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Electrical characteristics and inhomogeneous barrier analysis of Al/NPB/p-Si Schottky diodes

Wen-Chang Huang *, Chien-Chou Chen

Department of Electronic Engineering, Kun Shan University, No. 949, Da Wan Road, Yung-Kang City, Tainan Hsien 710, Taiwan, R.O.C.
Nano Technique Research and Development Center, Kun Shan University, No. 949, Da Wan Road, Yung-Kang City, Tainan Hsien 710, Taiwan, R.O.C.

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ABSTRACT

The current–voltage–temperature (I–V–T) characteristics of Al/NPB/p-Si Schottky diodes were discussed in detail in this paper. It shows an abnormal decrease of the Schottky barrier height and increase of ideality factor as the decrease of measured temperature. The series resistance was evaluated and it is found that the series resistance increases as the increase of the measurement temperature. The Gauss distribution of the inhomogeneous of the barrier was brought to discuss the contact interface. The characteristics have been interpreted based on the thermionic emission (TE) mechanism with Gaussian distribution of the barrier heights of $\bar{\phi}_{b0}$ is 0.96 eV and standard deviation σ_{so} is equal to 0.13 V. In addition, the $\ln(I_0/T^2)$ vs. $1/T$ plot yields the effective Richardson constant of 1.47×10^{-2} A cm^{-2} K^{-2} for the Al/NPB/Si diode which is lower than the known value of 32 A cm^{-2} K^{-2} for Si. This deviation is attributed to the inhomogeneous barrier heights and potential fluctuations at the contact interface that consists of low and high barrier areas. The modified Richardson plot shows a straight line relationship between $\ln(J_s/T^2) - (q^2\sigma_{so}^2/2k^2T^2)$ vs. $1000/T$, and gives a value of A^* = 30.1 A cm^{-2} K^{-2}.

1. Introduction

Organic semiconductors have attracted increasing interest owing to their potential application in various electronic and electro-optical devices such as optical switches [1], batteries [2], field effect-transistors [3], solar cells [4], and organic light-emitting diodes [5]. The organic semiconductor also shows the advantages of low synthesis costs and relative easiness of handling. These advantages make this kind of materials attractive for the above-mentioned applications.

The metal/semiconductor (MS) contact is a simple and important technology in semiconductor devices. The performance of the Schottky diodes is dominated by the properties of the barrier of the contact interface. The quality of the barrier is evaluated by the Schottky barrier height and ideality factor, n. For an ideal case of the Schottky barrier, its barrier height is simply the difference between the metal work function and the election affinity of the semiconductor and the ideality factor n is equal to 1. In a practical Schottky barrier [6–8], the current–voltage (I–V) characteristics of the MS contacts usually deviate from the ideal thermionic emission (TE) current model. In general, the electrical characteristics of a Schottky diode are greatly controlled by the interface quality. The interface properties show a great influence on the device performance. For a metal/organic/semiconductor Schottky barrier diode, the organic thin film on semiconductor modifies the electronic properties of MS contacts. Campbell et al. [9] have introduced an organic thin film at the semiconductor/organic interface and thus change the effective Schottky barrier height. The effective Schottky barrier could be changed by introducing an organic thin layer between metal and semiconductor. They reported that the changes in the Schottky barrier height were more than 500 meV. Because of modified contact barriers, the Schottky diodes with thin organic layer were superior than conventional Schottky diodes. Furthermore, some scientists made many researches on metal/organic/semiconductor Schottky diode with different methods of formation of organic compound at metal/semiconductor interface and then evaluated the Schottky barrier height and ideality factor. Kılıcoglu et al. [10] reported an Al/tetraamide-I/p-Si diode with a barrier height value of 0.75 eV and an ideality factor value of 1.77. Aydoğan et al. [11] discussed the current–voltage (I–V) characteristics of Al/polypyrrole(PPy)/p-Si structure with a function of temperature. Yakuphanoglu and Lee [12] presented an Ag/Zn(Phen)q/p-Si diode which shows a barrier height of 0.71 eV with the ideality factor of 2.05. They also [13] discussed the Ag/FSS/p-Si Schottky diode and found an improved Schottky barrier height than the conventional Ag/p-Si diode. Aydin et al. [14] presented an electrical characterization of Al/MEH-PPV/p-Si Schottky diode by current–voltage and capacitance–voltage methods. They showed that the organic interfacial layer formed at metal/semiconductor substrate has a rectification behavior in

* Corresponding author. Tel.: +886 6 2727175x530.
E-mail address: wchuang@mail.ksu.edu.tw (W.-C. Huang).

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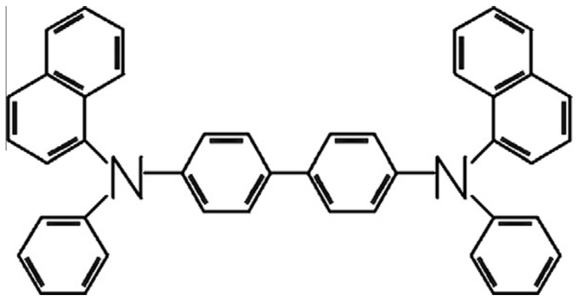

Fig. 1. The chemical structure of NPB.

which the values of Schottky barrier height and ideality factor are greater than those of the conventional metal/semiconductor structures [15]. So, the metal/organic/semiconductor Schottky diode not only shows the potential to improve the barrier height but also attracts us to investigate the information about organic/inorganic interface. In this paper, the organic material, *N*,*N*′-diphenyl-*N*,*N*′-bis(1-naphthyl-pheny1)-(1,1′-biphenyl)-4,4′-diamine (NPB) [16] is used to be an interfacial film between metal and silicon. Fig. 1 shows the chemical structure of NPB. It is one of the most widely used Hole Transport Layer (HTL) in organic light emitting diode. The energy band gap of NPB is 2.9 eV and the electron affinity is 2.3 eV [16,17]. The diode structure, Al/NPB/p-Si is designed to obtain a high quality Schottky diode.

The analyses of the *I–V* characteristics of the Schottky diodes obtained at room temperature do not give us sufficient information about the charge transport process across the MS interface. The temperature dependence of the *I–V* characteristics gives a better description of the conduction mechanism and allows us to understand various processes involved of the carrier transportation at the contact interface. For a conventional MS contact, it shows a decrease in the Schottky barrier height and an increase in ideality factor with a decrease of the measured temperature [18–25]. The decrease in the Schottky barrier height at low temperatures leads to non-linearity in the activation energy; and it is shown in the plot of $\ln(J_s/T^2)$ vs. $1000/T$. The decrease in Schottky barrier height and increase in ideality factor at lower temperatures have been explained [18–25] on the basis of a thermionic emission mechanism with the effect of the barrier heights with a Gaussian distribution. The series resistance, R_s is also an important parameter in the diode characteristics. The values of R_s can be obtained by using a method developed by Cheung and Cheung [26] in the high current range of the *I–V* characteristics. The value of the series resistance will give us information about the discussion of the interface characteristics of the diode.

For a more detailed inspection of the current transport mechanism on the Al/NPB/p-Si diode, the temperature dependent measurement of the *I–V* characteristic is performed. The barrier height and ideality will be evaluated at each measurement temperature. The Cheung and Cheung methods will also used to discuss the barrier height and series resistance effect. The inhomogeneity of barrier height of the diode will be discussed in the temperature dependent *I–V* measurement.

2. Experiment

The p-type Si(100) substrate with the resistivity of 5–10 Ω cm was used in the preparation of the Schottky diode. The silicon wafer was chemically cleaned by using the RCA cleaning process. The ohmic contact of the backside was made by evaporating aluminum (Al) on the back surface of the substrate, and then was annealed at 550 °C for 5 min. The native oxide on the front surface of the substrate was removed in buffered oxide etch (BOE) solution and finally the wafer was rinsed in de-ionized water for 30 s before forming organic layer on the p-type Si substrate. The wafer with backside ohmic contact and then was cut into pieces to form the thin film layer of NPB on their front surfaces. Thermal evaporator was used to deposit NPB on the front surface of p-Si substrate in a vacuum of 4×10^{-5} Torr chamber. The deposition rate was about 0.1–0.2 nm/s, as determined using a quartz-crystal thickness monitor. The circle contact electrode was defined by using a shadow mask at front surface of the sample during deposition. The contact electrode, Al was chosen in the Schottky diode. The thickness of the Al is 1000 Å, and the Schottky contacts electrode were circles with diameters of 200, 300 and 400 μm respectively. All metallic surfaces were cleaned by acetone and methanol before processes. Temperature dependent *I–V* measurement was performed by using semiconductor parameter analyzer. The temperature range was varied from 213 to 353 K.

3. Results and discussion

For a Schottky barrier diode, current transport is due to majority carriers and it is described by thermionic emission (TE) [15] over the interface barrier. The effective barrier height ϕ_b and ideality factor n are determined by using the thermionic emission current voltage expression:

$$I = I_s\left[\exp\left(\frac{q(V - IR_s)}{nkT}\right) - 1\right] \quad (1)$$

$$\text{where } I_s = AA^*T^2\exp[-q\phi_b/kT] \quad (2)$$

where R_s is the series resistance of the diode, V is the applied voltage, q is the electronic charge, k is the Boltzmann constant, T is the absolute temperature, A is the diode contact area, A^* is the effective Richardson constant, ϕ_b is the effective Schottky barrier height (SBH) at zero bias, and n is the ideality factor. Theoretical A^* value of 32 A cm^{-2} K^{-2} is used for Si. The saturation current density, J_s, is obtained by extrapolating the linear region of the forward *I–V* curves to the zero applied voltage and the ϕ_b values are calculated from Eq. (2). The values of ideality factor n are obtained from the slope of linear region of forward *I–V* plots, and they were derived from $n = q/kT[\partial V/\partial(\ln J)]$.

Fig. 2 shows the temperature dependent current–voltage (*I–V–T*) characteristics of the Al/NPB/p-Si. It shows the *I–V* characteristics of the diode in the temperature range from 213 to 353 K. The saturation current density decreased as the temperature decreased. The reverse leakage current density also shows the

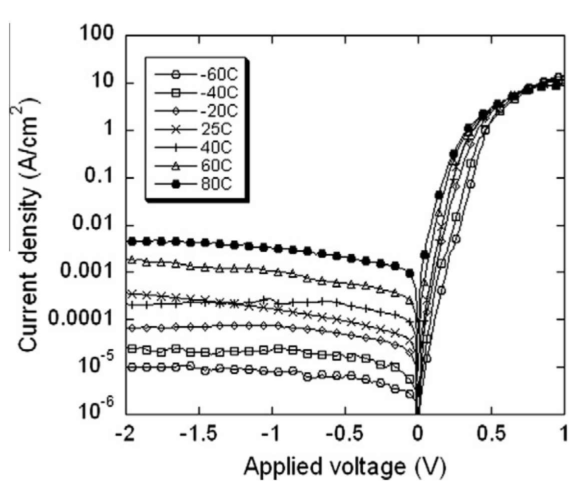

Fig. 2. The *I–V–T* characteristics of the Al/NPB/p-Si diodes.

same tendency. The saturation current density, J_s, of the diode is 3.28×10^{-5} A/cm^2 at the room temperature measured sample. The effective Schottky barrier height which derived from the TE model is 0.65 eV at the 300 K measurement. Its ideality factor is 1.33 and shows a straight line over four decade of the plot. For the reverse leakage current, the current density of the diode is 3.65×10^{-4} A/cm^2 at the reverse bias voltage of -2 V. The value of the Schottky barrier height of Al/NPB/p-Si is higher than that ($\sim$0.58 eV) of the conventional Al/p-Si diode [15]. It shows a slightly lower value of barrier height than that of some other metal/organic/Si diode. For example, the barrier height of the Al/tetraamide-I/p-Si diode [10] is 0.75 eV, of the Al/polypyrrole(PPy)/p-Si diode [11] is 0.78 eV, of the Ag/Zn(Phen)q/p-Si diode [12] is 0.71 eV, of the Ag/FSS/p-Si diode [13] is 0.72 eV and of the Al/MEH-PPV/p-Si diode [14] is 0.80 eV. The temperature dependent Schottky barrier height and ideality factor of the diode are displayed in Fig. 3. The Schottky barrier height and the ideality factor of the diode were determined from the intercepts and slopes of the forward biased current at each temperature, respectively. The ideality values were obtained from the fit of the equation of straight lines in the forward bias region of the *I–V* plot, and the series resistance effect is small. It is found that the Schottky barrier height increased and the ideality factor decreased as the measured temperature increased. The values of the Schottky barrier height and ideality factor are 0.68 eV and 1.19 at the 353 K-measured diode, and are 0.51 eV and 1.71 at 213 K-measured diode, respectively. Since the current transport across the metal/organic/semiconductor interface is a temperature activated process, electrons at low temperatures are able to surmount the lower barriers and therefore the current transport will be dominated by current flowing through the patches of lower Schottky barrier height and a larger ideality factor [27]. As the temperature increases, more and more electrons gain sufficient energy to surmount the higher barrier. As a result, the dominant barrier height will increase with the temperature. The current transport comes close to an ideal Schottky diode characteristic, so the ideality factor decreased and near to ideal value of $n = 1$ at high temperature measurement. An apparent increase in the ideality factor and a decrease in the barrier height at low temperatures are also caused possibly by other effects such as inhomogeneities of barrier height and non-uniformity of the interfacial charges [28]. This effect gives rise to an extra current, and the overall characteristics of the extra current still remain consistent with the TE process [29].

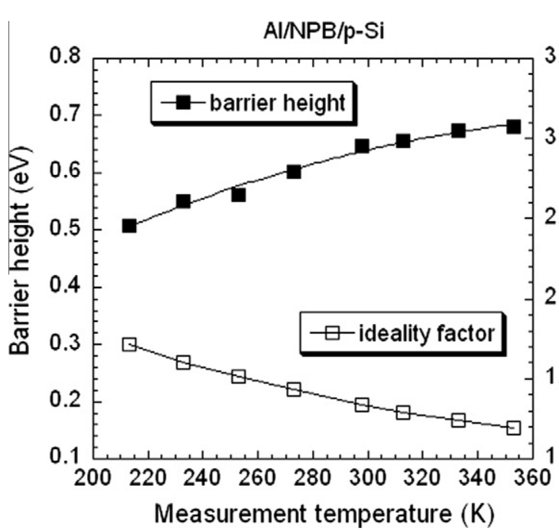

Fig. 3. The temperature dependent of the effective barrier and ideality factor of the Al/NPB/p-Si diodes.

According to Cheung and Cheung [26], the forward biased *I–V* characteristics for a large applied voltage ($V > 3kT/q$) from the TE model of a Schottky diode with series resistance can be expressed as Eq. (1). The IR_s term indicates the voltage drop across the series resistance of the diode described in the equation. The values of the series resistance can be determined from following equations:

$$\frac{dV}{d(\ln I)} = \frac{nkT}{q} + IR_s \tag{3}$$

$$H(I) = V - \left(\frac{nkT}{q}\right) \ln\left(\frac{I}{AA^*T^2}\right) \tag{4}$$

where $H(I)$ is given by

$$H(I) = n\phi_b + IR_s \tag{5}$$

The series resistance can be found from the slope of the $dV/d(\ln I)$ vs. I plots, and nkT/q is obtained at the interception of the y-axis, as indicated by Eq. (3). Fig. 4 shows the relations between $dV/d(\ln I)$ vs. I of the diode at various temperatures. The R_s value of the diode can be evaluated from the slopes of each curve. The values of n and R_s were calculated, yielding values of $n = 1.42$ and $R_s = 86\ \Omega$ for the Al/NPB/Si diode at room temperature. It should be noted that the value of n obtained from the $dV/d(\ln I)$ vs. I curves is larger than that of the forward-bias $\ln I$ vs. V plot. This can be attributed to the effect of series resistance and interface states and to the voltage drop across the interfacial layer [11]. The ideality factor increased from 1.23 to 1.83 as the measured temperature decreased from 353 to 213 K. While, the R_s values decreased from 137 to 57 Ω as the measured temperature decreased from 353 to 213 K.

Fig. 5 shows the plots of $H(I)$ vs. I of the diode measured at various temperatures. Using the value of the n obtained from Eq. (3), the value of the Schottky barrier height is obtained from the y-axis intercept. The value of the Schottky barrier height of the diode is 0.60 eV at room temperature. The barrier height increased from 0.50 to 0.67 eV, and the series resistance increased from 53 to 101 Ω as the temperature increased from 215 to 353 K.

The barrier height and ideality that derived from the Cheung's model were summarized at Fig. 6. A barrier height of 0.67 eV with the ideality factor of 1.23 was obtained at the 353 K measurement. A value of 0.60 eV of the barrier height with the ideality factor of 1.42 was obtained from the room temperature measurement. The barrier height increased and ideality factor decreased as the temperature is increased. Similar results are also obtained from the TE model of the diode.

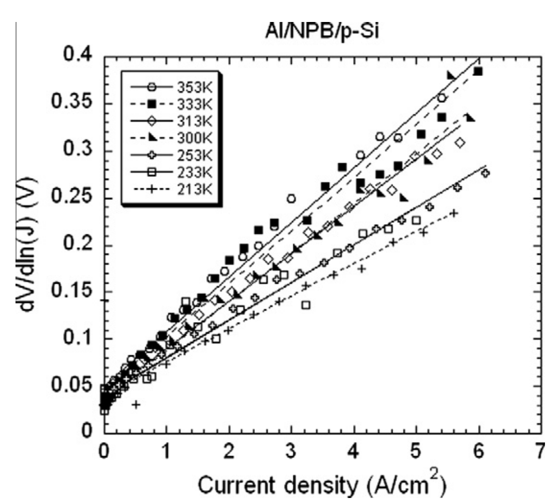

Fig. 4. The plot of $dV/d(\ln J)$ vs. J of the Al/NPB/p-Si diode.

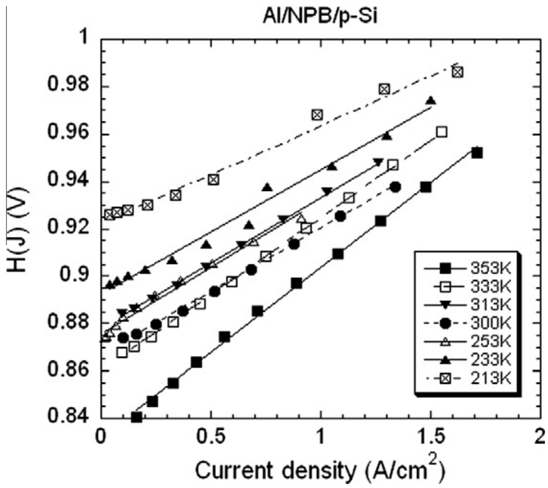

Fig. 5. The plot of $H(J)$ vs. J of the Al/NPB/p-Si diode.

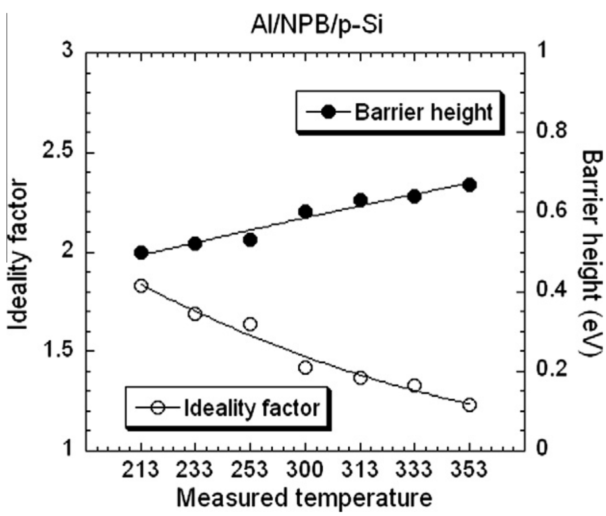

Fig. 6. Temperature dependent of barrier height and ideality of the Al/NPB/p-Si, by Cheung' model.

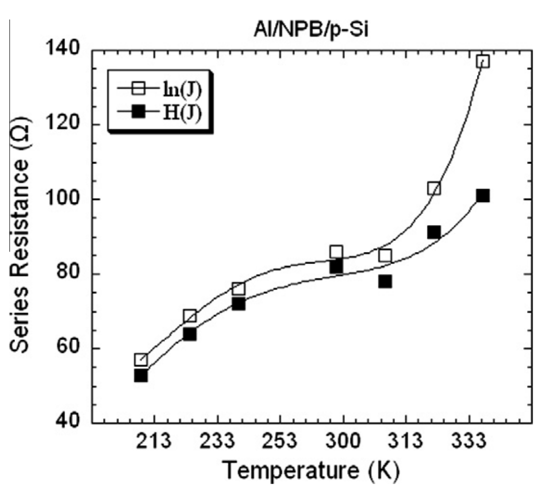

Fig. 7. Temperature dependent of series resistance of the Al/NPB/p-Si, by Cheung' model.

The series resistance of the diode that derived from the Cheung's model was depicted in Fig. 7. It shows the series resistance increased as the measurement temperature is increased.

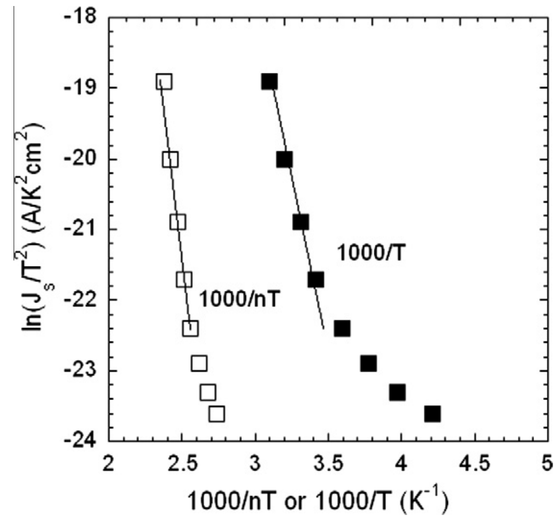

Fig. 8. The Richardson plot of the Al/NPB/p-Si diode.

The increase of the series resistance in the temperature range (213–353 K) has been found in the Sn/polypyrrole/n-Si structure [30]. For a silicon substrate, the carrier concentration belongs to extrinsic region in the temperature region (213–353 K) [31]. So, the majority carrier concentration of the silicon substrate is unchanged as the measured temperature increased from 213 to 353 K. The mobility of the carrier is dominated by the lattice scattering. As the temperature increased, the lattice scattering would also increase [31]. On the contrary, the increase of the lattice scattering would reduce the mobility of the carrier. The resistivity of the silicon substrate is ρ, and which $\rho = (pq\mu)^{-1}$ for p-Si. So the series resistance R_s would increase as the increase of the measured temperature, which was due to the increase of the resistivity.

Fig. 8 shows the Richardson plot of $\ln(I_s/T^2)$ vs. 1000/T or 1000/nT. The dependence of $\ln(I_s/T^2)$ vs. 1000/T is found to be non-linear in the temperature measured; however, the dependence of $\ln(I_s/T^2)$ vs. 1000/nT gives a straight line. The non-linearity of the conventional $\ln(I_s/T^2)$ vs. 1000/T is due to the temperature dependence of the barrier height and ideality factor. The Richardson constant of $1.47 \times 10^{-2}\ \mathrm{A\,cm^{-2}\,K^{-2}}$, which is much lower than the known value of $32\ \mathrm{A\,cm^{-2}\,K^{-2}}$ for p-Si was obtained. The deviation in the Richardson plots was mainly due to the spatially inhomogeneous barrier heights and potential fluctuations at the contact interface [18,29,32,33]. That is, for the passing through of the carrier to the metal/semiconductor junction, it preferentially passed through the lower barriers in the potential distribution.

The Schottky barrier height inhomogeneity of the Al/NPB/Si diode was considered by Gaussian distribution of the barrier heights. It assumed a Gaussian distribution of the Schottky barrier heights with a mean value $\bar{\phi}_b$ and a standard deviation σ_s. The relations are shown below:[34]

$$P(\phi_b) = \frac{1}{\sigma_s\sqrt{2\pi}} \exp\left[-\frac{(\phi_b) - \bar{\phi}_b}{2\sigma_s^2}\right] \tag{6}$$

where $\frac{1}{\sigma_s\sqrt{2\pi}}$ is the normalization constant.

The total current I at the forward bias voltage V is given by

$$I(V) = \int_{-\infty}^{+\infty} I(\phi_b, V)P(\phi_b)d\phi \tag{7}$$

On integration, the total current can be expressed as,

$$I(V) = I_s \exp\left(\frac{qV}{n_{ap}kT}\right) \times \left[1 - \exp\left(-\frac{qV}{kT}\right)\right] \tag{8}$$

where $I_s = AA^* T^2 \exp\left(-\frac{q\phi_{ap}}{kT}\right)$ (9)

The parameters, I_s is saturation current, ϕ_{ap} is apparent barrier height and n_{ap} is apparent ideality factor at zero bias, respectively. The apparent barrier height and apparent ideality can be expressed as:

$$\phi_{ap} = \bar{\phi}_{b0}(T=0) - \frac{q\sigma_{so}^2}{2kT} \quad (10)$$

$$\left(\frac{1}{n_{ap}} - 1\right) = \rho_2 - \frac{q\rho_3}{2kT} \quad (11)$$

It is assumed that the standard deviation σ_s and the mean value of the Schottky barrier height $\bar{\phi}_b$ are the voltages dependent. These voltage dependent in linearly on Gaussian parameters that are given by $\bar{\phi}_b = \bar{\phi}_{b0} + \rho_2 V$ and $\sigma_s = \sigma_{so} + \rho_3 V$, where ρ_2 and ρ_3 are the voltage coefficients that depend on the temperature and they quantify the voltage deformation of the barrier height distribution.

Fig. 9 shows the Schottky barrier height and ideality factor vs. $1/T$ of the Al/NPB/p-Si Schottky diode according to Gaussian distribution of the barrier heights. The plot of ϕ_{ap} vs. $1/2kT$ gives a straight line, and $\bar{\phi}_{b0}$ and σ_{so} are obtained from the intercept and slope, respectively. The mean value $\bar{\phi}_{b0}$ is 0.96 eV and standard deviation σ_{so} is equal to 0.13 V, respectively, were obtained from the least-square linear fitting of the data. For a homogeneous barrier height, its value of σ_{so} should be very small. On the other hand, a larger value of σ_{so} will give a inhomogeneous Schottky barrier height. Herein, the value of σ_{so} (0.13 V) is not small. It shows the existence of the inhomogeneous of barrier between at the junction of the Al/NPB/Si diode. The temperature dependence of the ideality factor can be evaluated through equation: $n = q/kT[\partial V/\partial(\ln J)]$. The fitting data of the ideality factor showed as the circle-dot in Fig. 9. The fitting data showed a straight line that gives voltage coefficients ρ_2 and ρ_3 from the intercept and slope of the plot where ρ_2 = 0.21 V and ρ_3 = −0.023 V from the experimental data. The linear behavior of the $(1/n_{ap}) - 1$ vs. $q/2kT$ plot confirms that the ideality factor does indeed denote the voltage deformation of the Gaussian distribution of the barrier height.

By combining the Eqs. (9) and (10), it can obtain a relation of modified Richardson plot. The equation was shown as:

$$\ln\left(\frac{I_0}{T^2}\right) - \left(\frac{q2\sigma_{so}^2}{2k^2T^2}\right) = \ln(AA^{**}) - \frac{q\bar{\phi}_{b0}}{kT} \quad (12)$$

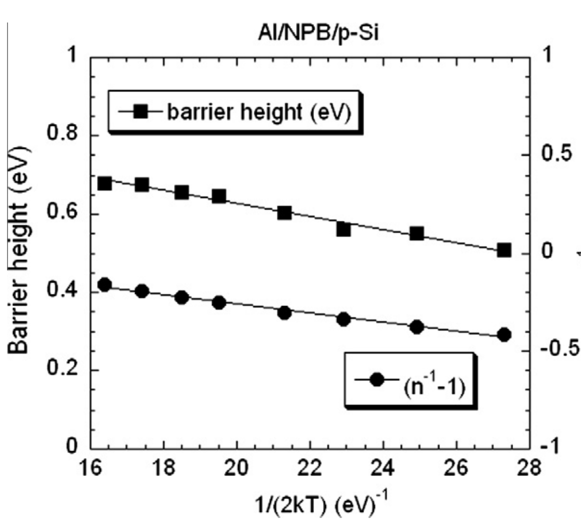

Fig. 9. The barrier height and ideality factor vs. $1/T$ of the Al/NPB/p-Si Schottky diode according to Gaussian distribution of the barrier heights.

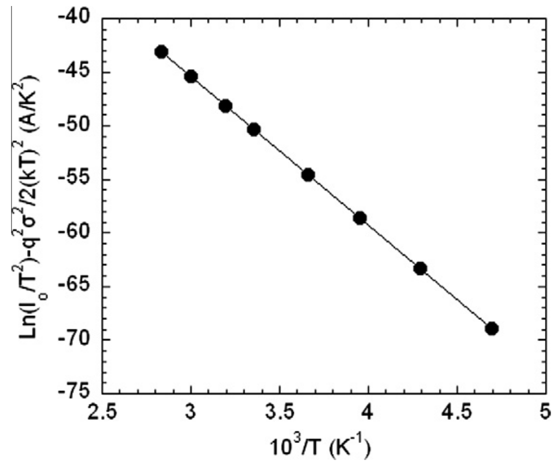

Fig. 10. The modified Richardson plot of the Al/NPB/p-Si diode according to Gaussian distribution of the barrier heights.

The modified Richardson plot $\ln(J_s/T^2) - (q^2\sigma_{so}^2/2k^2T^2)$ vs. $1000/T$ of the diodes was obtained and shown in Fig. 10. The plot according to Eq. (12) should also be a straight line with the slope and the intercept at the ordinate directly yielding the mean barrier height $\bar{\phi}_{b0}$ and A^*, respectively. It can be seen that the modified Richardson plot has quite a good linearity over the whole temperature range. It corresponds to an activation energy around $\bar{\phi}_{b0}$. By fitting of the data, $\bar{\phi}_{b0} = 0.98$ eV and A^* = 30.1 A cm^{-2} K^{-2} are obtained. The value of activation energy (0.98 eV) is very close to the mean value barrier height (0.96 eV). The Richardson constants are in close agreement with the theoretical value of A^* value of 32 A cm^{-2} K^{-2}. For a unmodified Richardson plots, it shows the activation energy of 0.45 eV and the Richardson constant is equal to 1.47×10^{-2} A cm^{-2} K^{-2}. The deviation in the Richardson plots proved the spatially inhomogeneous barrier heights and potential fluctuations at the junction interface. While, as the inhomogeneous effects by Gauss distribution was taken into consideration, the modified Richardson plot shows a straight line relationship between $\ln(J_s/T^2) - (q^2\sigma_{so}^2/2k^2T^2)$ vs. $1000/T$, and gives a reasonable value of Richardson constant.

4. Conclusion

A detailed discussion of the I–V–T characteristics of Al/NPB/p-Si Schottky diodes is displayed in the paper. It shows an abnormal increase of the effective barrier height and decrease of ideality factor as the measure temperature is increased. Similar phenomena are also found by the Cheung and Cheung's model. The series resistance is evaluated and it is found that the series resistance increased as the increase of the measured temperature. The distribution of the barrier height is inhomogeneous that is present at the interface. These characteristics have been interpreted on the basis of the TE mechanism with Gaussian distribution of the barrier heights of $\bar{\phi}_{b0}$ is 0.96 eV and standard deviation σ_{so} is equal to 0.13 V. In addition, The Richardson plot and modified Richardson give the evidence of the spatial inhomogeneous barrier heights and potential fluctuations at the interface.

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