Electrical characteristics and interface states of Au/poly(ethylmethacrylate)/n-InP organic-modified Schottky diode at room temperature

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The current-voltage (I-V), capacitance-voltage-frequency (C-V-f) and conductance-frequency (G-f) characteristics of a fabricated Au/poly(ethylmethacrylate) (PEMA)/n-InP Schottky barrier diode have been investigated at room temperature. The Au/PEMA/n-InP structure exhibits a good rectifying behaviour. The ideality factor and barrier height of Au/PEMA/n-InP structure are found to be 1.24 and 0.74 eV from the forward I-V characteristics, respectively. The PEMA layer increases the effective barrier height of the structure since this layer creates a physical barrier between the Au metal and the n-InP. From the C-V characteristics, the diffusion potential and barrier height values are estimated as 0.757 V and 0.81 eV, respectively. Further, the energy distributions of the interface states and their relaxation times τ of the Au/PEMA/n-InP Schottky structure are determined from C-f and G-f characteristics. Experimental results show that both the interface state density N_{ss} and the relaxation time τ of the interface states decreased with bias voltage. The frequency dependence of the R_s is attributed to the distribution density of interface states.

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1. Introduction

Metal/semiconductor (MS) diodes with a low ideality factor using thin interfacial films are critical for the electronic devices. To obtain such diodes based on inorganic semiconductors such as Si, GaAs, and InP, polymeric or non-polymeric organic compounds can be used as contacts to continuously control the barrier height (BH) at certain semiconductor interfaces [1-5]. Such organic compounds have drawn in considerable attention since their ease of device processing, low cost, suitability for large-area devices, and large range of applications in electronic and optoelectronic devices [6-8]. There have been numerous studies performed to investigate the electronic properties of different organic thin films on semiconductors [9,10]. But, most inorganic materials have higher electron mobilities than organic materials. Thus, there have been made attempts to make high performance electronic devices that take an advantage of both organic and inorganic semiconductors. The formation of organic thin films on inorganic semiconductor substrates can modify the electronic properties of the MS contacts, because the Schottky barrier heights of MS contacts are changed by the formation of a dipole layer between the semiconductor and the organic film [11].

Indium phosphide (InP) is an attractive semiconductor material for high speed electrical and optoelectronic devices due to its superior characteristics such as large direct band gap, high electron mobility, high surface velocity and breakdown voltage [12-13]. It is difficult to obtain a Schottky barrier height (SBH) greater than 0.5 eV [14-17], due to large current for metal-InP substrate at room temperature. Various methods can be adopted to enhance the effective barrier height of the InP based Schottky contacts such as insertion on interlayer between metal and semiconductor [18-20] and depinning the Fermi level by using a high work function metal [21]. Assuming that the surface Fermi level pinning is used by high surface state density, passivation technology is necessary to reduce the surface states of InP. In order to fabricate metal-interlayer-semiconductor Schottky structure with an enhanced barrier height, it is important to introduce organic layer on semiconductors in which surface passivation and insulating film deposition are carried out successively [22].

In recent years, conducting polymers have received much attention since their wide range of device applications. Many researchers have investigated by using various organic materials as the interfacial layers at metal-semiconductor junction [23-27]. For example, Gullu *et al* [23] investigated the rectifying junction characteristics of methyl red (MR) organic film on n-type InP substrate, reported that the MR film increases the effective barrier height by influencing the space charge region of the n-InP. Farag *et al* [24] studied the rectification and barrier height inhomogeneity in Al/Rhodamine-B based Schottky diode. They reported that the diode parameters extracted from the I-V and C-V characteristics were strongly influenced by the temperature. Gullu *et al* [25] investigated the electrical properties of Cu/phenolsulfonphthalein (PSP)/n-InP Schottky diode by current-voltage (I-V) and capacitance-voltage (C-V) measurements. They found that the barrier height of the Cu/PSP/n-InP Schottky diode was higher (0.82 eV) than that of Cu/n-InP Schottky diode. Reddy *et al* [26] studied the effect of annealing temperature on electrical properties of Au/polyvinyl alcohol/n-InP Schottky diode, found that the interlayer PVA increase the barrier height of the conventional Au/n-InP Schottky diode. Very recently, Reddy *et al* [27] investigated the electrical properties of Au/polymethyl methacrylate (PMMA)/n-InP Schottky barrier diode at different annealing temperatures using I-V and C-V techniques, reported that the Au/PMMA/n-InP structure shows excellent rectifying behavior. They also reported that the interface state density and series resistance have a significant effect on the electrical characteristics of Au/PMMA/n-InP Schottky barrier devices.

The aim of the present work is to fabricate and characterize the Au/PEMA/n-InP Schottky diode formed by insertion of poly(ethylmethacrylate) (PEMA) interlayer between n-InP semiconductor and Au metal. In this work, PEMA is chosen as an interfacial layer because it is methacrylic ester polymer and has excellent chemical resistance, high surface resistance and offers high optical transparency [28]. Specially, PEMA as a polymer waveguide and as optical and/or electronic components has become important. In this paper, an attempt is made to investigate the electrical characteristics of Au/PEMA/n-InP Schottky barrier diode using current-voltage (I-V), capacitance-voltage (C-V), capacitance-frequency (C-f) and conductance-frequency (G-f) measurements at room temperature.

2. Experimental details

The Au/poly(ethylmethacrylate)/n-type InP Schottky barrier diodes were prepared using one side polished n-InP wafer with a carrier concentration of 5×10^{15} cm^{-3} (as received from the manufacturer). The wafer was chemically cleaned with warm trichloroethylene, acetone and methanol by means of ultrasonic agitation for each step 5 min to remove contaminants followed by rinsing in deionized water and dried in N_2 flow. Then, the wafer was etched with HF (49%) and H_2O (1:10) for 30 s to remove the native oxides from the substrate. An ohmic contact was made by thermal evaporation of indium (In) on the rough side of the n-InP. Afterwards, low resistance ohmic contacts were formed by annealing at 350°C for 1 min in N_2 atmosphere using rapid thermal annealing (RTA) system. Then, the poly(ethylmethacrylate) (PEMA) solution was directly formed on the polished side of the n-InP wafer by using spin coating (Spin coater, Model No. WS-650Mz-23NPP, 60 s at 2000 rpm) method and evaporated by itself for drying of the solvent in nitrogen atmosphere for 1 hour. The thickness of the film was found to be about 30 nm by profilometer. The thickness of the organic film so obtained across the full substrate was uniform. Finally, the contacting electrode with diameter of 0.7 mm on PEMA was made by evaporation of gold (Au) with a thickness of 50 nm through stainless steel mask by e-beam evaporation system at a pressure of 5×10^{-6} mbar. Thus, the Au/PEMA/n-InP Schottky barrier diodes were obtained. The current-voltage (I-V) and capacitance-voltage (C-V) measurements were carried out by using a computer controller Keithley 2400 voltage source and automated deep level transient spectrometer (DLS-83D) at room temperature and in the dark, respectively. Capacitance-frequency (C-f) and conductance-frequency (G-f) characteristics of Schottky diode was also measured using a LCR meter (model No: PSM 1700) at various biases at room temperature.

3. Results and discussion

The forward-bias I-V characteristics of Schottky barrier diodes for qV>3kT with a thin interfacial layer (MIS) is considered, according to the thermionic emission (TE) theory, the current across a diode can be expressed as [29]

$$I = I_o \exp\left(\frac{qV}{nkT}\right)\left[1-\exp\left(\frac{-qV}{kT}\right)\right] \tag{1}$$

with

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

where I_o is the saturation current, q is the electron charge, V is the applied voltage, T is the absolute temperature, n is the ideality factor, k is the Boltzmann's constant, A is the contact area, A^{**} is the effective Richardson's constant (9.4 A cm^{-2} k^{-2} for n-InP based on the effective mass (m^*=0.078 m_o)) [30], and Φ_b is the Schottky barrier height (SBH). From Eqs. (1) and (2) ideality factor n and barrier height Φ_b are given by

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

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

A plot of ln(I) versus V is a straight line with a slope of q/(nkT) and the intercept on y-axis yields I_o. Using Eq. (4), barrier height (Φ_b) can be calculated. The experimental semi-logarithmic forward and reverse bias I-V characteristics of the Au/PEMA/n-InP Schottky diode are shown in Fig. 1. The barrier height and ideality factor are found to be 0.74 eV and 1.24 for the Au/PEMA/n-InP Schottky diode. It is noted that the barrier height achieved for the Au/PEMA/n-InP Schottky diode is higher than that of the as-deposited Au/PMMA/n-InP Schottky diode [27].

Normally, Schottky barriers to n-InP yield low barrier heights. Szydlo and Oliver [31] and Benamara *et al* [32] reported that the barrier height of Au/n-InP contacts was about 0.46 and 0.44 eV respectively. Further, Shi *et al* [33] found that the barrier height of Au/n-InP contact was 0.51 eV. Our experimental results show that the barrier height obtained for the Au/PEMA/n-InP Schottky diode is higher than the reported values [31,32,33]. This indicates that the PEMA interfacial layer has modified the barrier height value of MS n-InP Schottky diode in significant rate by influencing the space charge region of the InP substrate.

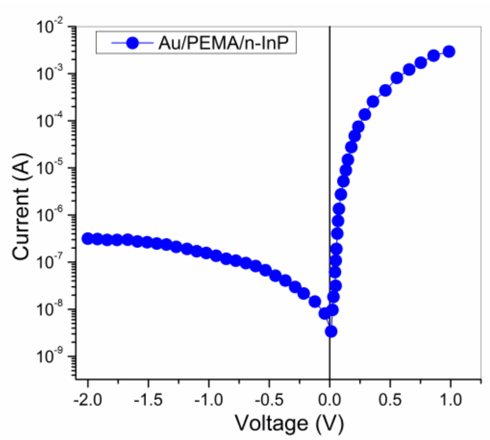

Fig. 1. The reverse and forward I-V characteristics of the Au/PEMA/n-InP Schottky diode at room temperature.

Fig. 2 shows a plot of $1/C^2$ as a function of bias voltage for the Au/PEMA/n-InP Schottky diode measured at 1 MHz at room temperature. The C–V relationship for the Schottky diode is given by [34]

$$\frac{1}{C^2} = \left(\frac{2}{\varepsilon_S q N_d A^2}\right)\left(V_{bi} - \frac{kT}{q} - V\right) \quad (5)$$

where ε_s is the permittivity of the semiconductor ($\varepsilon_s = 11\varepsilon_o$, ε_o is the dielectric constant $=8.85\times10^{-12}$ F/m), V is the applied voltage and A is the surface area of the diode, N_d is the doping concentration and V_{bi} is the built-in voltage at zero-bias, and it can be obtained by extrapolation of the $1/C^2$–V plot to the voltage axis as 0.732 V for the Au/PEMA/n-InP Schottky diode. In addition, the doping concentration for the Schottky diode is obtained as 1.01×10^{15} cm^{-3}. Using the obtained V_{bi} values the diffusion potential values at zero-bias were calculated using the following relation

$$V_d = V_{bi} + \frac{kT}{q} \quad (6)$$

and it is found as 0.757 V for the Au/PEMA/n-InP Schottky diode. The barrier height is given by

$$\Phi_{b(c-v)} = V_d + \frac{kT}{q}\ln\left(\frac{N_c}{N_d}\right) \quad (7)$$

The density of states in the conduction band edge is given by $N_c=2(2\pi m^* kT/h^2)^{3/2}$, where $m^*=0.078m_o$, and its value was 5×10^{15} cm^{-3} for n-InP at room temperature [35]. Measurements showed that the barrier height of Au/PEMA/n-InP Schottky diode is 0.81 eV, which is larger than the barrier height obtained from the I–V measurement (0.74 eV).

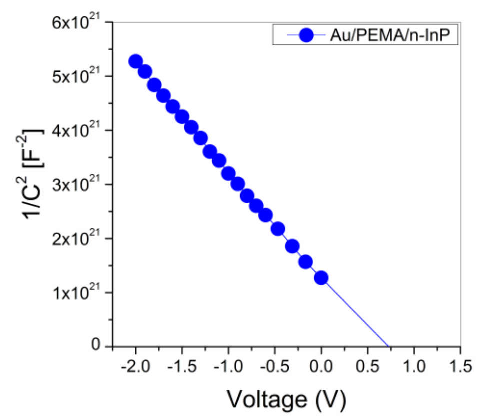

Fig. 2. Plot of $1/C^2$ versus V for the Au/PEMA/n-InP Schottky diode at room temperature.

A relatively large discrepancy between the barrier heights obtained by I–V and C–V techniques could be associated with the barrier height inhomogeneities such as non-uniformity of the interfacial layer thickness and distributions of the interfacial charges [36]. The current across the interface depends exponentially on barrier height and it is sensitive to the distribution of interface states at the interface [17, 37]. The capacitance is insensitive to potential fluctuations on a length scale of less than the space-charge region, and C-V method averages the BH over the whole area. C-V measurements are generally less prone to interface states, so that the determined barrier height is considered more reliable, though the depletion width can be altered by the interface defects if they are deeper into the space charge region.

Further, the capacitance-frequency (C-f), conductance-frequency (G-f) and series resistance-frequency (R_s-f) measurements of Au/PEMA/n-InP Schottky structure have been carried out at room temperature. Fig. 3 shows the forward bias C-f characteristics of the Au/PEMA/n-InP Schottky structure at different voltages from 0.00 to 0.50 V. It can be seen from Fig. 3, the measured capacitance is almost constant up to a certain value of the frequency in the lower side of the frequency scale. As well, the higher value of capacitance at low frequency is due to excess capacitance resulting from the interface states that can follow the a.c. signal. At low frequencies, the interface states can follow the a.c. signal while at high frequency they cannot follow the a.c. signal. At the high frequency region, the capacitance values originate from only space charge capacitance. Hence, the diode capacitance decreases rapidly at the high frequencies [38]. Fig. 4 shows the experimental G-f characteristics of Au/PEMA/n-InP at room temperature at various bias voltages. As can be seen from Fig. 4, the conductance has remained almost constant up to a certain value of the frequency in the lower side of the frequency scale. As the frequency is increased further, the diode conductance showed a continuous increase at all of the applied voltage.

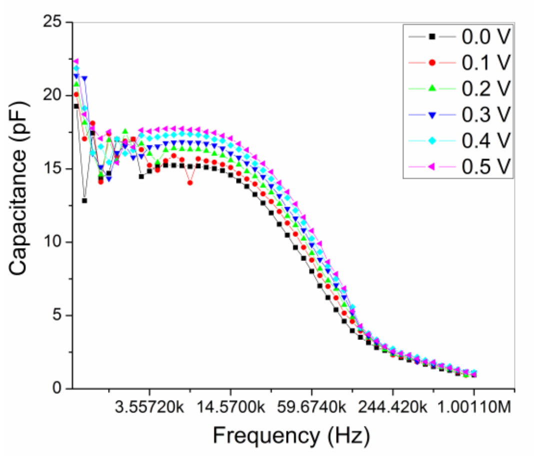

Fig. 3. The experimental C-f curves of the Au/PEMA/n-InP Schottky diode (0.0-0.5 V with steps of 0.1) at room temperature.

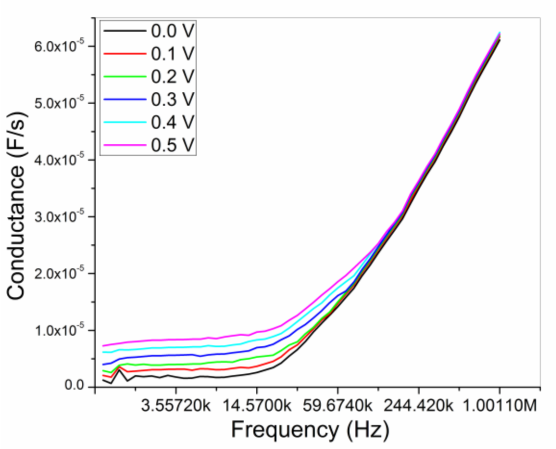

Fig. 4. The experimental G-f curves of the Au/PEMA/n-InP Schottky diode (0.0-0.5 V with steps of 0.1) at room temperature.

Now, the density distribution of the interface states from the experimental C-f and G-f measurements (the conductance method) has been calculated for the Au/PEMA/n-InP Schottky structure. The interface state conductance for this structure can be expressed according to Nicollian [39] and Goetzberg [40] as

$$G_{ss} = \frac{AqN_{ss}}{2\tau}\ln(1+\omega^2\tau^2) \tag{8}$$

where $\omega = 2\pi f$ is the angular frequency and τ is relaxation time constant of the interface states which can be written as

$$\tau = \frac{1}{V_{th}\sigma N_d}\exp\left(\frac{qV_d}{kT}\right) \tag{9}$$

N_{ss} is the interface state density, σ is the capture cross-section of interface states, V_{th} is the thermal velocity of carrier, N_d is the doping concentration and A is the contact area.

The conductance of the interface states G_{ss} is given by [40, 41]

$$G_{ss} = \frac{C_{ox}^2 G}{(C_{ox}-C)^2+(G/\omega)^2} \tag{10}$$

where G and C are the experimental measured diode conductance and capacitance of the diode, respectively, the capacitance of the interfacial layer plus PEMA film C_{ox} is determined from the high-frequency values of C. Besides, the energy of the interface states E_{ss} with respect to the bottom of the conduction band (E_c) at the surface of the semiconductor for n-type semiconductor is given by [42]

$$E_c - E_{ss} = q(\Phi_b - V) \tag{11}$$

The quantity G_{ss}/ω given in Fig. 5 is calculated from the C and G versus frequency measurements (Figs. 3 and 4) with help of Eq. (10). The G_{ss}/ω versus ω behaviour can be explained by the presence of an almost continuous distribution of interface state energy levels. At a given bias, the Fermi level fixes the occupancy of these interface trap levels. Hence, an interface charge density will be at the n-InP surface which determines the relaxation time constant of the related interface states. The peak height reduction is associated to the interface trap levels will occur as the a.c. signal corresponds to this time constant. If the frequency is slightly different from the relaxation time constant, peak heights are reduced because trap levels do not respond to the signal. Hence, the peak height reduction is a function of frequency. Also, the peak value depends on the capture rate, that is, on the interface state level occupancy that is determined by the applied bias [43]. The curves go through maxima at $\omega\tau = 1.98$ with values of $(G_{ss}/\omega)_{max}$ $=0.40qAN_{ss}$ [39,40]. The ordinates and frequencies of the maxima yield density of the interface states and their time constant, τ. After that, the dependence of N_{ss} and τ on the bias is converted to a function of E_{ss} using Eq. (11).

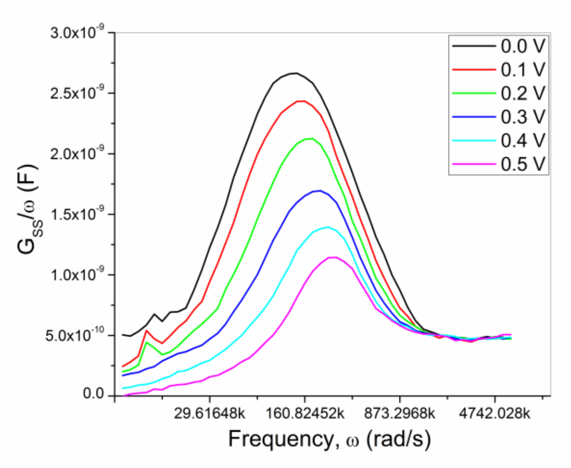

Fig. 5. G_{ss}/ω versus ω characteristics of the Au/PEMA/n-InP Schottky diode at various biases (0.0-0.5 V).

The energy distribution of the interface states and their relaxation time constants obtained from the experimental G_{ss}/ω versus ω characteristics of the Au/PEMA/n-InP Schottky diode at room temperature is shown in Fig. 6. The interface state densities and their relaxation times are in the range of 1.08×10^{13} $eV^{-1}cm^{-2}$ and 1.41×10^{-5} s at (E_c-0.74) eV to 4.64×10^{12} $eV^{-1}cm^{-2}$ and 0.70×10^{-5} s at (E_c-0.24) eV, respectively. It can be seen from Fig. 6, both the interface state density and the relaxation time constants of the interface states decrease with bias voltage. Aydogan *et al* [44] reported that the interface states were strongly influenced the properties of the PANI/*p*-Si/Al structure which could generate large number at the semiconductor surface when the polymers deposited onto the inorganic semiconductor. Gullu *et al* [23] determined interface properties of Au/methyl-red/n-InP contact, they found that the interface state density values varied from 4.35×10^{12} $cm^{-2}eV^{-1}$ to 1.04×10^{12} $cm^{-2}eV^{-1}$. The interface state density of the Au/PEMA/n-InP diode is consistent with those of above mentioned Schottky diodes with organic interlayer.

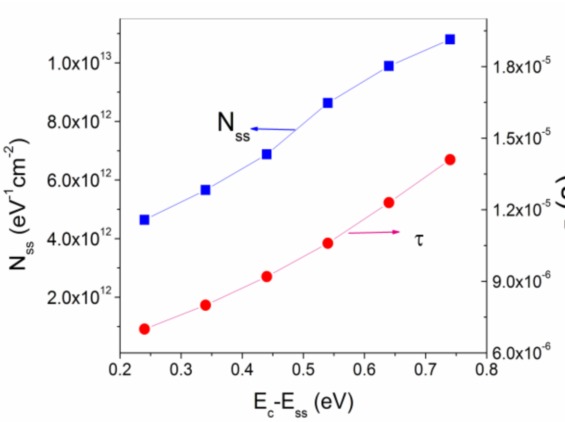

Fig. 6. Energy distribution plots of the interface state density and their time constant obtained from the G_{ss}/ω versus ω characteristics for the Au/PEMA/n-InP Schottky diode at room temperature.

Another important parameter for Schottky barrier diode is the series resistance (R_s). For the Au/PEMA/n-InP Schottky diode, the frequency dependent series resistances can be calculated from the experimental C-V-f measurements as [40]

$$R_s = \frac{G}{G^2 + (\omega C)^2} \tag{12}$$

where C is measured capacitance, and G is conductance values. The series resistance of Au/PEMA/n-InP structure as function of the frequency is calculated by using Eq. (12). Fig. 7 shows the frequency dependence of the series resistance for different bias voltages at room temperature. As can be clearly seen from Fig.7, the series resistance R_s does not change almost with frequency at low frequencies, whereas, it decreases at high frequencies and reaches a constant value. The frequency dependence of the R_s is attributed to the distribution density of interface states [45].

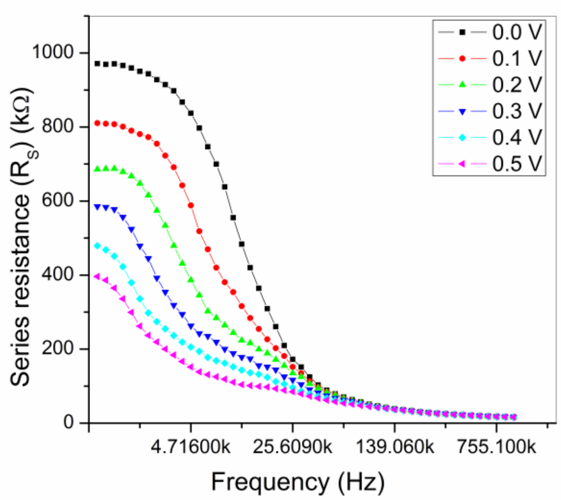

Fig. 7. Plot of series resistance versus frequency of the Au/PEMA/n-InP Schottky diode at room temperature.

4. Conclusions

In conclusion, the current-voltage (I-V), capacitance-voltage-frequency (C-V-f) and conductance-frequency (G-f) characteristics of the prepared Au/PEMA/n-InP Schottky barrier diode have been investigated with different bias voltages at room temperature. The Au/PEMA/n-InP Schottky barrier diode shows good rectification behaviour. The estimated barrier heights of Au/PEMA/n-InP Schottky barrier diode are 0.74 eV (I-V) and 0.81 eV (C-V). The modification of the interfacial potential barrier for Au/n-InP Schottky diode is obtained using a thin organic PEMA interlayer. The difference in the barrier heights obtained from I-V and C-V measurements is discussed. It is noted that the measured capacitance is almost constant up to a certain value of the frequency, after this value the capacitance decreases with increasing frequency. The higher values of capacitance at low frequencies are due to excess capacitance resulting from the interface states that can follow the a.c. signal. Besides, the energy distribution of the interface states and their relaxation time constants are calculated from the C-f and G-f characteristics of the Au/PEMA/n-InP Schottky barrier diode at room temperature. The interface state density (N_{ss}) values and the relaxation time constants show an exponential rise with bias from the bottom of the conduction band towards the midgap.

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