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Investigation of photovoltaic properties of amorphous InSe thin film based Schottky devices

K Yılmaz[1], M Parlak[2] and Ç Erçelebi[2]

[1] Pamukkale University, Science and Arts Faculty, Physics Department, 20020 Denizli, Turkey
[2] Middle East Technical University, Physics Department, 06531 Ankara, Turkey

E-mail: kyilmaz@pau.edu.tr

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Abstract
In this study, device behavior of amorphous InSe thin films was investigated through *I–V*, *C–V* and spectral response measurements onto SnO_2/p-InSe/metal Schottky diode structures. Various metal contacts such as Ag, Au, Al, In and C were deposited onto amorphous p-InSe films by the thermal evaporation technique. The best rectifying contact was obtained in a SnO_2/p-InSe/Ag Schottky structure from *I–V* measurements, while the Au contact had poor rectification. Other metal contacts (Al, In and C) showed almost ohmic non-rectifying behaviors for all samples. The ideality factor and barrier height values with the Ag contact were found to be 2 and 0.7 eV, respectively.

1. Introduction

Considerable research activity has been undertaken in the field of metal–semiconductor junctions as photovoltaic solar energy converters. InSe which has attracted particular attention in the last decade is a layered semiconductor whose direct energy gap is around 1.2–1.3 eV at room temperature [1–4]. The indirect gap which is 50 meV below the direct gap is weak enough not to be observable in absorption measurements. The chemical bonds in these materials are almost complete within the layer which make the surfaces of these materials free of dangling bonds and suitable for device applications [5]. Most of the work in the literature on InSe-based Schottky devices is about n- or p-type single crystals or polycrystalline thin films [6–10]. Thus, our study presented in this work is focused on characterization of amorphous p-type InSe thin film based Schottky devices.

2. Experimental details

Amorphous InSe thin films were deposited onto unheated soda-lime and SnO_2 (TO) coated glass substrates by the thermal evaporation method using 99.99% pure In_2Se_3 single crystal powder as a source material. The deposition process was carried out under a vacuum of 10^{-5} Torr by keeping the source temperature at around 800 °C. Various metals such as Au, Ag, In and Al were achieved onto the a-InSe thin films as the top point contacts with the area of around 7.85×10^{-3} cm^2 by the thermal evaporation method in order to form the sandwich structure of TO/a-InSe/metal. Also, C (colloidal graphite) was pasted onto the films as point contacts. Prior to the device characterization, structural, electrical and optical properties of the InSe thin films, which were deposited on insulating glass substrates, were determined. Structural analyses of the films were carried out by using the JSM-6400 scanning electron microscope equipped with energy dispersive x-ray facility (EDXA) and a Rigaku Miniflex x-ray diffractometer. Electrical properties of both films and devices were measured using a Keithley 220 constant current source and a Keithley 619 electrometer. Temperature-dependent current–voltage characteristics were investigated using a Janis liquid nitrogen VPF series crysostat. The Hall effect measurements of the films were carried out by the same system except a constant magnetic field of 0.97 T was applied parallel to the *c*-axis (perpendicular to the film surface) using a Walker Magnion model FCC-4D magnet. Optical properties were studied by means of transmission and spectral response measurements. The transmission measurements were made by a double beam Perkin-Elmer UV/VIS lambda

2S spectrometer. Spectral response analyses were performed by using an Oriel MS 257 monochromator together with the HP 4140 picoammeter/dc voltage source.

3. Results and discussion

3.1. InSe thin film properties

The structural properties of the InSe thin films deposited on glass substrates were examined through XRD and EDXA analyses which have shown that as-grown InSe films were composed of about 49% In and 51% Se and no other impurity atoms were found in the structure. The XRD and electrical measurements have indicated that undoped InSe thin films deposited on glass substrates were amorphous with p-type conductivity lying in the range of 10^{-4}–10^{-5} Ω^{-1} cm^{-1} at room temperature. The temperature-dependent *I–V* and Hall effect measurements have shown that the conductivity and carrier concentration increase with increasing absolute temperature while mobility is almost temperature independent in the studied temperature range of 100–430 K which reveals that the dominant scattering mechanism is neutral impurity scattering. Carrier concentration and mobility values of InSe films at room temperature were determined to be in the range of 10^{12}–10^{13} cm^{-3} and 2.7–82 cm^2 V^{-1} s^{-1}, respectively. The detailed conduction mechanisms of the InSe films were investigated in a temperature region of 100–430 K and have been reported previously [11, 12]. It was found that thermal excitation is dominant above 200 K in which region conductivity increases sharply with temperature whereas below 200 K, temperature dependence is weak and conduction is dominated by variable-range hopping (VRH).

3.2. TO/a-InSe/metal Schottky devices

Theoretically, it is known that p-type semiconductors make the rectifying junction with metals whose work functions are less than those of semiconductors. However, reported experimental results have shown that InSe makes good rectifying barriers with low work function materials as well as with high work function metals (such as Pt or Au) which was attributed to the complex impurity structure of InSe due to its compensating nature [2]. According to the referred study, the barrier with the low work function metal is a typical Schottky structure with the negative space charge region; however for the case of a high work function metal (Au), the barrier is created by ionized deep donor levels. In this study, among all the TO/a-InSe/metal (In, Al, Ag, Au, C) structures, the best rectifying behavior was observed with the Ag contact, while diodes with the Au top contact have shown slight rectification. In, Al and C contacts result in almost ohmic non-rectifying behavior for all samples. Aluminum is known to form an oxidized layer which may easily become a blocking contact and not diffuse into the film that result in a non-rectifying behavior. Indium contacts were supposed to be rectifying because the work function of indium is less than the electron affinity of InSe; however, the *I–V* characteristics showed an almost ohmic behavior for these contact materials. This may be due to the In atoms that diffuse during the thermal evaporation into the InSe film and combine with other Se atoms in InSe [8]. Liquid colloidal graphite is used to achieve cold contact onto a-InSe thin films without thermal evaporation. Carbon has a work function greater than that of InSe; thus carbon is expected to be ohmic with p-InSe thin film which is observed by the measured current–voltage characteristics. The almost ohmic non-rectifying current–voltage characteristics of sandwich structures with Al, In and C top electrodes are illustrated in figure 1 on a semi-logarithmic scale.

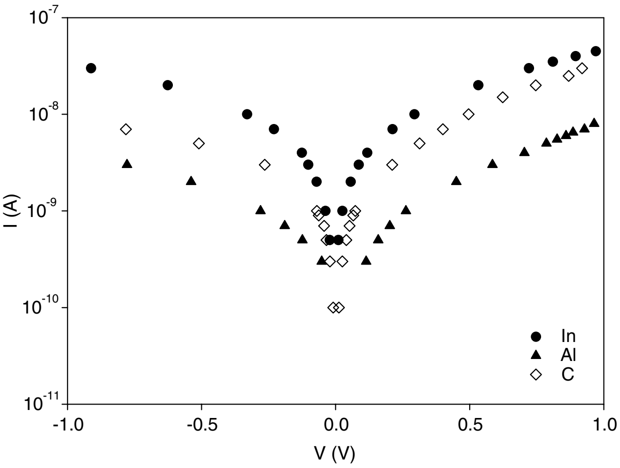

Figure 1. The non-rectifying current–voltage characteristics of TO/p-InSe/(In, Al, C) structures.

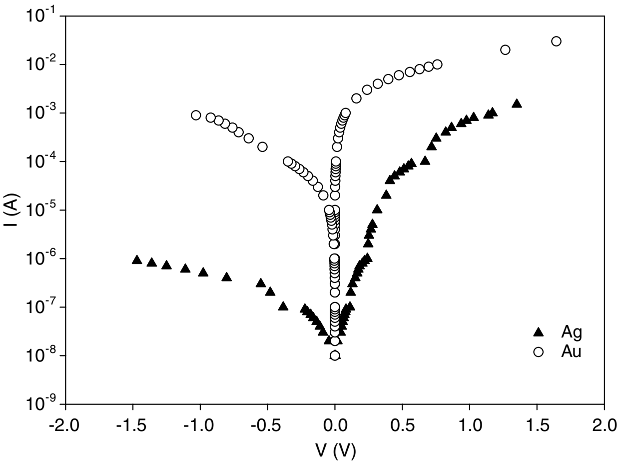

Figure 2. Typical rectifying current–voltage characteristics of TO/p-InSe/(Ag, Au) structures.

The *I–V* curves of typical rectifying structures of a-InSe/Ag and a-InSe/Au are shown in figure 2. Theoretically, the unexpected result of rectifying Au contacts might be due to the presence of deep donor levels in p-InSe films and the complex impurity structure of the films [2].

In the case of best rectifying system, TO/a-InSe/Ag, which we took into consideration for the rest of the analysis, the device is forward biased when the TO side is made positive with respect to the Ag electrode. The barrier is a typical Schottky barrier, formed when electrons are transferred from the metal to the semiconductor. The space charge region will be formed due to the capture centers for electrons in InSe. Thus, we may suggest a potential barrier at the interface. The forward current increases exponentially with increasing

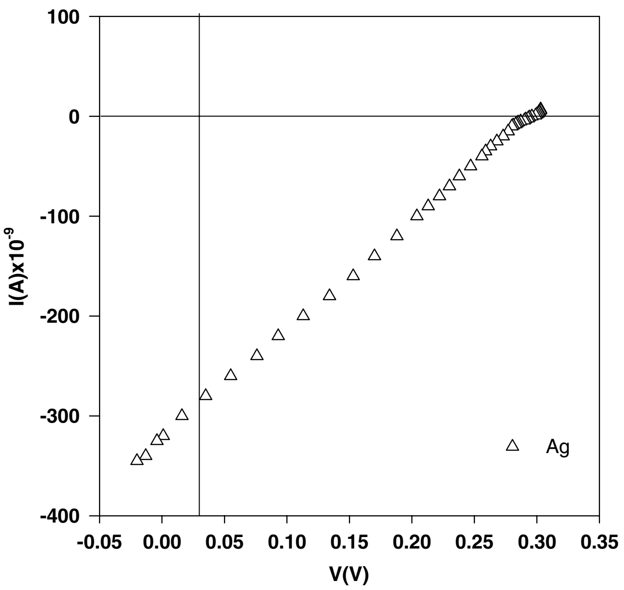

Figure 3. The current–voltage characteristic under illumination (AM1 condition) for a Schottky diode with an Ag top electrode.

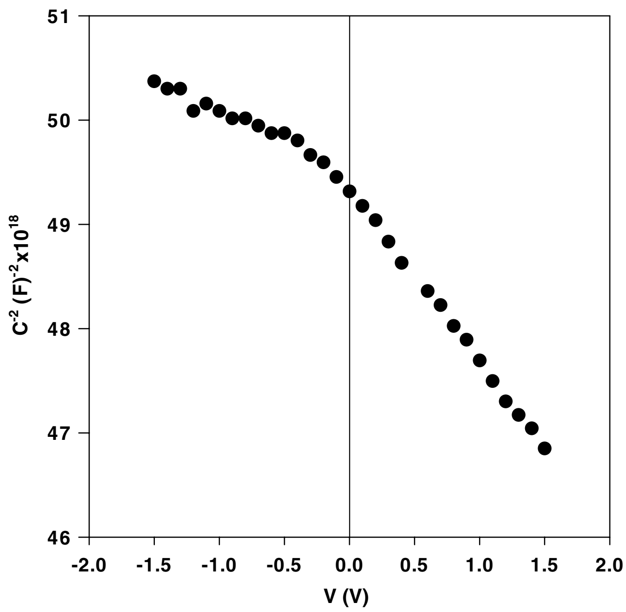

Figure 4. The plot of C^{-2}–V at 10 kHz under reverse bias of the TO/p-InSe/Ag system.

voltage whereas reverse current increases slowly up to the breakdown voltage after which irreversible breakdown occurs. The forward current is related to the applied voltage; for the Schottky barrier diodes it is given by the following relation:

$$I = I_s \left(\exp\left(\frac{qV_a}{nkT} \right) - 1 \right) \qquad (1)$$

where n is the diode ideality factor, V_a is the applied voltage and I_s is the saturation current given by the expression,

$$I_s = A^{**}AT^2 \exp\left(-\frac{q\phi_b}{kT} \right). \qquad (2)$$

In this equation, A is the area of the diode, A^{**} is the Richardson constant and ϕ_b is the barrier height. The ideality factor and the barrier height for the TO/a-InSe/Ag system were calculated by using equations (1) and (2) from the semi-logarithmic plot of the current–voltage characteristic of the diode. The ideality factor and the barrier height at room temperature were found to be around 2 and 0.7 eV, respectively. The deviation from ideality is attributed to the highly defective structure of the amorphous InSe film. The conduction mechanism is thought to be recombination in the depletion region through the localized states. As seen in figure 3, the current–voltage characteristic of TO/InSe/Ag system under illumination shows a straight line which indicates the effect of high series resistance found to be around 588 Ω in comparison with the sheet resistance of the film which was calculated to be around 100 Ω. The open-circuit voltage (V_{oc}) measured by taking the Ag electrode side as a positive terminal of voltage output and short circuit current (I_{sc}) were determined to be 300 mV and 3.2×10^{-7} A ($\sim$40 μA cm^{-2}), respectively.

C–V measurements indicated that junction capacitance is almost independent of the applied reverse bias, seen in figure 4. This may be attributed to the high resistivity of the InSe film of which the whole thickness may be depleted. However, frequency-dependent C–f measurements have been performed in the range of 1–1200 kHz and it was found that capacitance changes with frequency at each voltage value.

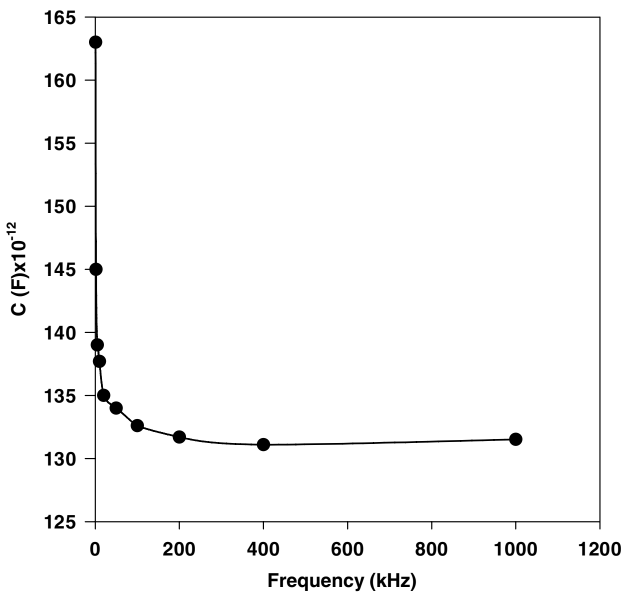

Figure 5. The variation of capacitance with frequency at zero bias.

Figure 5 shows the capacitance–frequency dependence at the zero bias. The variation of capacitance with frequency at low frequencies is stronger than at higher frequencies, which is the indication of the presence of interface states at the junction.

The number of interface states (N_{IS}) can be roughly estimated by using the following expression:

$$N_{IS} = \frac{(C_L - C_H)}{q} \qquad (3)$$

where C_L and C_H denote the low and high frequency capacitance values, respectively. At the zero bias and room temperature, the number of interface states was calculated from equation (3) to be around 2×10^8 cm^{-2} V^{-1}.

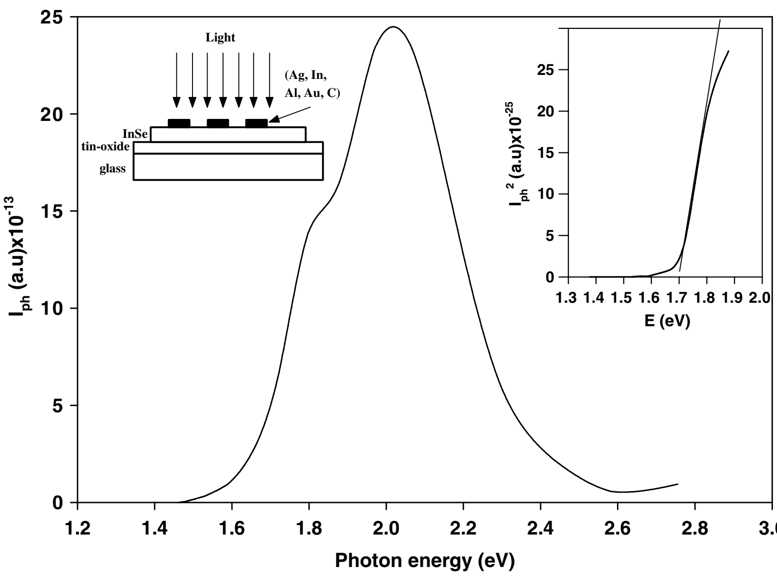

Figure 6. Spectral response of a typical p-InSe/Ag Schottky structure. The insets on the left side and right side illustrate the schematic view of the device geometrical configuration and the Fowler plot, respectively.

The spectral response distribution of TO/p-InSe/Ag structure illuminated from the Ag side in the photon energy range of 1.5–2.6 eV is given in figure 6. The short circuit photocurrent increases gradually with increasing incoming photon energy after the long wavelength threshold followed by a sharp increase corresponding to the transition between the band tails. The curve goes through a small shoulder around 1.8 eV which may be related to interface states. The photocurrent starts to decrease after 2 eV with increasing energy of the incoming photons because the photons at these energies are absorbed at or near the surface where recombination velocities are higher than those of the bulk of the semiconductor.

$$I_{ph}^2 \propto (h\nu - E_g). \qquad (4)$$

The band gap of the amorphous p-InSe thin films was obtained from the Fowler plot (in the inset of figure 6) according to equation (4). The extrapolation of the Fowler expression gives a value around 1.7 eV which is in well agreement with the values given in the literature [10].

4. Conclusion

The photovoltaic and diode properties of the amorphous p-InSe thin film based Schottky devices have been analyzed. The sandwich structure of SnO_2/a-InSe/Ag system has shown the best photovoltage and rectifying characteristics while the systems with Au top contact have shown some rectification with a poor photovoltage. Other top electrodes (Al, In, C) used in this work indicate almost ohmic characteristics. *C–V* and *C–f* measurements have indicated the presence of interface states at the junction which would limit the photocurrent due to the recombination of the charge carriers at the junction. High series resistance of the rectifying structures also limits the device efficiency which could be overcome by using a doping process to reduce the resistance of InSe thin films.

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