Solid State Communications 152 (2012) 381–385

Contents lists available at SciVerse ScienceDirect

Solid State Communications

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

High barrier Schottky diode with organic interlayer

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ARTICLE INFO

Article history:
Received 7 June 2011
Received in revised form
29 September 2011
Accepted 6 December 2011
by R. Phillips
Available online 11 December 2011

Keywords:
A. Organic film
B. Schottky barrier
C. Ideality factor

ABSTRACT

A new Cu/*n*-InP Schottky junction with organic dye (PSP) interlayer has been formed by using a solution cast process. An effective barrier height as high as 0.82 eV has been achieved for Cu/PSP/*n*-InP Schottky diodes, which have good current–voltage (I–V) characteristics. This good performance is attributed to the effect of formation of interfacial organic thin layer between Cu and *n*-InP. By using capacitance–voltage measurement of the Cu/PSP/*n*-InP Schottky diode the diffusion potential and the barrier height have been calculated as 0.73 V and 0.86 eV, respectively. From the I–V measurement of the diode under illumination, short circuit current (I_{sc}) and open circuit voltage (V_{oc}) have been extracted as 0.33 μA and 150 mV, respectively.

1. Introduction

Indium phosphide (InP) is one of the most promising semiconductor materials for microwave and optoelectronic devices, field effect and high-speed field effect transistors, Schottky junction etc [1–4]. The barrier height (BH) of *n*-InP Schottky junctions is fixed to the value of around 0.4 eV irrespective of the metal work function. Effort has been devoted to forming InP Schottky junctions with a high barrier. An enhancement of the barrier height up to 0.7–0.8 eV has been achieved by fabricating metal–interlayer–semiconductor (MIS) Schottky junctions [2]. The transport properties of the metal–semiconductor (MS) contacts have been observed to be significantly affected by the presence of the interfacial oxide layer. Thus, the barrier height has been increased by about 140 meV for the Au/*n*-InP diode by means of the interfacial oxide grown by the use of absorbed water vapor [5].

In recent years there has been growing interest in the field of thin organic semiconducting films due to their successful application in optical and electronic devices. In addition, organic materials have now reached the early stages of commercialization with the technological success of thin film organic optoelectronic devices, particularly organic light-emitting devices and with their improving efficiency, manufacturing yield and long-term stability [6–11]. Owing to their stability and barrier height enhancement properties, organic materials have been employed particularly in electronic devices [12–15]. It has been seen that the various contacts including conductive organic thin films show good rectification and enhancement of BH properties [12–18].

New electrical properties of the MS contacts can be promoted by means of the choice of suitable organic semiconductor [10]. Phenolsulfonphthalein (PSP) organic dye is a pH indicator, bright red and crystalline powder that is frequently used in cell biology laboratories. Due to its conjugated structure, we have chosen PSP as an organic material. PSP is known chemically as 4, 4; -(3H-2, 1-benzoxathiol-3-ylidene) bis-phenol, S, S-dioxide with molecular formula $C_{19}H_{14}O_5S$. The molecular structure of the PSP is given in Fig. 1. The structure of organic dyes has attracted considerable attention recently due to their wide applicability in the light-induced photo isomerization process, and their potential usage for the reversible optical data storage [19]. PSP organic material has been considered as one of the most stable organic semiconductors for various electronic and optoelectronic applications and has not been used for the fabrication of different electronic devices. Our aim is to investigate the electrical properties of Cu/PSP/*n*-InP MIS diode by the insertion of PSP organic layer between *n*-InP semiconductor and Cu metal by using current–voltage (I–V) and capacitance–voltage (C–V) measurements and is to compare the electrical parameters of the Cu/PSP/*n*-InP MIS diode with those of conventional MS diodes.

2. Experimental details

MIS structure was prepared by using one side polished (as received from the manufacturer) *n*-type InP wafer in this study. The wafer was chemically cleaned with $3H_2SO_4 + H_2O_2 + H_2O$ (a 20 s boil). The native oxide on the front surface of *n*-InP

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doi:10.1016/j.ssc.2011.12.007

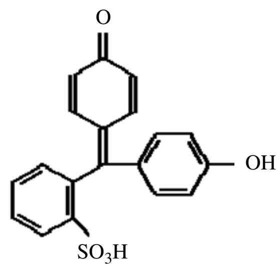

Fig. 1. Chemical structure of phenolsulfonphthalein (PSP).

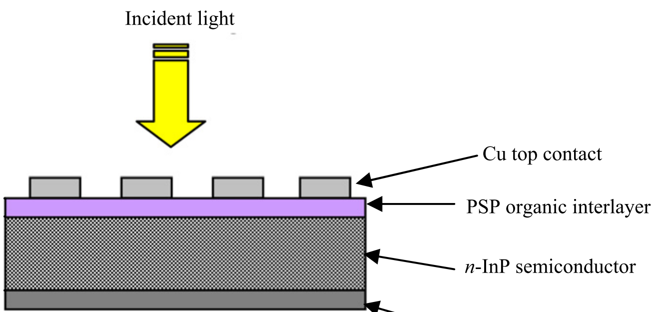

Fig. 2. (Color online) A schematic cross-section of the Cu/PSP/n-InP structure.

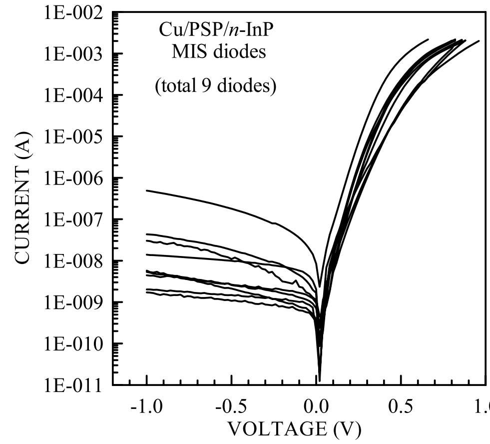

Fig. 3. Current–voltage characteristics of the Cu/PSP/n-InP Schottky devices (total 9 diodes) at room temperature and in dark.

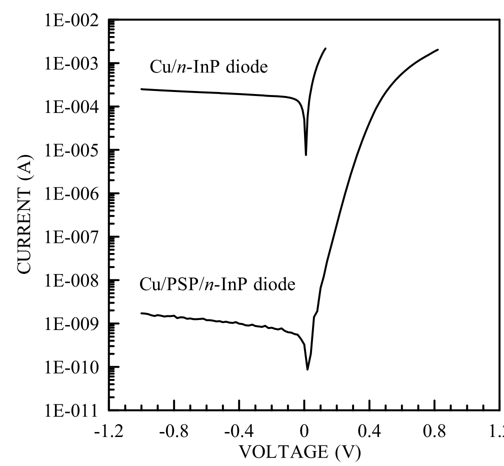

Fig. 4. Current–voltage characteristics of one of the Cu/PSP/n-InP MIS devices and a conventional Cu/n-InP MS diode at room temperature and in dark.

was removed in a HF : H_2O (1:10) solution and finally the wafer was rinsed in deionized (DI) water for 30 s. Before forming PSP layer on n-InP substrate, the ohmic contact was made by evaporating indium metal on the back of the substrate, followed by a temperature treatment at 350 °C for 60 s in N_2 atmosphere.

After the cleaning procedures and ohmic metallization were carried out, PSP film was directly formed by PSP solution (wt 0.2% in methanol) on the front surface of n-InP wafer, and evaporated by itself for drying of solvent in N_2 atmosphere for one day. Here, we selected an amount of 12 μL of the PSP solution by considering and testing various factors that could effect a given PSP film thickness and homogeneity depending on the solution concentration and substrate area. The quality of organic thin films should be also related to other factors, such as the film-forming ability, the molecular symmetry and structure [20]. The contacting top metal dots with diameter of 1.0 mm were formed by evaporation of Cu metal. We also fabricated Cu/n-InP reference diode without the organic layer to compare with the electrical parameters of the Cu/PSP/n-InP device. All evaporation processes were carried out in a vacuum coating unit at about 10^{-5} mbar.

The I–V and C–V measurements of the Cu/PSP/n-InP structure (please see Fig. 2) were performed by KEITHLEY 487 Picoammeter/Voltage Source and HP 4192A (50 Hz–13 MHz) LF IMPEDANCE ANALYZER, respectively.

3. Results and discussion

According to the thermionic emission (TE) theory, the forward-bias I–V characteristics of Schottky contacts for $qV > 3kT$ can be expressed as [21]

$$I = I_0 \exp\left(\frac{qV}{nkT}\right) \tag{1}$$

where V is the applied voltage, n is the ideality factor and I_0 is the saturation current determined by

$$I_0 = AA^*T^2 \exp\left(-\frac{q\Phi_b}{kT}\right), \tag{2}$$

where A is the diode area, A^* is the effective Richardson constant, k is the Boltzmann constant, T is the absolute temperature, q is the electron charge and Φ_b is the barrier height. From Eqs. (1) and (2), ideality factor n and barrier height Φ_b can be written as:

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

and

$$\Phi_b = \frac{kT}{q}\left(\frac{\ln(AA^*T^2)}{I_0}\right), \tag{4}$$

respectively.

Fig. 3 shows the experimental reverse and forward bias I–V characteristics of the Cu/PSP/n-InP MIS contacts (total 9 diodes) formed on the same n-type InP semiconductor substrate. As clearly seen from Fig. 3, all Cu/PSP/n-InP MIS devices have good rectifying properties. As seen from Fig. 3, there is a linear region on a logarithmic scale at low voltages, in contrast to higher currents that show a curvature due to a series resistance (R_s) for the MIS devices. The ideality factors n and BHs Φ_b for each diodes have been obtained from the slopes and the current axis intercepts of the linear regions of the corresponding forward bias I–V plots, respectively. Fig. 4 shows the experimental I–V characteristics of the reference (Cu/n-InP) diode and one of the Cu/PSP/n-InP MIS Schottky device. This figure indicates that the leakage current of the Cu/PSP/n-InP Schottky device decreases in significant rate with

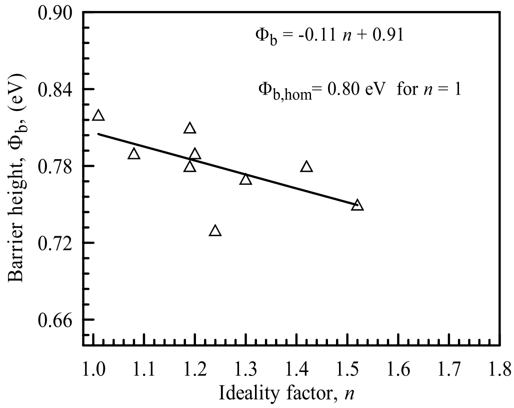

Fig. 5. Barrier height *versus* ideality factor plot of the Cu/PSP/n-InP MIS devices.

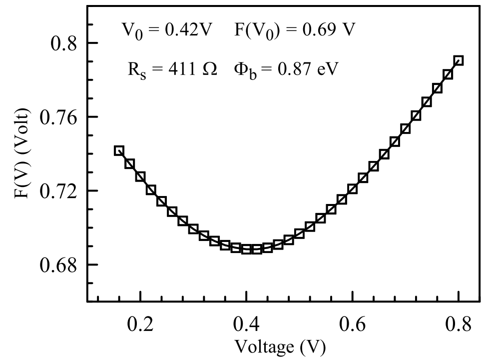

Fig. 6. $F(V)$ *vs.* V plot of the Cu/PSP/n-InP structure.

respect to that of MS reference Schottky diode. The ideality factor and barrier height for one of the Cu/PSP/n-InP contacts is calculated 1.01 and 0.82 eV, respectively. This ideality factor value is equal to expected value, 1.01 or 1.02 [22]. The barrier height value of 0.82 eV calculated for one of the Cu/PSP/n-InP contacts is higher than value of 0.45 eV for Cu/n-InP conventional diode shown in Fig. 4. This value appears to be one of the highest barrier values ever reported for the metal/n-InP diodes modified by an interlayer. For example, Jones et al. [23] reported a Φ_b value of about 0.87 eV for poly(pyrrole)/n-InP structure. Sakamoto et al. [1] obtained a value of 0.83 eV for Au/n-InP MIS structure with PN_x interlayer. The findings indicate that the PSP organic thin layer formed on n-InP inorganic substrate has modified the Φ_b value of MS InP Schottky diode in significant rate by influencing the space charge region of the inorganic substrate [24,25]. Thereby, it is known that the PSP organic thin film forms a physical barrier between the metal and the n-InP substrate, preventing the metal from directly contacting the InP surface [24–28]. According to Roberts and Evans [24], the change in the Φ_b in the Cu/PSP/n-InP device could be attributed to the substrate band bending originated from the PSP organic thin interlayer.

The interfaces of MS junctions were implicitly assumed to be laterally uniform and the contacts were characterized by their BHs and ideality factors [22,29–37]. However, Tung et al. [30,33] and Rau et al. [37] have already pointed out that inhomogeneities may play an important role and have to be considered in the evaluation of experimental I–V characteristics. The application of standard procedures gives effective BHs and ideality factors only. Both parameters vary from diode-to-diode even if they are identically prepared. To statistically investigate these parameters it gives us scientific information about interfacial and electrical properties of organic thin film and MIS device. As is well known, the homogeneity or uniformity of the Schottky BH is an issue with important implications on the theory of Schottky BH formation and important ramifications for the operation of Schottky barrier diodes and contacts [30,33]. Moreover, as mentioned in Ref. [29], the homogeneous BHs rather than effective BHs of individual contacts should be used to discuss theories on the physical mechanism that determine the BHs of MIS contacts. Thus, provided the semiconductor substrate is well characterized then the homogeneous Schottky BH may be obtained from I–V characteristics of even one contact [29]. Mönch and co-workers [22,29] showed experimentally and Tung and co-workers [30,33] reported theoretically, that a correlation exists between effective BHs and ideality factors, which may approximated by a linear relationship [22,34]. Also, several authors have reported experimental evidence that nanometer-sized lateral variations in BHs exist [35–38]. In this work, the values of BH and ideality factor for the Cu/PSP/n-InP MIS diodes as seen in Fig. 5 range from 0.73 eV to 0.82 eV, and from 1.01 to 1.52, respectively. Lateral homogeneous barrier height has been calculated as 0.80 eV by extrapolation of BH *vs.* ideality factor curve given in Fig. 5.

It is well known that the downward concave curvature of the forward bias current–voltage plots at sufficiently large voltages is caused by the presence of series resistance, apart from the interface states, which are in equilibrium with the semiconductor [39–41]. The R_s values have been calculated by using a method developed by Norde [40]. The following function has been defined in the modified Norde's method [40]:

$$F(V) = \frac{V}{\gamma} - \frac{kT}{q} \ln\left(\frac{I(V)}{AA^*T^2}\right) \tag{5}$$

where γ is the first integer (dimensionless) greater than n. $I(V)$ is current obtained from the I–V curve. Once the minimum of the F *vs.* V plot is determined, the value of barrier height can be obtained from Eq. (5), where $F(V_0)$ is the minimum point of $F(V)$ and V_0 is the corresponding voltage.

$$\Phi_b = F(V_0) + \frac{V_0}{\gamma} - \frac{kT}{q}. \tag{6}$$

Fig. 6 shows the $F(V)$–V plot of the junction. From Norde's functions, R_s value can be determined as;

$$R_s = \frac{kT(\gamma - n)}{qI}. \tag{7}$$

From the F–V plot by using $F(V_0) = 0.69$ V and $V_0 = 0.42$ V values, the values of Φ_b and R_s of the Cu/PSP/n-InP structure have been determined as 0.87 eV and 411 Ω, respectively. There is a difference between the values of Φ_b obtained from the forward bias $\ln I$–V and Norde functions.

Another fundamental property in the metal/interlayer/semiconductor interfaces is transmission probability at the interface. This property, described by the coefficient κ, represents the fraction of sufficiently energetic charge carriers that manage to cross the interface. In intimate MS interfaces, κ is often assumed to be one, with values less than one typically attributed in some small part to quantum mechanical reflection and/or phonon scattering [23,42]. Interfaces with an interfacial layer have a κ that is exponentially related to the thickness and potential barrier of the layer [23,42]: $\kappa = \exp[-(8m^*\chi)^{1/2}\delta/\hbar]$. Here m^* is the effective tunneling mass of free carriers, χ is the effective Φ_b value presented by the thin interfacial layer or the energy difference between the conduction-band edge of the semiconductor and that of the interfacial layer, and δ is the thickness of the interfacial layer. In this study, the transmission coefficient κ for Cu/PSP/n-InP structure was calculated as 2.35×10^{-6}, as stated in Refs. [23,42], by using the Fig. 4. Jones et al. [23,42] reported the κ values of 0.22 and 0.004 for the PPy/p-InP and the PPy/n-InP devices, respectively. Jones et al. [42] evaluated these different values according to some

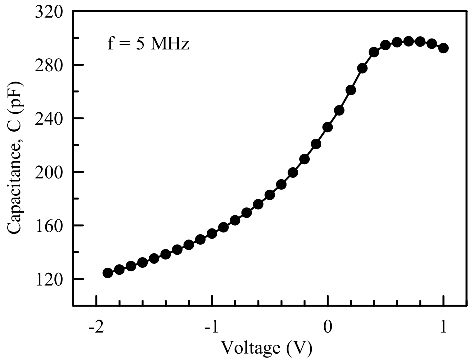

Fig. 7. High frequency (5 MHz) C–V characteristic of the Cu/PSP/n-InP MIS capacitor.

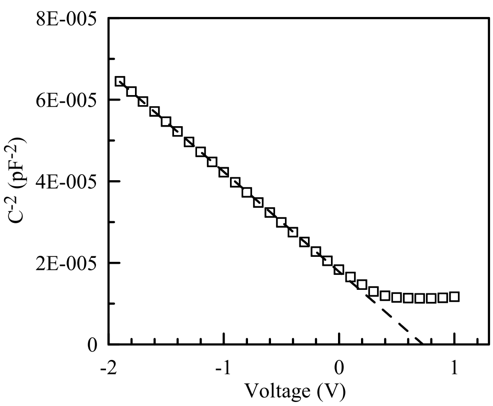

Fig. 8. High frequency (5 MHz) C^{-2}–V characteristic of the Cu/PSP/n-InP MIS capacitor.

points; such as the explanation based on interfacial layer and analysis of liquid redox couple/semiconductor interface. It can clearly be seen that our result is a reasonable value for the κ value when compared with the other reports [23,42].

In Schottky structures, the depletion layer capacitance can be written as [21]:

$$\frac{1}{C^2} = \frac{2(V_d + V)}{q\varepsilon_s A^2 N_d} \tag{8}$$

where ε_s is the dielectric constant of n-InP, V_d is the diffusion potential at zero bias and is determined from the extrapolation of the linear C^{-2}–V plot to the V axis. The value of barrier height can be calculated by the relation

$$\Phi_b(C\text{–}V) = V_d + V_n \tag{9}$$

where V_n is the potential difference between the Fermi level and the bottom of the conduction band of n-InP and can be calculated by knowing the carrier concentration N_d and it is obtained from the following relation:

$$V_n = \frac{kT}{q} \ln\left(\frac{N_c}{N_d}\right) \tag{10}$$

where $N_c = 4.9 \times 10^{17}$ cm^{-3} is the density of effective states in the valence band.

Fig. 7 shows the high frequency (5 MHz) C–V characteristic of one of the Cu/PSP/n-InP MIS capacitor with a gate bias sweep from +1 to −2 V at a rate of 0.1 V s^{-1}. As shown in the Fig. 7, C–V curve has a peak due to series resistance and interface layer effects. From the slope and voltage axis intersect of C^{-2}–V plot shown in Fig. 8 by using C–V data, diffusion potential, barrier height and free carrier dopant density have been calculated as 0.73 V, 0.84 eV and

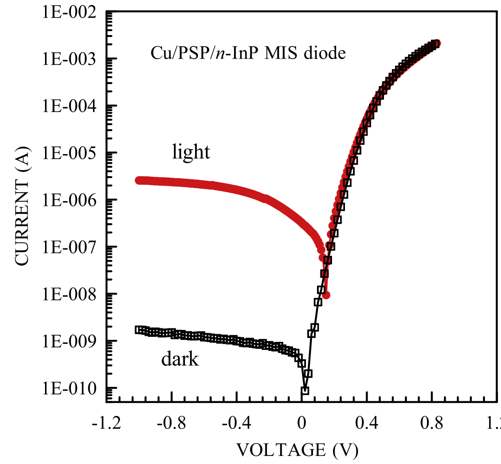

Fig. 9. Dark and illuminated I–V characteristics of one of the Cu/PSP/n-InP MIS devices at room temperature.

7.47×10^{15} cm^{-3}, respectively. It can be seen that the barrier height obtained from I–V measurement is lower than that obtained from C–V measurement as expected by Ref. [32]. According to Werner and Guttler [32] the inhomogeneities/defects at the MS interface may cause to such differences in the barrier heights determined from the I–V and the C–V measurements.

The effect of white light on the Cu/PSP/n-InP diode is shown in Fig. 9. The reverse current increases by almost three orders when white light is incident on the device. The short circuit current (I_{sc}) and open circuit voltage (V_{oc}) values for the device have been extracted as 0.33 μA and 150 mV, respectively. The structure could be attractive as a low impedance optical detector.

4. Conclusion

In conclusion, the barrier heights of the Schottky structures may be tuned by using the thin interlayers of organic dye molecules. By means of the choice of the organic molecule, the device can be designed to exhibit the desired properties. This work reported here proposes that the PSP interlayer should be considered, among other candidates, as a potential thin film for the novel MIS devices. In summary, we have studied as follows: (a) introducing to a new degree of freedom in the control of fundamental device parameters by the inclusion of well-defined PSP thin interlayers in the Cu/n-type InP inorganic MS Schottky diodes, (b) capacitance properties of the device, and (c) photovoltaic characteristic of the MIS structure.

Acknowledgments

Dr. Gullu wishes to thank Dr. M. Çankaya from Biology Department, Erzincan University and Dr. Ö. Barış from Biology Department, Atatürk University for organic material supply.

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