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Electrical Characterization of Sn/InSe: Mn Crystal Grown by Bridgman/ Stockbarger Method

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ABSTRACT

In this study, the electrical properties of InSe:Mn semiconductor grown by Bridgman-Stockbarger method have been examined. The current-voltage (I-V) measurements of Sn/InSe:Mn Schottky diode have been performed with 20 K increments in the range 140-380 K**.** The experimental barrier height (BH) decreased while ideality factor (n) increased as the temperature decreased. The experimental values of BH and (n) range from 0.496 eV and 3.926 at 140 K to 1.00 eV and 1.227 at 380 K. This behaviour has been attributed to the barrier in homogeneities by assuming a Gaussian distribution of barrier heights at the metal-semiconductor interface. From the temperature-dependent I–V characteristics of the Sn/InSe:Mn diode, Richardson constant A* has been calculated as 256.53 A / cm^2K^2 and 313.33 A/cm^2K^2 from a $\ln(I_0/T^2)$-$(kT)^{-1}$ plot for the two temperature regions, Respectively.

Keywords: InSe:Mn, Schottky diode, ideality factor

1 INTRODUCTION

It is well known that the single crystals of $A^{III}B^{VI}$ type compounds, in particular of Indium Selenide (InSe), crystallize in a layered structure where each layer contains two In and two Se close-packed sub layers with the stacking sequence Se–In–In–Se [1]. InSe is a layered semiconductor, which can be cleaved to yield high-quality surfaces and has been shown a new class of materials for solar energy conversion applications [2–3]. The bonding between two adjacent layers is of the weak Van der Waals type, while with in the layer the bonding is predominantly covalent. Depending on the packing of the layers the indicated single crystals form various modifications, in which the positions of band edges are determined by interlayer interactions. Binary semiconductor compounds such as InSe are of wide spread technological and scientific interest owing to their practical applications in the areas of visible and infrared light emitting diodes, infrared detectors, optical parametric oscillators, nonlinear optics, solar cells, optical frequency conversion, second harmonic generation devices and many other electro-optical devices.

Schottky barrier diodes (SBDs) are of the most simple of the MS (metal–semiconductor) contact devices due to their technological importance [4–5]. In particular, the Schottky diodes have important applications in bipolar integrated circuits such as clamps, load resistor, couplers, and level shifters [6,7]. Moreover, Schottky diodes with low barrier height (BH) play an important role in devices operating at cryogenic temperatures as infrared detectors, sensors in thermal imaging, microwave diodes, gates of transistors and infrared and nuclear particle detectors [7–8]. Therefore, analysis of the current voltage (I–V) characteristics of the SBDs at room temperature only does not give detailed information about their conduction process or the nature of barrier formation at the MS interface [8–9]. In the present study, the current-voltage (*I-V*) measurements of Sn/InSe:Mn Schottky diode have been performed with 20 K increments in the range 140-380 K**.** The temperature-dependent barrier characteristics of the diodes were interpreted by assuming Gaussian spatial distribution of barrier height.

2 EXPERIMENTAL PROCEDURE

The Schottky diodes were made with InSe:Mn single crystal samples cleaved from a large crystal ingot which was grown from non-stoichiometric melt by the Bridgman– Stockbarger method at our crystal growth laboratory. For the constituent of polycrystalline $A^{III}B^{VI}$, the first important step in obtaining high quality crystals is the purity of the basic elements which are being involved in the structure. These elements were weighed in a stoichiometric ratio accurate to 0.1 mg. The total mass of the elements was about 40g. The basic criteria for this choice were; first a sufficient need to justify the cost of one run, second minimal loss of the material in case of breakage. This stoichiometric ratio necessary to produce 40g InSe was calculated using the following relationships:

$M_{In} = (M_{Se}/A_{Se})A_{In}$

with total mass,

$M_{In}+M_{Se} = 40$ g where, M and A are total and atomic masses, respectively.

InSe:Mn (0.03wt%Mn) single crystals were grown by using the Bridgman/Stockbarger method at the same time. Sealed quartz ampoule was annealed at 950°C for 15h in the out gassing furnace designed in our laboratories. The temperature of quartz ampoule was decreased to room temperature in 24h. The mix In–Se (0.03wt%Mn) put into quartz ampoule and quartz ampoule was sealed under a vacuum of 10^{-6} mbar. Quartz ampoules were coated with carbon. The crucible was suspended in the middle of the vertical furnace with two zone designed. The temperature of furnace was increased to 950°C and stayed at that temperature for 1 h and then decreased to 750°C and stayed at that temperature for 5h. The temperature of lower zone of furnace was reduced to 50°C. The prepared InSe:Mn single crystal ingots were 10mm in diameter and about 60mm in length. The ingots had no cracks or voids on the surface. No polishing or cleaning treatments were carried out on the cleaved faces of the samples because of the natural mirror-like cleavage faces. They were cleaved into perpendicular planes of naturally cleaved planes. InSe:Mn samples were cleaved from the ingots with a razor blade and cut into 155 μm thickness.

The back ohmic contact was realized by evaporating indium followed by heat treatment at 300°C for 3 min. in N_2 atmosphere on the freshly cleaved InSe:Mn. No further polishing or cleaning treatment was required because of the natural mirror-like cleavage faces of the samples. The Schottky contacts were formed by evaporating Sn as dots with diameter of about 0.5 mm on the front surface of the InSe:Mn.

The current–voltage (I–V) characteristics of the devices were measured in the temperature range 140–380 K using a Leybold Heraeus closed-cycle helium cryostat that enables us to make measurements in the temperature range 140–380 K, and a Keithley 487 Pico ammeter/Voltage Source in dark conditions. The sample temperature was always monitored by a copper-constantan thermocouple and a Windaus MD850 electronic thermometer with sensitivity better than ± 0.1 K.

The forward-bias current through a uniform metal–semiconductor interface due to thermionic emission can be expressed as [4]:

$$I = I_0 \left[\exp\left(\frac{qV}{nkT} \right) - 1 \right] \quad (1)$$

where I_0 is the saturation current defined by

$$I_0 = AA^* T^2 \exp\left(-\frac{q\phi_{ap}}{kT} \right) \quad (2)$$

where, the quantities V, A, A^*, T, k, q, ϕ_{ap} and n are the forward-bias voltage, the effective diode area, effective Richardson constant for InSe:Mn, temperature in Kelvin, Boltzmann constant, electronic charge and the zero bias apparent BH and ideality factor, respectively. From Eq. (1), n can be written as

$$n = \frac{q}{kT} \left(\frac{dV}{d(\ln I)} \right) \quad (3)$$

From the temperature-dependent I–V characteristics of the Sn/InSe:Mn diode, Richardson constant A* has been calculated as 256.53 A / cm^2K^2 and 313.33 A / cm^2K^2 from a $\ln(I_0/T^2)$-$(kT)^{-1}$ plot for the two temperature regions respectively.

The electrical I–V measurements of the five Sn/InSe:Mn/In Schottky diodes were carried out in the temperature range 140–380 K with a temperature step of 20 K, and the I–V characteristics of one of the dots are given in Fig.1. These I–V plots shift towards the higher bias side with decrease in temperature. The experimental values of the barrier height ϕ_{ap} and the ideality factor n for the device were determined from intercepts and slopes of the forward-bias ln(I) versus V plot at each temperature, respectively. The temperature-dependent I–V characteristics of the dots were very near each other. The characteristics of the dots were very near each other. The standard error for the ideality factor and barrier height values was calculated at each temperature. The standard error should be considered as different from the standard deviations derived from the Gaussian distributions value being a measure of the barrier homogeneity. The experimental values of BH and (n) range from 0.496 eV and 3.926 at 140 K to 1.00 eV and 1.227 at 380 K respectively.

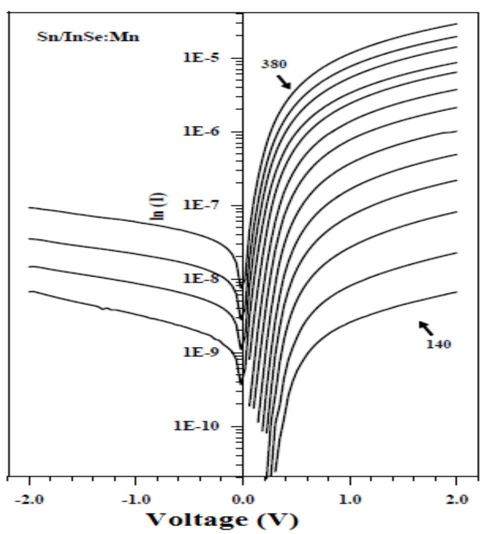

Figure 1: Experimental forward-bias current–voltage characteristics of a typical Sn/InSe:Mn/In Schottky contact in the temperature range 140-380 K. Measurements were carried out with a temperature step of 20 K.

The experimental barrier height (BH) decreased while ideality factor (n) increased as the temperature decreased Fig. 2 (indicated by closed triangles) shows the values of n as a function of temperature. The experimental value of n increased with a decrease in temperature as can be seen in Fig. 2. The experimental values of ϕ_{ap} (indicated by open triangles in Fig. 3) as a function of the temperature decreased with a decrease in temperature. Standard error for the ideality factor and barrier height values was calculated at each temperature. The standard error should be considered as different from the standard deviations derived from the Gaussian distributions value being a measure of the barrier homogeneity. Fig. 4 (indicated by open triangles) shows a conventional activation energy ln (I_0/T^2) versus 1/T plot according to Eq. (2).

The continuous curves show estimated values of ideality factor using characteristic tunnelling energy for two Gaussian distributions of barrier heights with ρ_2=0,325 $\rho_{3=}$ 0,0331 V in 220 K - 380 K (the curve 1) and ρ_2=0,156 $\rho_{3=}$ 0,0145 V in 140–220 K (the curve 2).

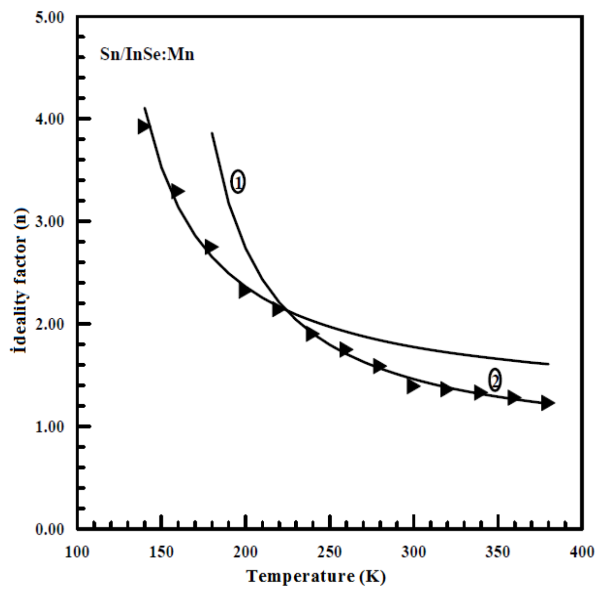

Figure 2: Temperature dependence of the ideality factor for the Sn/InSe:Mn/In Schottky contact (the filled triangles).

An experimental ln(I_0/T^2) versus 1/T plot shows significant deviation from linearity at low temperatures while it should yield a straight line with a slope given by a BH at 0 K, ϕ_{bo} (T = 0). The experimental data are seen to fit asymptotically to a straight line at higher temperatures only. An activation energy value of 0.36 eV from the slope of this straight line was obtained for the device. Bowing of the experimental ln(I_0/T^2) versus 1/T curve may be caused by the temperature-dependent of the BH and ideality factor due to the existence of the surface in homogeneities of the InSe:Mn substrate [9–10]. As will be discussed below, the deviation in the Richardson plots may be due to the spatially inhomogeneous BHs and potential fluctuations at the interface that consist of low and high barrier areas [9–11,12–13], that is, the current through the diode will flow preferentially through the lower barriers in the potential distribution. As explained in refs [9–11,12–13], since current transport across the MS interface is a temperature activated process, at low temperatures, current transport will be dominated by current flowing through the patches of lower SBH and larger ideality factor. As the temperature increases, the dominant BH will increase with the temperature and bias voltage [9–11, 12–13].

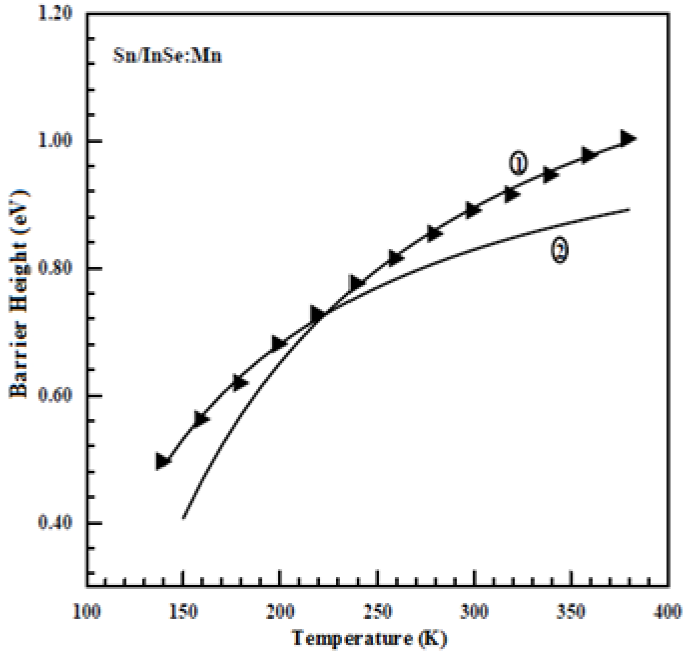

Figure 3:The continuous curve related to the filled circles represents estimated values of ϕ_b using thermionic field emission theory for two Gaussian distributions of barrier heights with ϕ_b=1.384 eV and σ_s = 0,159 V in 220–380 K (the curve 1) and ϕ_b=1,126 eV and σ_s = 0,124 V in 140–220 K (the curve 1).

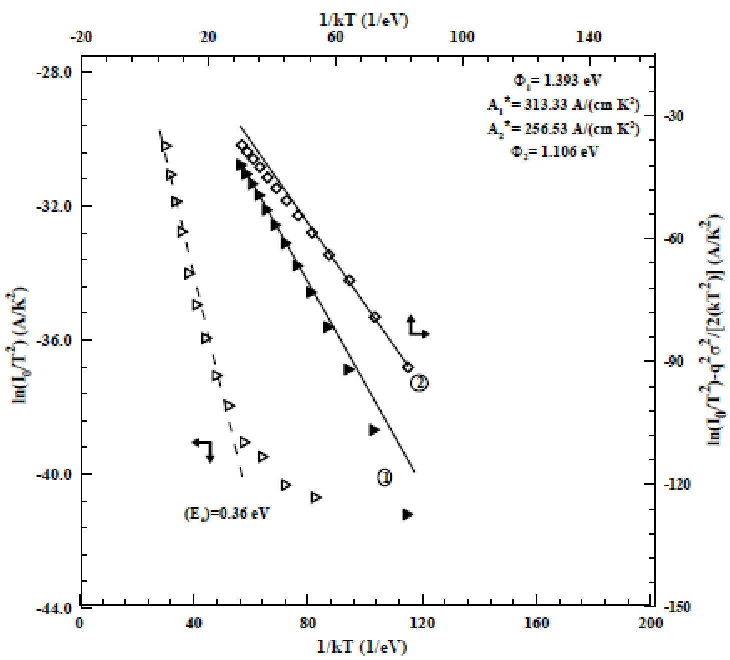

Figure 4: Richardson plot of the $\ln(I_0/T^2)$ vs. 1/T plot (the open triangles) and modified Richardson $\ln(I_0/T^2 - q^2\sigma_s^2/2k^2T^2)$ vs. 1/T plot for the Sn/ InSe:Mn/In Schottky diode according to two Gaussian distributions of barrier heights.

The decrease in the barrier height with a decrease in temperature can be explained by the lateral distribution of BH if the barrier height has a Gaussian distribution of the barrier height values over the Schottky contact area with the mean barrier height ϕ_b and standard deviation σ_s, and by thermionic field emission (TFE) [13–15]. Indeed, the ideality factor and the I–V barrier height and all functions derived from them can be fitted to two different theoretical models [14–15]. The standard deviation is a measure of the barrier homogeneity. The Gaussian distribution of the BHs yields the following expression for the BH [11–16]:

$$\phi_{ap}=\phi_b-\frac{q\sigma_s^2}{2kT} \quad (4)$$

Where ϕ_{ap} is the apparent BH measured experimentally. The above expression for the apparent barrier height construction was used already by Song et al. [16] and also by Werner and Gὒttler [10]. The temperature dependence of is usually small and can be neglected. The observed variation of ideality factor with temperature in the model is given by [8]

$$\left(\frac{1}{n_{ap}}-1\right)=-\rho_2+\frac{q\rho_3}{2kT} \quad (5)$$

where n_{ap} is apparent ideality factor and ρ_2 and ρ_3 quantify the voltage deformation of the BH distribution.

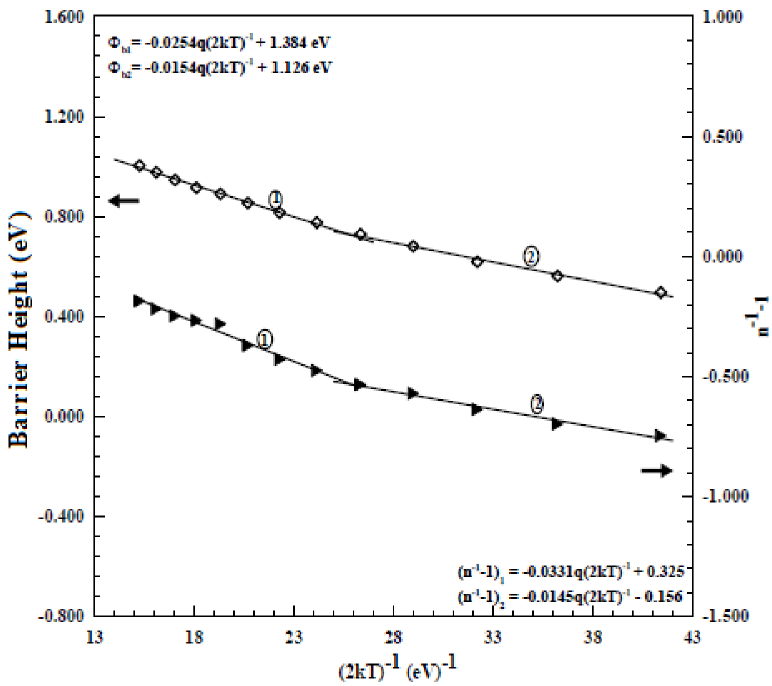

Figure 5: Zero-bias apparent barrier height (the open triangles) and ideality factor (the filled triangles) vs. 1/(2 kT) curves of the Sn/InSe:Mn/In Schottky contact according to two Gaussian distributions of BHs.

The linearity of the apparent barrier height or ideality factor versus 1/T curves in Fig. 5, and the continuous curves in Figs. 2, 3 and 5 show that the temperature-dependent experimental data of the Sn/InSe:Mn/In Schottky contact are in agreement with the recent model which is the related to thermionic emission over a Gaussian BH distribution [11–16]. Fitting of the experimental I–V data to Eqs. (2) and (3) gives ϕ_{ap} and n_{ap}, respectively, which should obey Eqs. (4) and (5). Thus, the plot of ϕ_{ap} versus 1/T (Fig. 5) should be a straight line with the intercept at the ordinate determining the zero bias mean BH ϕ_{bo} and a slope giving the zero bias standard deviation σ_s. The above observations indicate the presence of two Gaussian distributions of barrier heights in the contact area. When the dots have been considered, the intercepts and slopes of these straight lines given two sets of values of ϕ_{bo} and σ_s as 0.124 V 1,393 eV in the temperature range 220 –380 K (the distribution 1), and as 0.157 V 1,106 V in the temperature range

140 – 220 K (the distribution 2). Furthermore, the ϕ_{ap} values estimated from Eq. (4) over the entire temperature range 140–320 K using the two ϕ_{bo} and σ_s are shown by the continuous curves 1 and 2 in Fig. 3. That is, the continuous solid lines related to the open triangles in Fig. 3 represent the data estimated with these parameters using Eq. (4).

The existence of a double Gaussian in Schottky diodes was already experimentally proven by BEEM [17–18]. These changes were ascribed to the chemical treatment of the semiconductor surface [19–20]. Likewise, as indicated also by Chand and Kumar [21], the existence of a double Gaussian in the metal/semiconductor contacts can be attributed to the nature of the in homogeneities themselves in the two cases. This may involve variation in the interface composition/phase, interface quality, electrical charges and non stoichiometry, etc. They are important enough to electrically influence the I–V characteristics of the Schottky diodes, at particularly low temperatures. Thus, I–V measurements at very low temperatures are capable of revealing the nature of barrier in homogeneities present in the contact area. That is, the existence of a second Gaussian distribution at very low temperatures may possibly arise due to some phase change taking place on cooling below a certain temperature. Furthermore, the temperature range covered by each straight line suggests the regime where the corresponding distribution is effective [21].

Similarly, as can be clearly seen from Fig. 5, the plot of nap versus 1/T should also possess different characteristics in the two temperature ranges because the diode contains two barrier height distributions. The values of ρ_2 obtained from the intercepts of the experimental nap versus 1/T plot are -0.325 in 220–380 K range (the distribution 1) and 0.156 in 140–220 K range (the distribution 2), whereas the values of ρ_3 from the are -0.0331 V in 140–220 K range and -0.0145 V in 140–220 K range. The linear behaviour of this plot demonstrates that the ideality factor indeed expresses the voltage deformation of the Gaussian distribution of the Schottky BH. The continuous solid lines in Fig. 4 represent data estimated with the above values of ρ_2 and ρ_3 using characteristic tunnelling energy equation. As can be seen, the computed values exactly coincide with the experimental results in the respective temperature ranges for two different distributions. As can be seen from the n_{ap} versus 1/T plot, ρ_3 value or the slope of the distribution 1 is larger than that of the distribution 2, therefore we may point out that the distribution 1 is wider and relatively higher barrier height with bias coefficients ρ_2 and ρ_3 being smaller and larger, respectively. Thus, we can say that the distribution 2 at very low temperatures may possibly arise due to some phase change taking place on cooling below a certain temperature. As indicated above, the conventional activation energy $\ln(I_o/T^2)$ versus 1/T plot has showed nonlinearity at low temperatures.

To explain these discrepancies, according to the Gaussian distribution of the BH, we can be rewritten:

$$\ln\left(\frac{I_0}{T^2}\right) - \left(\frac{q^2\sigma_s^2}{2k^2T^2}\right) = \ln(AA^*) - \frac{q\Phi_{bo}}{kT} \qquad (6)$$

Using the experimental I0 data, a modified $\ln(I_0/T^2 - q^2\sigma_s^2/2k^2T^2)$ versus 1/T plot can be obtained according to Eq. (6) and should give a straight line with slope directly yielding the mean ϕ_{bo} and the intercept (=lnAA^*) at the ordinate determining A^* for a given diode area A. The $\ln(I_0/T^2 - q^2\sigma_s^2/2k^2T^2)$ values were calculated for both two values of s obtained for the temperature ranges of 220–380 K and 140–220 K. Thus, the closed triangles and open squares in Fig. 4 have given the $\ln(I_0/T^2 - q^2\sigma_s^2/2k^2T^2)$versus 1/T plots for both two values of σ . The best linear fitting to these modified experimental data are depicted by solid lines in Fig. 4 which represent the true activation energy plots in respective temperature ranges.

The statistical analysis yielded zero bias mean BH ϕ_{bo} of 1,393 eV (in the range 220–380 K) and 1.106 eV (in the range 140–220 K). These values match exactly with the mean BHs obtained from the ϕ_{ap} versus 1/T plot in Fig. 5. The intercepts at the ordinate give the Richardson constant A^* as 256,53 ($A/cm^2 K^2$) (in 220–380 K range) and 313,33 ($A/cm^2 K^2$) (in 140–220 K range) without using the temperature coefficient of the BHs. If the current transport is controlled by the thermionic field emission theory, the relationship between the current and voltage can be expressed [4].

3 CONCLUSION

In this research, InSe:Mn single crystals have been grown by using the Bridgman/Stockbarger method. The ingots have no cracks and voids on the surface in ingots. There is no process to polish and clean treatments at cleavage faces of these samples because of the natural mirror-like cleavage faces. InSe has specific impurities arising from its crystal structure. When transition element is doped into InSe single crystals, these impurities are eliminated by the transition elements from the crystal structure during the growth process. It has been concluded from the I-Measurements that the band gap energy and ideality factor values for the InSe:Mn becomes 0,496 eV, n=3,936 at 140 K, 0,89 eV n=1,390 at 300 K and 1.00 eV n= 1,227 at 380 K, respectively. The electrical measurements have also shown that the temperature-dependent current–voltage (I–V) characteristics of Sn/InSe:Mn/In Schottky diodes can be explained by the double Gaussian distribution of BHs. Furthermore, the modified the $\ln(I_0/T^2-q^2\sigma_s^2/2k^2T^2)$versus 1/T plot for the two temperature regions have given ϕ_{bo} and A* as 1,393 eV and 1,106 eV, and 256,53 and 313,33 (A/cm^2 K^2), respectively. Furthermore, in the temperature range 140–380 K, it has concluded that the experimental values of ideality factor are in agreement with the curve obtained using the characteristic energy value and the coefficient of barrier height value thus; we have seen that the current through the junction can also be connected with TFE.

4 ACKNOWLEDGEMENTS

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REFERENCES

[1] Mooser E. (1976). in:(Ed.), Physicsand Chemistry of Material with Layered Structure Riedel:Dordrecht

[2] Kovalyuk Z. D. and Katerynchuk V. M. (2005). I V Mintyanskii, A I Savchuk, O M Sydor, Mater.Sci.Eng. B118, 147

[3] Gürbulak B., Kundakçı M., Ateş A and Yıldırım M..(2007). M, Phys.Scr.75, 424

[4] Rhoderick E. H. and Williams R. H.(1988). Metal–semiconductor Contacts, second ed.(Clarendon, Oxford).

[5] Morimoto T.(1995). IEEE Trans. Electron. Dev. 42, 915

[6] Huang S. H., Tian Y. and Lu F.(2004). Appl. Surf. Sci. 234, (1–4) , 362

[7] Özdemir A. F., Türüt A. and Kökçe A.(2006). Semicond. Sci. Technol. 21 (3),298

[8] Chand S and Kumar J.(1995). Semicond. Sci. Technol. 10, 1680

[9] Wenckstern H., Biehne G., Rahman R. A., Hochmuth H., Lorenz M. and Grundmann M. (2006). Appl. Phys. Lett. 88, (9), 092102

[10] Werner J. H. and Gùttler H. H.(1991). J. Appl. Phys. 69, 1522

[11] Karataş Ş., Altındal Ş., Türüt A. and Özmen A.(2003). Appl. Surface Sci. 217,250

[12 Karataş Ş. and Altındal Ş.(2005). Mater. Sci. Eng. B 122, 133

[13] Horváth Z. J.(1996). Solid-State Electron,39, 176

[14] Ayyildiz E., Cetin H. and Horváth Z. J.(2005). Appl. Surf. Sci. 252, 1153

[15 Horvath Z. J., Rakovics V., Szentpali B., Pûpoki S.and Zdansky K. (2003). Vacuum 71, 113

16] Song Y. P., Van Meirhaeghe R. L., Lafle´r W. H. and Cardon F.(1986) . Solid-State Electron 29, 633

[17] Vanalme G. M., Goubert L., Van Meirhaeghe R. L., Cardon F. and van Daele P.(1999). Semicond. Sci. Technol. 14, 871

[18] Vanalme G .M., Van Meirhaeghe R. L., Cardon F.and Van Daele P.(1997). Semicond. Sci. Technol. 12, 907

[19] Biber M., Çakar M. , Türüt A. and Mater J.(2001). Sci-Mater. Electron. 12 , 575

[20] Kampen T., Schuller A., Zahn D. R. T., Biel B., Ortega J., Perez R. and Flores F. (2004). Appl. Surf. Sci. 234, (1–4), 341.

[21] Chand S. and Kumar J.(1996). Semicond. Sci.Technol. 11,1203

[22] Duman S., Gurbulak B. and Turut A. (2007). Applied Surface Science 253, 3899–3905

[23] Gürbulak B., Şata M., Dogan S., Duman S., Ashkhasi A. and Keskenler E. F. (2014). Physica E 64, 106–111