lamp which is calibrated by Moll type II thermopile that has light detectivity in the range of 200–5000 nm.

3. Results and discussion

The physical nature of growth and the structural phases of the $TlInS_{1.8}Se_{0.2}$ crystals are investigated by the scanning electron microscopy (SEM) and X-ray diffraction techniques. Fig. 1(a), (b) and (c) displays the scanning electron microscopy images for the Se doped $TlInS_2$ crystals being recoded for magnifications of 9300, 60,000 and 120,000, respectively. As seen from Fig. 1(a), the crystal is composed of very dense sequentially stacked microlayers layers. It is clear in Fig. 1(b) that when these layers are enlarged further it appear in groups. Further enlargement (Fig. 1(c)) shows stacked layers each of ~ 120 nm thick. The side of each layer is straight indicating the ability of cleaving thin layers from the free standing crystals. This property makes the produced crystals of high quality and attractive for use in nanotechnology applications [11]. Studies on crystal growth and layering have shown that the grown crystals at slow rates result in large, flat and spacer nucleation islands [12]. The larger the grown layer, the less the roughness, the better the defect symmetrical distributions and the higher the crystal quality. It is reported that, the lower growth rate of the nucleation layer could enhance the surface mobility of crystal atoms, and improve the nucleation layer's crystal quality [12]. Fig. 1(d) display the qualitative evaluation of the crystal composition. As the figure shows, the crystal is composed of Tl, In, S and Se only. No peaks that are assigned to any additional impurity was observed. The stoichiometric composition comprises the expected ratio of doping which represents 5.26–6.50% of the total atomic content. The deviation in values never exceeds 4% of the measured value indicating that the crystals are highly homogeneous.

Fig. 2 displays the X-ray diffraction patterns for the crystal under investigation. The patterns contained two main major peaks located at 2θ= 24.30° and 49.15° exhibiting relative intensity values of 100% and 90%, respectively. All the X-ray diffraction patterns are subjected to software analysis with the help of TREOR 92 and Crystdiff software packages. No one exact solution for particular cell is obtainable. The correct solution comprises two dominant structural phases. Namely, the peaks which are observed at 2θ value of 12.35°, 21.95°, 24.30°, 44.20° and 49.15° are indexed assuming monoclinic unit cell with lattice parameters of a = 8.071, b = 15.566, c = 4.1931 Å and β = 92.25° (displayed in Fig. 3(a) for $TlInS_2$ and Fig. 3(b) for $TlInS_{1.8}Se_{0.2}$). The peaks which appear at 55.95, 62.4, 68.35° correspond to a tetragonal unit cell of lattice parameters a = 9.272 and b = 3.876 Å. The decision about the most appropriate lattice parameters is based on finding no difference between the measured and the theoretically optimized 2θ values. The presence of the tetragonal phase (illustrated in Fig. 3(c) for $TlInS_2$ and Fig. 3(d) for $TlInS_{1.8}Se_{0.2}$) as minor phase can also be guessed from the broadening of the peak located at 49.15° which is shown in the inset of the Fig. 2. Since the most two intensive peaks are related to monoclinic structure, the tetragonal phase can be regarded as minor phase. On the other hand, the deviation of the lattice parameters