Microelectronic Engineering 107 (2013) 200–204

Contents lists available at SciVerse ScienceDirect

Microelectronic Engineering

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

Barrier heights engineering of Al/p-Si Schottky contact by a thin organic interlayer

Wen Chang Huang [a,*], Tien-Chai Lin [b], Chia-Tsung Horng [a], Chien-Chou Chen [a]

[a] Department of Electro-Optical Engineering, Kun Shan University, No. 949, Da-Wan Rd., Yong-Kang Dist., Tainan City 71003, Taiwan, ROC
[b] Department of Electrical Engineering, Kun Shan University, No. 949, Da-Wan Rd., Yong-Kang Dist., Tainan City 71003, Taiwan, ROC

ARTICLE INFO

Article history:
Available online 24 September 2012

Keywords:
Schottky diode
Barrier height
Ideality factor
Alq_3

ABSTRACT

The current–voltage (*I–V*) characteristics of the Al/Alq_3/p-Si Schottky diode shows rectified behavior with a potential barrier formed at the contact interface. The barrier height and the ideality factor values are 0.78 eV and 1.53, respectively. The barrier height of the Al/Alq_3/p-Si diode is larger than that ($\sim$0.58 eV) of the conventional Al/p-Si diode. It reveals that the organic film, Alq_3, controls the carrier transport of the diode at the contact interface. A linear relationship of $1/C^2$ *vs.* V plot under the reverse bias is shown and the effective barrier height is 0.69 eV by capacitance–voltage (*C–V*) measurement. The electrical characteristics of the diode are also discussed by using Norde's function and Cheung's method.

1. Introduction

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

The metal/semiconductor (MS) contact is an important technology in semiconductor devices applications. The properties of the barrier of the contact interface show great influence on the diode characteristics. The quality of the barrier is evaluated by the Schottky barrier height and the ideality factor, n. For an ideal case of a Schottky barrier diode (SBD), its barrier height is the difference between the metal work function of the contact metal and the electron affinity of the semiconductor and the ideality factor n is equal to 1. In a practical SBD [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 quality of the contact interface. The properties of the contact interface show a great influence on the device performance. For a metal/organic/semiconductor Schottky barrier diode, the organic thin film on the semiconductor modifies the electronic properties of MS contacts. There are many scientists that are devoted to the study of the organic Schottky barrier diode. Campbell et al. [9] introduced an organic thin film at the metal/semiconductor interface and thus changed the effective Schottky barrier height. They reported that the changes in the Schottky barrier height were more than 500 meV and the Schottky diodes with thin organic layers were superior to conventional Schottky diodes. 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 temperature dependent *I–V* characteristics of Al/Polypyrrole(PPy)/p-Si Schottky diode. Yakuphanoglu et al. [12] presented an Ag/Zn(Phen)q/p-Si diode and showed a barrier height of 0.71 eV with the ideality factor of 2.05. The Ag/FSS/p-Si Schottky diode [13] also found an improved Schottky barrier height compared to the conventional Ag/p-Si diode. Aydin et al. [14] presented an electrical characterization of Al/MEH-PPV/p-Si Schottky diode through *I–V* and *C–V* measurements. They showed that the organic interfacial layer formed at the metal/semiconductor substrate has a rectification behavior in which values of the Schottky barrier height and the ideality factor are greater than the conventional metal/semiconductor structures [15]. Therefore, 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, Tris (8-hydroxyquinolinato) aluminum (Alq_3), is used to be an interfacial organic film between metal and silicon. The Alq_3 is a coordination complex wherein aluminum is bonded in a bidentate manner to the conjugate base of three 8-hydroxyquionline ligands [16]. Fig. 1 shows the chemical structure of Alq_3. It is one of the most widely used Hole Transport Layer (HTL) in organic light emitting diodes. The energy band gap of Alq_3 is 2.7 eV, which is referenced from the report of Ruhstaller et al. [17]. The HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) of the Alq_3 is 5.7

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

0167-9317/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.mee.2012.09.003

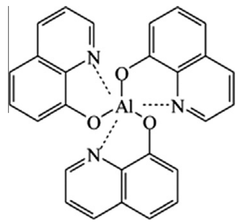

Fig. 1. The chemical structure of Alq_3.

and 3.0 eV, correspondingly. The Schottky diode, Al/Alq_3/p-Si, is designed to obtain a high quality electrical characteristic. The analyses of the *I–V* characteristics of the Schottky diodes were based on the thermionic emission model. The *C–V* measurement was used to evaluate the diode characteristics under the reverse bias. The values of R_s can be obtained by using a method developed by Cheung and Cheung's model [18] in the high current range of the *I–V* characteristics. The Norde's function [19,20] for the discussion of barrier height and series resistance was also stressed. The value of the series resistance will give us information about the discussion of the interfacial characteristics of the diode.

2. Experimental

The preparation of the Schottky diode was processed on a p-type Si (100) substrate with the resistivity of 5–10 Ω-cm. The silicon wafer was chemically cleaned by using the RCA cleaning process before the metal deposition. Aluminum was evaporated through a thermal evaporation system on the back surface of the substrate for ohmic contact of the diode. After the aluminum deposition, the sample was annealed at 550 °C for 5 min in a furnace system for the formation of ohmicity. The native oxide on the front surface of the substrate was removed in the buffered oxide etch (BOE) solution and finally the wafer was rinsed in de-ionized water for 30 s before forming the organic layer on the p-type Si substrate. The wafer with backside ohmic contact was then cut into pieces to form the thin film layer of Alq_3 on their front surfaces. Thermal evaporator was used to deposit the organic film, Alq_3, 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 the front surface of the sample during deposition. The contact electrode, Al, was chosen in the Schottky diode. The thickness of Al is 1000 Å, and the Schottky contact electrodes were circular with diameters of 200, 300 and 400 μm, respectively. The *J–V* measurement was performed by using the semiconductor parameter analyzer. The *C–V* characteristic of the diode was also evaluated in the voltage range from −4 to 4 V at the frequency of 10 kHz.

3. Results and discussion

In the evaluation, the quality of a Schottky barrier diode, Schottky barrier height, ideality factor, and reverse leakage current are the crucial parameters. The current transport of a Schottky diode is due to the majority carriers and is described by the thermionic emission (TE) [15] over the interface barrier. The effective barrier height, ϕ_b, and the ideality factor, *n*, are determined by using the thermionic emission current voltage expression:

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

where

$$I_s = AA^*T^2 \exp[-q\phi_b/kT] \tag{2}$$

where *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, R_s is the series resistance of the diode, A^* is the effective Richardson constant, ϕ_b is the effective Schottky barrier height 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 *J–V* curves to the zero applied voltage, and the ϕ_b values are calculated from Eq. 2. The values of the ideality factor, *n*, are obtained from the slope of linear region of forward *J–V* plots, and were derived from $n = q/kT[\partial V/\partial(\ln J)]$. Fig. 2 shows the *J–V* characteristics of the Al/Alq_3/p-Si. The saturation current density, J_s, of the diode is 8.45×10^{-6} A/cm^2 at the room temperature measured sample. The effective Schottky barrier height which derived from the TE model is 0.78 eV at the 300 K measurement. Its ideality factor is 1.53 and shows a straight line over four decades of the plot. For the reverse leakage current, the current density of the diode is 1.48×10^{-4} A/cm^2 at the reverse bias voltage of −6 V. The value of the Schottky barrier height of Al/Alq_3/p-Si is higher than that (∼0.58 eV) of the conventional Al/p-Si diode [15]. It shows a comparable value of barrier height with that of some other organic interfacial layered Schottky diode. Kılıcoglu et al. [10] reported a barrier height of 0.75 eV in the Al/tetraamide-I/p-Si diode, Aydoğan et al. [11] presented a Al/Polypyrrole(PPy)/p-Si Schottky diode with a barrier of 0.78 eV, and Yakuphanoglu et al. [12] showed a barrier height of 0.71 eV in the Ag/Zn(Phen)q/p-Si Schottky diode [12], that of 0.72 eV in the Ag/FSS/p-Si Schottky diode [13], and that of 0.80 eV in the Al/MEH-PPV/p-Si diode [14]. The value of 1.53 of *n* for the Al/Alq_3/p-Si Schottky diode indicates the presence of an insulator layer on the inorganic semiconductor surface [21–23]. That is, there is probably an insulating oxide layer between Alq_3 and p-Si substrate, for the front surface of the silicon substrate is exposed to air before the deposition of the organic Alq_3 layer. The interfacial oxide layer can be formed by vapor absorbed onto the surface of substrate.

The *C–V* characteristics of the diode measured from 4 to −4 V at the frequency of 10 kHz is shown in Fig. 3. The capacitance decreases as the applied voltage derived from 4 to −4 V which reveals that a depletion region exists at the Alq_3 and Si substrate, and the width of the depletion region increases with the reverse bias. For the forward biased capacitance, the capacitance of the diode is 2.93 nF at the forward voltage of 4 V. The junction of the p-Si substrate becomes more depleted as the applied voltage was reversed.

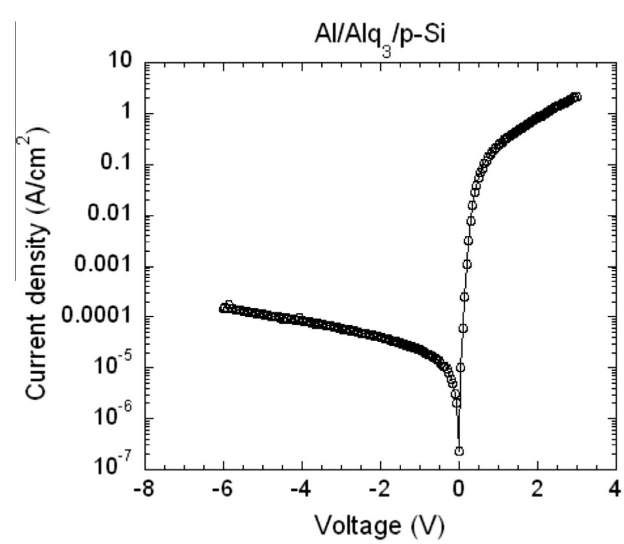

Fig. 2. The *J–V* characteristics of the Al/Alq_3/p-Si diodes.

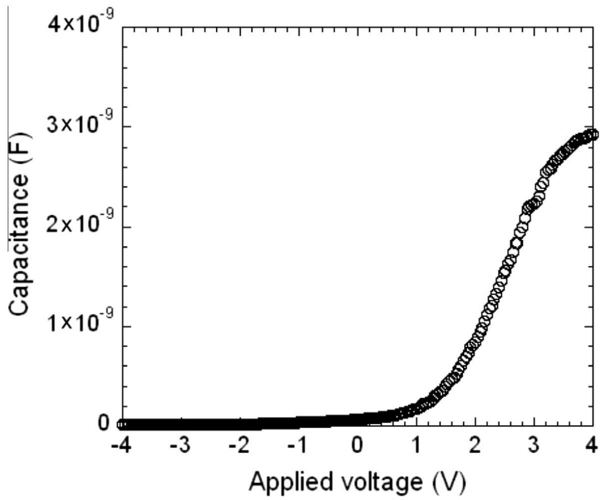

Fig. 3. The C–V characteristics of the Al/Alq_3/p-Si diode.

And the increase of the depletion width results in a decrease of the capacitance. The capacitance is nearly constant at the reverse biased region and its value is equal to 0.0113 nF at the voltage of −4 V. The depletion capacitance is in serial with the capacitance of the organic film.

The plots of $1/C^2$ *vs.* *V* is linear which indicates the formation of Schottky junction [24]. Therefore, it follows a standard Mott–Schottky relationship: $\frac{1}{C^2} = \frac{2[V_{bi} - V - kT/q]}{q\varepsilon_o\varepsilon_s A^2 N_A}$ where *C* is the diode capacitance, V_{bi} is the built in voltage, ε_s is the semiconductor dielectric constant, ε_o is the permittivity in vacuum, *V* is the applied voltage, q is the charge, *A* is the diode active area, *kT/q* is the thermal voltage at 300 K, and N_A is the charge carrier concentration. The value of V_p was obtained from the following relation: $V_p = kT\ln(\frac{N_v}{N_A})$. The value of the ϕ_b can be obtained by the relation: $q\phi_b = V_{bi} + V_p$. The charge carrier concentration can be determined from the slope of $1/C^2$ *vs.* *V* plots. From the extrapolated intercept on voltage axis V_{bi} can be estimated. Fig. 4 shows the $1/C^2$–*V* plot of the diode that was measured at the frequency of 10 K Hz. It shows the built in voltage is V_{bi} = 0.54 V, the effective carrier concentration is 5.45×10^{16} cm^{-3}, the value of V_p is 0.15 V, and the effective barrier height is 0.69 eV, and this value of barrier height is lower than that (0.78 eV) of *I–V* measurement. In general, the barrier height deduced from *C–V* measurement is higher than that of *I–V* measurement [25,26]. The discrepancy can be due to the existence of the interfacial native oxide layer between the organic/semiconductor contact. It is also found that the value of barrier height deduced from *C–V* measurement is dependent on measurement frequency [27,28]. Aydogan et al. [27] shows a barrier height decreased from 0.932 to 0.480 eV as the operating decreased from 1 M to 0.5 kHz. At low frequencies, all the interface states affected by the applied signal are able to give up and accept charges in response to this signal. The interface state capacitance appears directly in parallel with the depletion capacitance, as this results in a higher total value of the capacitance for Schottky diodes than if no interface states were present. These effects not only cause a lower built in potential in the C^{-2} *vs.* *V* plots, but a lower barrier height. The measurement frequency of the sample is 10 K Hz which belongs to low frequency region. This shows a lower barrier height value compared to the *J–V* measurement.

According to the model developed by Cheung and Cheung [18], the forward biased *I–V* characteristics for a large applied forward 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 and the Schottky barrier height can be determined from the 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. 5 shows the relations between *dV/d(*ln *I) vs. I* of the diode. 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 = 1.76 and R_s = 10.58 K Ω for the Al/Alq_3/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 biased ln *J vs. V* plot. Because of the nonlinearity of the *J–V* characteristics, the values of the ideality factor obtained from

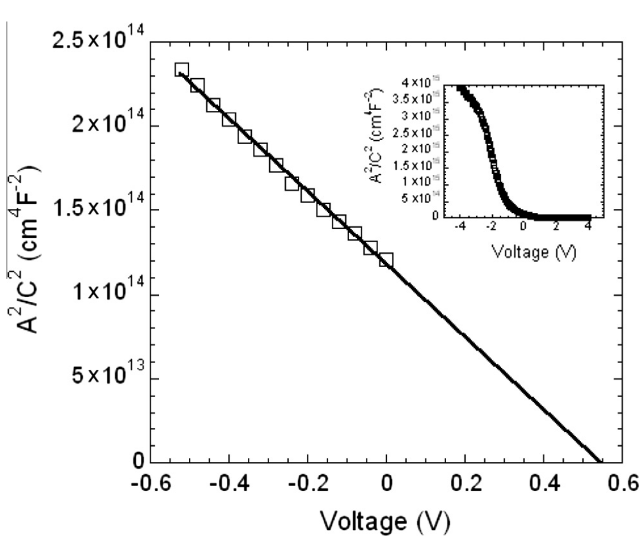

Fig. 4. The $1/C^2$ *vs.* applied voltage of the Al/Alq_3/p-Si diode.

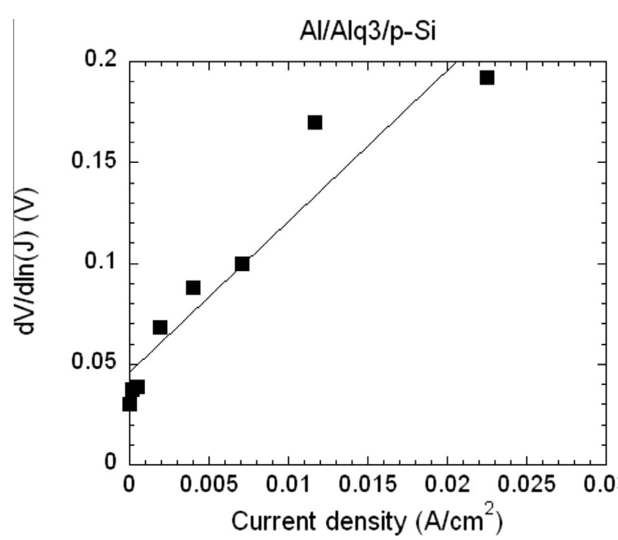

Fig. 5. The plot of *dV/d*(ln *J*) *vs.* *J* of the Al/Alq_3/p-Si diode.

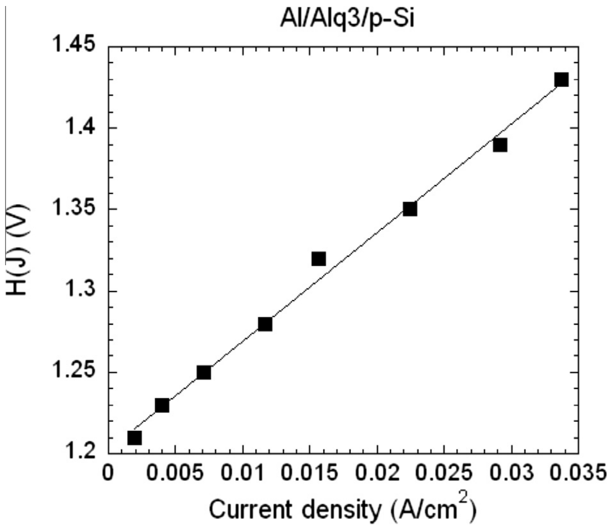

Fig. 6. The plot of *H(J) vs. J* of the Al/Alq_3/p-Si diode.

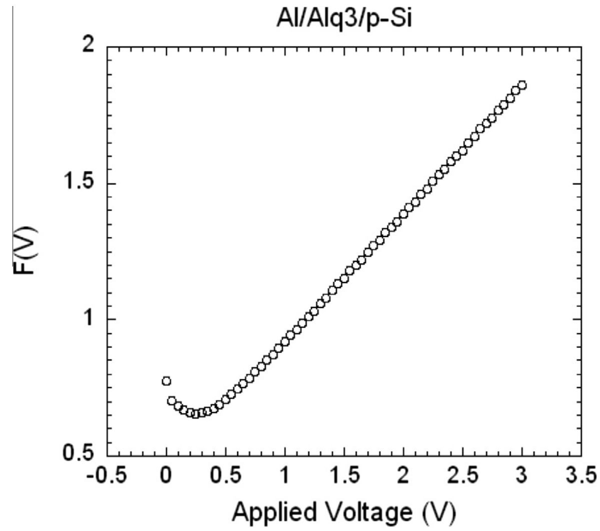

Fig. 7. The Norde plot of the Al/Alq_3/p-Si diode.

Cheung's functions can be higher than the values from the forward biased $J-V$ characteristics. The difference between the values of the ideality factors can be attributed to the fact that the first one is only under the effect of the interfacial properties and the second one is under the effect of both the interfacial properties and the series resistance [11].

Fig. 6 shows the plots of *H(I) vs. I* of the diode. Using the value of 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 0.68 eV at room temperature. The series resistance obtained by the plots of *H(I) vs. I* is 9.43 K Ω.

In the discussion of the series resistance, Norde [19,20] proposed a method to determine the value of the series resistance. According to the thermionic emission theory, the forward biased J–V characteristics of a Schottky barrier diode with the series resistance can be expressed as Eq. 1. In the equation, R_s is the series resistance and the IR_s is the voltage drop across the series resistance of the diode. Norde's function *F(V)* has been used to obtain the values of Schottky barrier height and the series resistance. The *F(V)* function is defined as

$$F(V) = \frac{V}{2} - \frac{kT}{q} \ln\left(\frac{J(V)}{A^*T^2}\right) \tag{6}$$

where *J(V)* is current obtained from the J–V curve. A plot of *F(V) vs. V* of the diode is shown in Fig. 7. From the plot of *F(V) vs. V*, the value of the barrier height of a diode can be determined as follows:

$$\phi = F(V_{\min}) - \left(\frac{1}{2} - \frac{1}{n}\right)V_{\min} - \frac{(2-n)}{n}\frac{kT}{q} \tag{7}$$

where $F(V_{\min})$ is the minimum value of $F(V)$ and $V_{\min}$ is the corresponding voltage. The series resistance R_s can be expressed as:

$$Rs = \frac{(2-n)kT}{qI_{\min}} \tag{8}$$

where $I_{\min}$ is the value of the forward current at the voltage $V_{\min}$ where the function *F(V)* exhibits a minimum. The value of the Schottky barrier height is 0.68 eV and R_s is 5.17 K Ω. For the barrier height, there is a good agreement with the values of ϕ_b obtained from Cheung's and Norde's functions. These values are lower than that from the standard ln J–V plot. This is may be due to the high value of series resistance. For a large series resistance can hinder the accurate evaluation of the barrier height from the standard ln $J-V$ plot. The value of the series resistance obtained from Norde's functions is lower compared to that obtained from Cheung's functions. This is because Cheung's functions are only applied to the non-linear region (high voltage region) of the forward biased ln $J-V$ characteristics. In addition, Norde's function is applied to the full forward biased ln $J-V$ characteristics of the diodes. In these regions, the slopes of the ln $J-V$ characteristic are higher than for the high voltage regions [28,29].

4. Conclusion

The $J-V$ characteristics of the Al/Alq_3/p-Si Schottky diode shows rectified behavior with a potential barrier formed at the contact interface. The values of the barrier height and the ideality factor are 0.78 eV and 1.53, in that order. The barrier height of the Al/Alq_3/p-Si diode is larger than that (~0.58 eV) of the conventional Al/p-Si diode. It reveals that the organic film, Alq_3, controls the carrier transport of the diode at the contact interface. A linear relationship of $1/C^2$ *vs. V* plot under the reverse bias is shown and the effective barrier height is 0.69 eV by C–V measurement. The electrical characteristics of the diode are also discussed by using Norde's function and Cheung's method. This shows consist results of the diode characteristics through these models.

Acknowledgement

This work was supported by the Science and Technology Park of the Republic of China through the contract of 100CP05. The authors would give thank to NDL for the technology support.

References

[1] S.V. Frolov, M. Liess, P.A. Lane, W. Gellermann, Z.V. Vardeny, M. Ozaki, K. Yoshino, Phys. Rev. Lett. 78 (1997) 4285.
[2] Z. Gadjourova, Y.G. Andreev, D.P. Tunstall, P.G. Bruce, Nature 412 (2001) 520.
[3] M. Takada, H. Yoshioka, H. Tada, K. Matsushige, Jpn. J. Appl. Phys. 41 (2002) 73.
[4] N.S. Sariciftci, D. Braun, C. Zhang, V.I. Srdanov, A.J. Heeger, G. Stucky, F. Wudl, Appl. Phys. Lett. 62 (1993) 585.
[5] J.H. Burroghs, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burn, A.B. Holmes, Nature 347 (1990) 539.
[6] W.C. Huang, S.H. Su, Y.K. Hsu, C.C. Wang, C.S. Chang, Superlattices Microst. 40 (2006) 644.
[7] W.C. Huang, T.F. Lei, C.L. Lee, Jpn. J. Appl. Phys. 42 (2003) 71.
[8] W.C. Huang, T.F. Lei, C.L. Lee, J. Appl. Phys. 78 (1995) 291.
[9] I.H. Campbell, S. Rubin, T.A. Zawodzinski, J.D. Kress, R.L. Martin, D.L. Smith, N.N. Barashkov, J.P. Ferraris, Phys. Rev. B 54 (20) (1996) 14321.
[10] T. Kılıcoglu, M.E. Aydın, G. Topal, M.A. Ebeoglu, H. Saygılı, Synth. Met. 157 (2007) 540.

[11] Ş. Aydoğan, M. Sağlam, A. Türüt, Y. Onganer, Mater. Sci. Eng.: C 29 (2009) 1486.
[12] F. Yakuphanoglu, B.J. Lee, Physica B 390 (2007) 151.
[13] M.E. Aydin, F. Yakuphanoglu, J. Phys. Chem. Solids 68 (2007) 1770.
[14] M.E. Aydin, F. Yakuphanoglu, J.H. Eom, D.H. Hwang, Physica B 387 (2007) 239.
[15] E.H. Rhoderick, R.H. Williams, Metal–Semiconductor Contacts, Clarendon, Oxford, 1988.
[16] R. Katakura, Y. Koide, Inorg. Chem. 45 (2006) 5730.
[17] B. Ruhstaller, S.A. Carter, S. Barth, H. Riel, W. Riess, J.C. Scott, J. Appl. Phys. 89 (2001) 4575.
[18] S.K. Cheung, N.W. Cheung, Appl. Phys. Lett. 49 (1986) 85.
[19] H. Norde, J. Appl. Phys. 50 (1979) 5052.
[20] K. Sato, Y. Yasumura, J. Appl. Phys. 58 (1985) 3655.
[21] A. Turut, F. Koleli, J. Appl. Phys. 72 (1992) 818.
[22] Y. Onganer, M. Saglam, A. Turut, H. Efeoglu, S. Tuzemen, Solid State Electron. 39 (1996) 677.
[23] M.H. Qiao, T. Cao, J.F. Deng, G.Q. Xu, Chem. Phys. Lett. 325 (2000) 508.
[24] K. Kudo, Curr. Appl. Phys. 5 (2005) 337.
[25] O. Gullu, M. Cankaya, O. Baris, M. Biber, H. Ozdemir, M. Gulluce, A. Turut, Appl. Surf. Sci. 254 (2008) 5175.
[26] A. Ashery, A.A.M. Farag, M.A. Salem, Microelect. Eng. 85 (2008) 2309.
[27] S. Aydogan, M. Saglam, A. Turut, Polymer 46 (2005) 10982.
[28] X. Zhang, F. Hai, T. Zhang, C. Jia, X. Sun, L. Ding, W. Zhang, Microelect. Eng. 93 (2012) 5.
[29] S. Sonmezoglu, S. Senkul, R. Tas, G. Cankaya, M. Can, Sol. Stat. Sci. 12 (2010) 706.