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ABSTRACT

The effect of the TiO₂ interfacial layer on rectifying junction parameters of Ag/TiO₂/n-InP/Au Schottky diodes has been investigated using current-voltage (I-V) measurements in the temperature range of 120–420 K with steps of 20 K. The barrier height is found to be 0.19 eV and 0.68 eV from current-voltage characteristics at 120 K and 420 K, respectively. At 120 K and 420 K, the ideality factor is found to be 3.52 and 1.01 for the Ag/TiO₂/n-InP/Au Schottky barrier diode, respectively. These results are gained by the thermionic emission theory at room temperature. Values of series resistances gained from the Cheung-Cheung method are compared with results gained from a modified Norde method. These experimental results indicate that series resistance decreases with an increase in temperature. The current-voltage (I-V) measurements showed that the diode with the TiO₂ interfacial layer gave a double Gaussian property in the examined temperature range. The Richardson constant is also calculated from a modified Richardson plot and is found to be very compatible with the theoretical value. Interface state density is also examined by using I-V characteristics.

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I. INTRODUCTION

Metal-Semiconductor (MS) structures are an important research area in the electronics industry. Formation and characterization of these structures may result in producing some useful technological devices. The reason why Schottky contacts attract much attention in the scientific world is because it is still not possible to explain correctly how the Schottky barrier is formed. Therefore, to understand and make a correct description of the Schottky barrier height (BH), many researchers make different investigations by using different materials and methods around the world. During these studies, different kinds of electronic devices are produced by researchers, such as optoelectronic devices, microwave devices, solar cells, detectors, and circuits with chips that can be used in qualified communication. In the electronics industry, MS contacts have a large application field. Results gained by measurements and calculations by using current-voltage (I-V) characteristics of MS structures are usually different from an ideal thermionic emission (TE) model. Therefore, examination of I-V characteristics only at room temperature is not enough for having knowledge about the barrier at the MS interface or conduction mechanisms of the diode. We can understand different

sides of conduction mechanisms by using temperature dependent I-V characteristics.^{1–3} According to analysis results of I-V characteristics of surface behavior diagrams (SBDs), it is seen that there is a decrease in BH, Φ_b , and an increase in the ideality factor n when the temperature decreases.⁴

The reason for the decrease in BH and the increase in the ideality factor when the temperature decreases is that other electrical abnormalities may be related to Schottky barrier height (SBH) inhomogeneity. Abnormal conduct in SBDs can be partly described by accepting that there are small regions with lower BH than the junction's main BH. This circumstance may affect the current across the MS contact with a great percentage. Tung and co-workers found larger ideality factors and smaller BHs when they increased the inhomogeneity of barriers.^{5–8} Schottky barrier inhomogeneity, which means potential fluctuations at the top of the barrier, may be caused by field emission at the interface.⁹ In many previous works, different operations are made in order to increase the naturally low BH of InP. Hattori and Izumi¹⁰ deposited the P_xO_y compound as an interfacial layer. Wada et al.¹¹ showed that forming a very thin oxide layer between metal and InP caused a decrease in leakage current and an increase in BH.

Hasegawa¹² showed that the SBH can be increased by using interfacial layers and attempted to describe the mechanisms related to the increasing of BH by using Fermi level pinning. Davis and co-workers¹³ investigated the effect of illumination over the interfacial layer and the changing in BH. Kamimura *et al.*¹⁴ formed an oxide layer at the interface by etching the sample into the Bromur solution at room temperature. As a result of these studies, it is seen that electrical behaviors of the devices are strongly dependent on the preparation process of semiconductor surface for contact and choosing the most suitable metal. In the present study, Ag/TiO₂/n-InP/Au Schottky barrier diodes were fabricated using the sputtering method with 120 Å thickness of the TiO₂ interfacial layer, after forming Au back contact on the n-InP substrate (Fig. 1). The purpose of adding TiO₂ on the interface is to examine its effect on device performance. Bilgili did this examination in his master's thesis for the first time in 2015¹⁵ and found out that as the thickness of the TiO₂ layer decreases, diode parameters get more ideal. As TiO₂ is grown on the interface by the sputtering method, it diffuses over n-InP better and changes the work function. This results in improvement of device performance. The influence of the TiO₂ interlayer on p-InP is also not investigated by anyone in the literature. But the influence of it is investigated for p-Si. If an estimation is made, because of the negative charge of oxygen in TiO₂, it will make a perfect contact on p-InP. It will affect the width of the depletion region, so the interface states and device performance will improve. I-V characteristics were measured and analyzed in the temperature range of 120–420 K by steps of 20 K.

II. EXPERIMENTAL PROCEDURE

Schottky barrier diodes were prepared on a 500 μm thick n-type InP semiconductor with orientation (100) and carriers concentration of $3.13 \times 10^{18} \text{ cm}^{-3}$. The wafer was degreased consecutively in trichloroethylene, acetone, and methanol by using ultrasonic agitation for 5 min in each step. The degreased was etched with HF:H₂O (1:10) for 30 s to remove native oxides on the surface. Back side ohmic contact was made by sputtering Au under 1×10^{-6} Torr pressure with a thickness of 150 nm. Then, samples were annealed at 325 °C for 4 min under a pure N₂ atmosphere. Before Schottky contacts of Ag, TiO₂ were deposited on the polished side of n-InP with a thickness of 120 Å. Schottky contacts with 0.75 mm

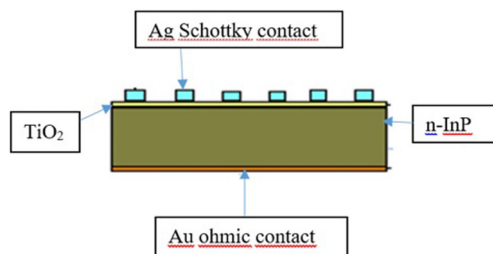


FIG. 1. The structure of the Ag/TiO₂/n-InP/Au Schottky barrier diode.

diameter were formed on the TiO₂ film on the sample by using a shadow steel mask. I-V measurements of the devices were carried out using a Keithley 2400 sourcemeter in the temperature range of 120–420 K using a temperature controlled vpf-475 cryostat. Sample temperature was monitored using a thermocouple close to the sample, and the temperature is controlled with a Lake Shore model 321 autotuning temperature controller. Temperature stability for each run was better than 0.1 K.

III. RESULTS AND DISCUSSION

A. Current-voltage characteristics (I-V)

According to TE, the equation related to the current between metal and semiconductor is

$$I = I_0 \exp\left(\frac{q(V - IR)}{nKT}\right) \left[1 - \exp\left(-\frac{q(v - IR)}{kT}\right)\right]. \quad (1)$$

Here I_0 is the saturation current. I_0 is found by y axis intercept of the $\ln(I)$ -V plot's linear part in the forward-bias region ($V = 0$). Saturation current I_0 is calculated by

$$I_0 = A A^{**} \exp\left(\frac{-q\Phi_{b0}}{kT}\right). \quad (2)$$

Here A is the diode area, Φ_{b0} is the barrier height, A^* is the Richardson constant, k is the Boltzman constant, and T is the temperature. (For n-InP, the Richardson constant is $9.4 \text{ A cm}^{-2} \text{ K}^{-2}$.) By using Eq. (2), Φ_{b0} can be calculated as

$$\phi_{b0} = \frac{kT}{q} \ln\left(\frac{AA^*T^2}{I_0}\right). \quad (3)$$

In the forward-bias region, $\ln(I)$ vs. V plot is expected to be linear. If this plot is not linear, this means that the ideality factor is large and the diode is not an ideal diode. The reason for this may be the existence of an interfacial layer or recombination at the interface. The ideality factor can be calculated as¹⁶

$$n = \frac{q}{kT} \left(\frac{dV}{d\ln I}\right). \quad (4)$$

Current-voltage characteristics of the produced diode are shown in Fig. 2 in the temperature range of 120–420 K.

According to the TE model, the ideality factor is calculated by the slope of experimental $\ln(I)$ vs. V plot. The barrier height at zero-bias is determined by the intercept of this plot. At 120 K and 420 K, the ideality factor is found to be 3.52 and 1.01 for the Ag/TiO₂/n-InP/Au Schottky barrier diode, respectively. The barrier height is found to be 0.19 eV and 0.68 eV for the same diode at the same temperatures. The change of the ideality factor and the barrier height vs. temperature is shown in Fig. 3.

According to this plot, the ideality factor decreases and the barrier height increases with an increase in temperature.

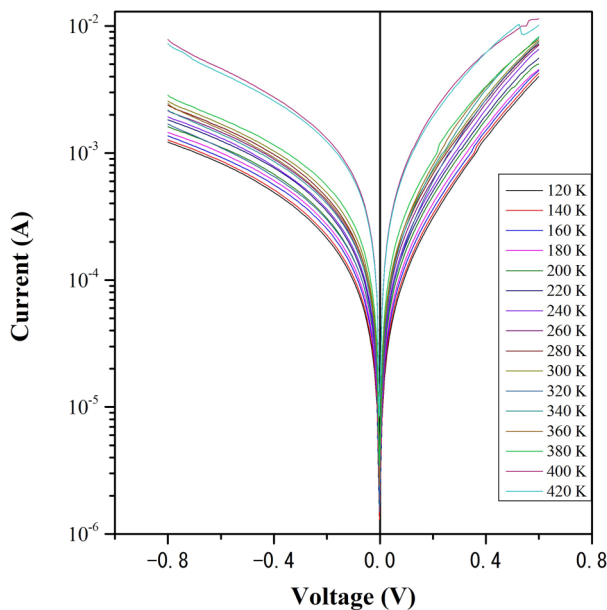


FIG. 2. Reverse and forward bias I-V characteristics of the Ag/TiO₂/n-InP/Au Schottky diode as a function of temperature.

This result indicates that both parameters are strongly dependent on temperature. Because current transport across the MS interface is dependent on temperature, at low temperatures, the current is formed by the carriers which surmount the lower barriers. As a result, the dominant barrier height decreases and the ideality factor increases. At high temperatures, the opposite of this process comes out.

In general, the semilogarithmic I-V plot's forward-bias low voltage region shows linearity. However, when the voltage

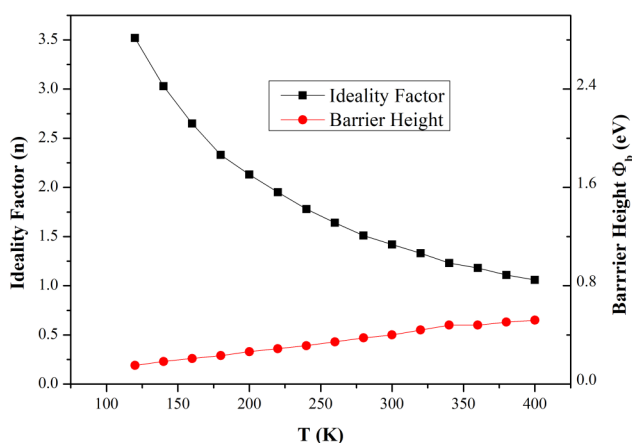


FIG. 3. Temperature dependence of the ideality factor and barrier height for the Ag/TiO₂/n-InP/Au Schottky diode.

increases, a deviation from linearity occurs. Some of the reasons for this are interface states and resistance caused by the oxide layer. Series resistance is one of the important parameters to let us understand the electrical characteristics. In order to determine series resistance, there are different methods. The first of these methods is the Cheung-Cheung method. By using this method, it is possible to determine parameters, such as n , R_s , and Φ_b . These parameters are determined by $dV/d(\ln I)$ vs. I and $H(I)$ - I function plots:¹⁷⁻¹⁹

$$dV/d(\ln I) = nkT/q + IR_s, \quad (5)$$

$$H(I) = IR_s + n\Phi_b. \quad (6)$$

As can be seen in Eqs. (5) and (6), the slope of $dV/d(\ln I)$ vs. I plot (Fig. 4) gives us series resistance (R_s) and intercept of y axis gives us the ideality factor (n). Also, the slope of $H(I)$ vs. I plot (Fig. 5) gives us series resistance and together with the ideality factor n , gained from $dV/d(\ln I)$ vs. I plot, intercept point gives us ($n\Phi_b$). We deduce Φ_b from this intercept point. By using this method, n , R_s , and Φ_b are calculated. Results can be seen in Tables I and II.

Because of the large value of series resistance, in spite of $\ln(I)$ vs. V plot, the Norde method is a more suitable method for determining the barrier height. This method is also improved for calculating series resistance. The only disadvantage of this method is the difficulty of determining the minimum point on the plot. According to the Norde method, the Norde function is given by the following equation,

$$F(V) = \frac{V}{\gamma} - \frac{1}{\beta} \ln \left(\frac{I(V)}{AA^{**}T^2} \right). \quad (7)$$

Here, $\beta = q/kT$ and γ is an integer greater than ideality factor.

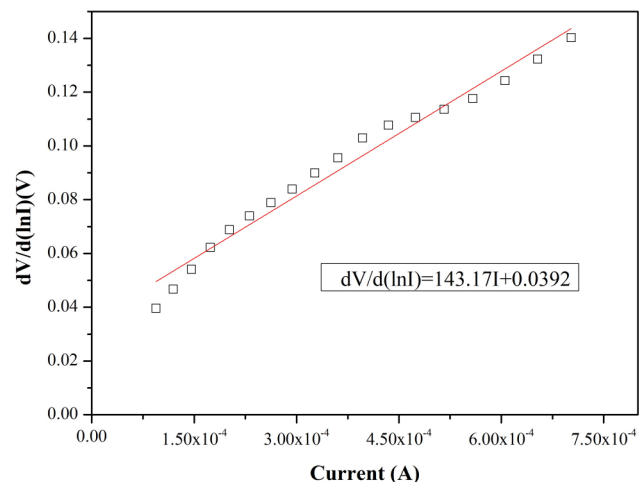


FIG. 4. Plot of $dV/d(\ln I)$ versus I for the Ag/TiO₂/n-InP/Au Schottky diode at room temperature.

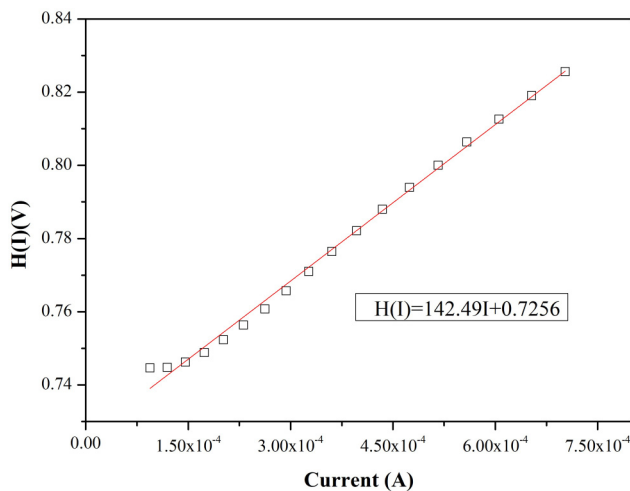


FIG. 5. Plot of $H(I)$ versus I for the Ag/TiO₂/n-InP/Au Schottky diode at room temperature.

$F(V)$ vs. V function has a minimum point as can be seen in Fig. 6, V_{\min} corresponds to F_{\min} . By using the following equation, the barrier height can be calculated

$$\varphi_b = F_{\min} + \frac{V_{\min}}{\gamma} - \frac{kT}{q}. \quad (8)$$

I_{\min} corresponds to V_{\min} and R_s is calculated by the following equation,^{20,21}

$$R_s = \frac{kT(\gamma - n)}{qI_{\min}}. \quad (9)$$

Results gained from this method are shown in Table III. As can be seen in Tables I–III, results gained from the Cheung-Cheung method and Norde method are in good agreement with each other.

Change of series resistance vs. temperature can be seen in Fig. 7. As can be seen in Fig. 7, series resistance decreases

TABLE I. Series resistance (R_s) and ideality factor (n) values according to the Cheung-Cheung method [$dV/d(\ln I)$].

T (K)	R_s (Ω)	n
120	307	3.87
140	282	3.42
160	273	2.86
180	239	2.62
200	213	2.33
220	194	2.16
240	186	1.9
260	158	1.81
280	146	1.65
300	143	1.51

TABLE II. Series resistance (R_s) and barrier height (Φ_b) values according to the Cheung-Cheung method, $H(I)-I$.

T (K)	R_s (Ω)	Φ_b (eV)
120	305	0.18
140	280	0.21
160	270	0.25
180	237	0.28
200	212	0.31
220	194	0.34
240	184	0.38
260	157	0.41
280	146	0.45
300	142	0.48

with an increase in temperature. This may be attributed to the higher energy of the carriers at higher temperatures so that they can move more freely toward the metal in the expanded interfacial layer with higher mobility.

An alternative method to calculate the barrier height is the Richardson plot (Fig. 8). The equation to draw this plot is

$$\ln\left(\frac{I_0}{T^2}\right) = \ln(AA^{**}) - \frac{q\Phi_{b0}}{kT}. \quad (10)$$

According to this equation, $\ln(I_0/T^2)$ vs. $1000/T$ plot is expected to give a straight line. The slope of this plot gives us the barrier height at $T = 0$ K. This value is also called activation energy. The slope line intercept point of this plot gives us the Richardson constant (A^*). For the Ag/TiO₂/n-InP/Au Schottky barrier diode, the Richardson constant and activation energy are calculated as $6.31 \times 10^{-7} \text{ A cm}^{-2} \text{ K}^{-2}$ and 0.23 eV, respectively.

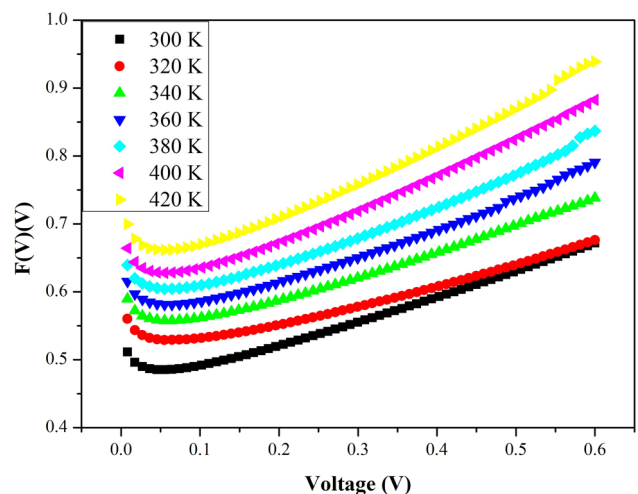


FIG. 6. Plot of $F(V)$ versus V for the Ag/TiO₂/n-InP/Au Schottky diode at 300–420 K.

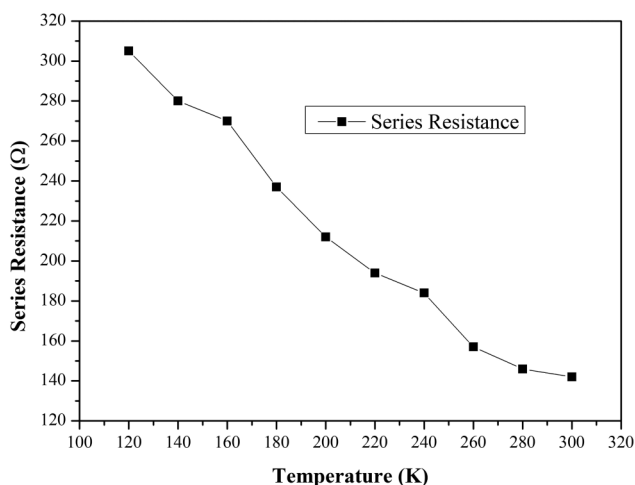
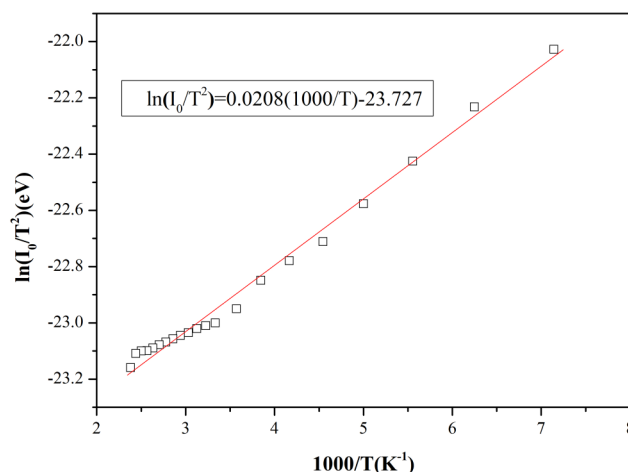
TABLE III. Series resistance (R_s) and barrier height (Φ_b) values according to the Norde method.

Temperature (K)	R_s (Ω)	Φ_b (eV)
300	82	0.48
310	139	0.5
320	145	0.52
330	99	0.54
340	97	0.55
350	92	0.57
360	67	0.57
370	74	0.59
380	43	0.6
390	31	0.6
400	28	0.62
410	31	0.64
420	28	0.66

This result is found too different from the theoretical value of the Richardson constant. Deviation in the result gained from the Richardson plot may be attributed to barrier inhomogeneity. Devi and co-workers,²² the Richardson constant A^* gained from I-V characteristics may be different from theoretical value because of the deviation in the calculated effective mass.

Plots for barrier height vs. ideality factor include two different linear parts. This may be explained by inhomogeneity in barrier heights.

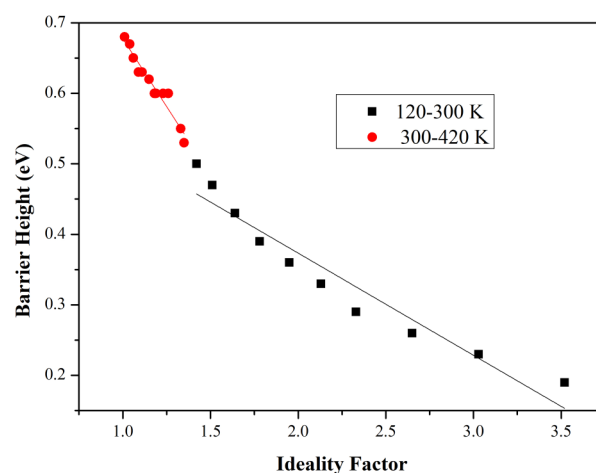
According to Fig. 9, homogeneous barrier heights are calculated by the intercept point on the barrier height axis for $n=1$. For the Ag/TiO₂/n-InP/Au Schottky barrier diode, the barrier height is determined as 0.66 eV and 1.06 eV for 120–300 K and 300–420 K temperature ranges, respectively. These results indicate that the current transport mechanism has a deviation from the TE model.

**FIG. 7.** Temperature dependence of series resistance of the Ag/TiO₂/n-InP/Au Schottky diode in the temperature range of 120–300 K.**FIG. 8.** Richardson plot of $\ln(I_0/T^2)$ versus $1000/T$ for the Ag/TiO₂/n-InP/Au Schottky diode.

The Gaussian distribution model is introduced by Song and coworkers in order to explain these deviations from the TE model. Vanalme *et al.* investigated double Gaussian in InP Schottky barriers in detail and this study is made in accordance with that study.²³ According to them, in the base of the deviations from the TE model, there is the spatial homogeneity of barrier heights. Spatial inhomogeneity is given by

$$P(\Phi_{b0}) = \frac{1}{\sigma_0 \sqrt{2\pi}} \exp \left[-\frac{(\Phi_{b0} - \bar{\Phi}_{b0})^2}{2\sigma_0^2} \right]. \quad (11)$$

Here, $P(\Phi_{b0})$ is the Gaussian distribution, $(\bar{\Phi}_{b0})$ is the mean barrier height, and (σ_0) is the standard deviation.^{24,25} According

**FIG. 9.** The zero-bias barrier height versus the ideality factor for the Ag/TiO₂/n-InP/Au Schottky barrier diode in the temperature range of 120–420 K.

to this equation, the current through the diode is given by

$$I(V) = \int_{-\infty}^{\infty} I(\Phi_{b0}, V) P(\Phi_{b0}) d\Phi. \quad (12)$$

If the term $I(\Phi_{b0}, V)$ in this equation is modified,

$$I(V) = AA * \exp \left[-\frac{q}{kT} \left(\bar{\Phi}_{b0} - \frac{q\sigma_0^2}{2kT} \right) \right] \exp \left(\frac{qV}{n_{ap}kT} \right) \times \left[1 - \exp \left(\frac{qV}{kT} \right) \right], \quad (13)$$

the equation is found. Here, the saturation current I_0 is calculated by the following equation:

$$I_0 = AA * \exp \left(-\frac{\Phi_{ap}}{kT} \right). \quad (14)$$

According to this model,

$$\Phi_{ap} = \bar{\Phi}_{b0}(T=0) - \frac{q\sigma_0^2}{2kT}. \quad (15)$$

Because temperature dependence of σ_0 is small it may be neglected. Temperature dependence of ideality factor is given by

$$\left(\frac{1}{n_{ap}} - 1 \right) = -\rho_2 + \frac{q\rho_3}{2kT}. \quad (16)$$

Here, n_{ap} is the experimental value of ideality factor. ρ_2 and ρ_3 are voltage deformations of the BH. There is a linear relation among ρ_2 , ρ_3 , and σ_0 . So following equations can be written as

$$\bar{\Phi}_b = \bar{\Phi}_{b0} + \rho_2 V, \quad (17)$$

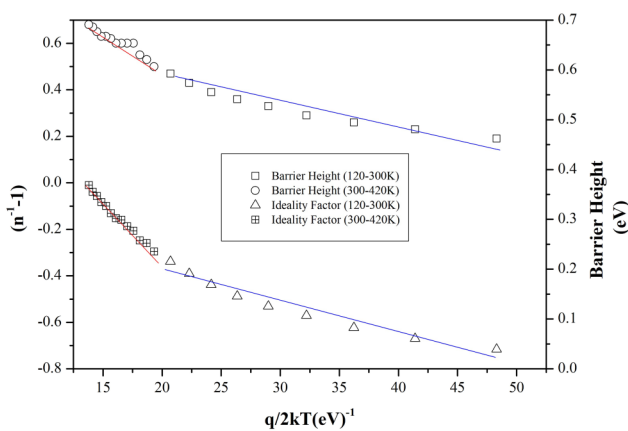


FIG. 10. The zero-bias barrier height and ideality factor versus $q/2kT$ curves and their linear fits for the Ag/TiO₂/n-InP/Au Schottky contact according to the Gaussian distribution of the barrier heights.

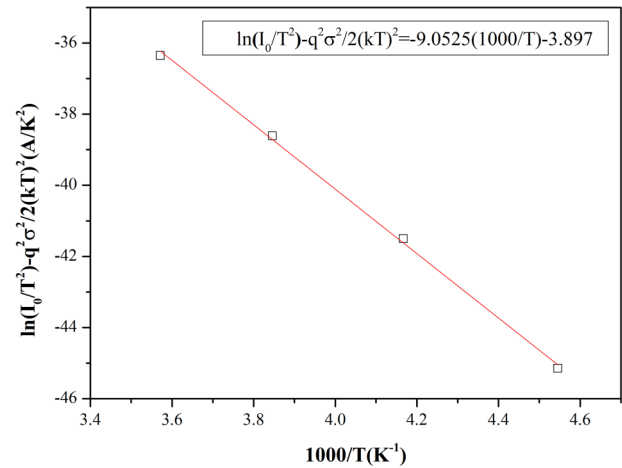


FIG. 11. Modified Richardson $\ln(I_0/T^2) - q^2 \sigma_0^2 / 2k^2 T^2$ versus $1000/T$ plot for the Ag/TiO₂/n-InP Schottky diode according to the Gaussian distribution of the barrier heights at low temperatures.

$$\sigma_{0s} = \sigma_{0c} + \rho_3 V. \quad (18)$$

If σ_0 is small, the barrier height is more homogeneous. According to Eqs. (14) and (15), Φ_{ap} vs. $q/2kT$ plot is expected to give a straight line. The slope of this line gives us σ_0 , and the intercept point on the y axis gives us the mean barrier height ($\bar{\Phi}_{b0}$). Also, $(n_{ap}^{-1} - 1)$ vs. $q/2kT$ plot is expected to be a straight line.²⁶⁻²⁸ The slope of this line is ρ_3 , and the intercept point on the y axis is ρ_2 . Φ_{ap} vs. $q/2kT$ and $(n_{ap}^{-1} - 1)$ vs. $q/2kT$ plots can be seen in Fig. 10.

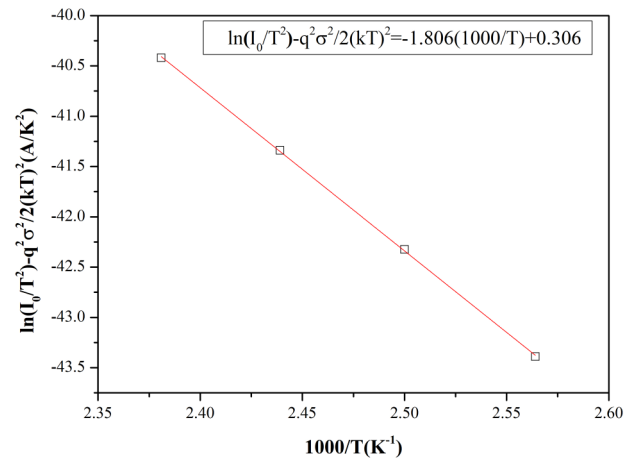


FIG. 12. Modified Richardson $\ln(I_0/T^2) - q^2 \sigma_0^2 / 2k^2 T^2$ versus $1000/T$ plot for the Ag/TiO₂/n-InP Schottky diode according to the Gaussian distribution of the barrier heights at high temperatures.

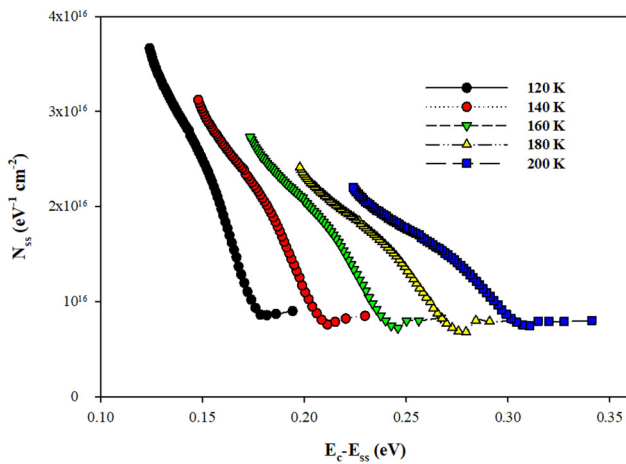


FIG. 13. Interface state density distribution profile as a function of $E_c - E_{ss}$ for the Ag/TiO₂/n-InP Schottky diode at 120–200 K temperature range.

($\bar{\Phi}_{b01}$), σ_{01} , ρ_2 , and ρ_3 are determined as 0.69 eV, 138 mV, -0.1125 V, and -0.0134 V in 120–300 K temperature range, respectively. ($\bar{\Phi}_{b02}$), σ_{02} , ρ_2 , and ρ_3 are determined as 1.25 eV, 257 mV, 0.6634 V, and -0.0498 V in 300–420 K temperature range, respectively. For the Ag/TiO₂/n-InP/Au Schottky barrier diode, the calculated mean barrier heights and standard deviations are too large to neglect, especially in the low temperature range. This situation implies that barrier distribution is inhomogeneous. If the Richardson equation is modified, the following equation is deduced:

$$\ln\left(\frac{I_0}{T^2}\right) - \left(\frac{q^2\sigma^2}{2k^2T^2}\right) = \ln(AA^*) - \frac{q\bar{\Phi}_{b0}}{kT}. \quad (19)$$

$\ln(I_0/T^2) - q^2\sigma_0^2/2k^2T^2$ vs. $1000/T$ plot is expected to be

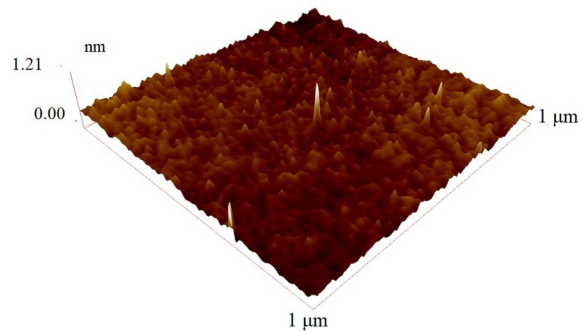
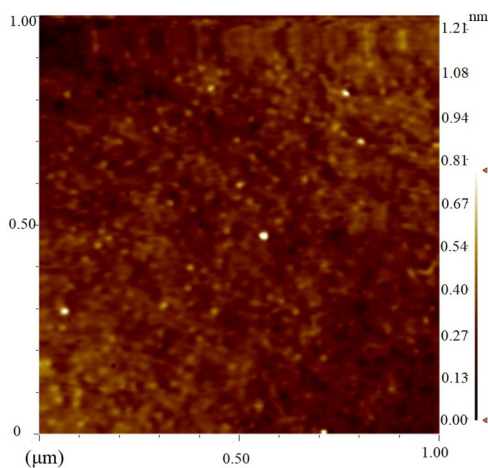


FIG. 14. AFM micrographs of the Ag/TiO₂/n-InP Schottky contacts as-deposited.

linear, the slope of this plot gives $\bar{\Phi}_b$ and intercept point on the y axis is the Richardson constant A^* (Figs. 11 and 12).^{29–31}

For the Ag/TiO₂/n-InP/Au Schottky barrier diode, $\bar{\Phi}_b$ and A^* are determined as 0.78 eV and $2.58 \text{ A cm}^{-2} \text{ K}^{-2}$ in 120–300 K temperature range and 1.39 eV and $20 \text{ A cm}^{-2} \text{ K}^{-2}$ in 300–420 K temperature range, respectively. These results for the Richardson constant are in good agreement with theoretical value.

Other effects influencing the current transport mechanism together with semiconductor's electrical properties are the thickness of the interfacial layer and interfacial state density. Especially in determining the barrier height and the ideality factor, the interface state density (N_{ss}) plays a significant role. If the interfacial layer is thick enough, the probability of conduction between metal and semiconductor is small. For this reason, the effective barrier height Φ_e is dependent on the applied voltage. Φ_e is calculated by the following equation:

$$\Phi_e = \Phi_{b0} + \left(\frac{d\Phi_e}{dV}\right)V = \Phi_{b0} + \beta V. \quad (20)$$

Here, $\beta = 1 - [1/n(V)]$ and it implies the change of effective barrier height with voltage. Also, the change of the ideality factor with voltage is described by Card and Rhoderick. According to them, $n(V)$ is calculated by the following equation:

$$n(V) = 1 + \frac{\delta}{\epsilon_i} \left[\frac{\epsilon_s}{W_D} + qN_{ss} \right]. \quad (21)$$

Here, W_D is the depletion region width, δ is the interfacial layer thickness, ϵ_s and ϵ_i are the dielectric constants of the semiconductor and interfacial layer, respectively. N_{ss} is the interface state density. By using Eq. (22), N_{ss} can be

calculated as follows:

$$N_{ss}(V) = \frac{1}{q} \left[\frac{\epsilon_i}{\delta} (n(V) - 1) - \frac{\epsilon_s}{W_D} \right]. \quad (22)$$

The difference between the bottom edge of the conduction band and interfacial state density energy is calculated as follows:²⁷

$$E_c - E_{ss} = q(\Phi_e - V). \quad (23)$$

The plot N_{ss} vs. $E_c - E_{ss}$ can be seen in Fig. 13 in the 120–200 K temperature range. This plot may be deduced from the forward bias of I–V characteristics. As can be seen in Fig. 13, the values of N_{ss} are approximately between 25×10^{15} and $9 \times 10^{15} \text{ cm}^{-2} \text{ eV}^{-1}$ at 200 K and between 38×10^{15} and $8 \times 10^{15} \text{ cm}^{-2} \text{ eV}^{-1}$ at 120 K. This means that the interface state density decreases with an increase in temperature as expected.

Atomic force microscopy (AFM) was employed to characterize the surface morphology of the n-InP wafer. The AFM image of the chemically cleaned n-InP wafer is shown in Fig. 14. Surface morphology of the cleaned sample is fairly smooth with a root mean square (RMS) roughness of 0.0668 nm as shown in Fig. 14.

IV. CONCLUSION

In summary, electrical properties of Ag/TiO₂/n-InP/Au Schottky diodes have been investigated by I–V measurements as a function of temperature. The barrier height is found to be 0.19 eV and 0.68 eV from current-voltage characteristics at 120 K and 420 K, respectively. With a decrease in temperature down to 120 K, BH decreases to 0.190 eV. Moreover, a modified Norde's function is used to calculate diode parameters including BHs and series resistance. Modification of the interfacial potential barrier of Ag/TiO₂/n-InP/Au is achieved by using a thin TiO₂ interlayer. A change in the barrier height and ideality factor upon increasing temperature of 120 K to 420 K may be ascribed to the pinholes that might be formed in the TiO₂ interlayer. These pinholes may be formed during the growth period of the structure. There may occur dislocation lines because of lattice mismatch or the difference in thermal expansion coefficients. At the end point of these lines on the interface, there formed a hole like tiny dots called pinholes. Pinholes act as a tip of a pipe and help increase the mobility of charges. The obtained results show that the interface state density and series resistance have a significant effect on the electrical characteristics of the produced diode. The Richardson coefficient and the mean barrier height are also calculated by using the modified Richardson plot, and they are found in good agreement with the literature.

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