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Electronic and optical properties of electrochemically polymerized polycarbazole/aluminum Schottky diodes

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We report the fabrication of organic Schottky diodes on indium tin oxide (ITO) coated glass by electrochemically polymerized polycarbazole (PCz) with configuration ITO/PCz/Al. The diode has been characterized in respect of electrical and optical properties. The study involves estimation of optical bandgap of the polymer from UV-visible spectroscopic measurements. The current-voltage (J-V) and capacitance-voltage (C-V) characteristics of the Schottky diode were subsequently used for extracting electronic parameters of the device such as ideality factor, barrier height, reverse saturation current, built-in potential, depletion width, doping concentration, etc. The photoresponse of the Schottky contact was measured by illuminating the device with a laser source operating at 650 nm having an incident optical power density of $10\ \mathrm{mW/cm^2}$. The device exhibits a high value of peak detectivity ($\sim 10^7\ \mathrm{cm\,Hz^{1/2}\,W^{-1}}$) near zero bias voltage and the same attains a value of the order of $10^9\ \mathrm{cm\,Hz^{1/2}\,W^{-1}}$ at a reverse bias of -6 V. © *2009 American Institute of Physics*.
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I. INTRODUCTION

With the advent of conducting polymers the researchers all over the world started exploring the potential of these materials as an alternative of inorganic semiconductors in making electronic and optoelectronic devices. A variety of electronic and optoelectronic devices based on conducting polymers have been developed and deployed in civil and military situations. These devices include polymer based Schottky diodes, tunnel diodes, thin-film field-effect-transistor in the metal-insulator-semiconductor and Schottky gate form, light-emitting diodes, and even photovoltaic devices. In view of the dramatic development in this field in the recent past it is predicted that polymer based electronic devices would be used as computer memory and logic circuits on computer chips in place of inorganic silicon. More interestingly, many of these organic polymers have excellent optical properties that would make them potential candidates for use as optoelectronic devices. Organic light-emitting diode is already commercially available as a low-cost optical source that can easily outperform more expensive inorganic counterparts based on III-V and II-VI materials. The conjugated conducting polymers have attracted increasing attention of the researchers because of their potential to replace inorganic semiconductors in the development of low-cost electronic and optoelectronic devices including electroluminescent devices, photovoltaic devices, and gas sensors. Currently the dominant materials used for making optoelectronic devices include a host of III-V and II-VI inorganic materials. These materials are not only expensive and fragile but also involve more complex and uneconomic processing technology. On the other hand, the synthetic polymers are much cheaper and require simple techniques for making electronic devices. These factors have actually motivated the researcher to study these materials as a viable alternative of silicon and other inorganic materials since the early inception of semiconducting polymers.

Conducting polymers have been extensively investigated over the past two decades in order to explore their fundamental physical properties, chemical properties, and their technological applications in various fields such as electronic and optoelectronic devices, chemical and biological sensors, soft actuators, artificial muscles, electromagnetic interference shielding, antistatic materials, and secondary batteries.[1–4] In recent years there has been much interest in organic semiconductor as new materials for flexible electronics devices, owing to their easy processing and potential for low-cost fabrication. Conducting polymers can be obtained by both chemical and electrochemical methods. Their properties can be tailored by modifying experimental conditions, in particular, in the case of electrochemical polymerization. Although spin coating technique is very convenient for deposition of the good quality film of conducting polymers, a large amount of material is lost during spin coating process. On the other hand electrochemical polymerization technique reduces the cost of the devices by minimizing the loss of material. Moreover, it is suitable for reproducibility and it has the ability to derive a homogenous thickness distribution with controlled electrochemistry of both processable and nonprocessable polymers. Polycarbazole (PCz) is one of relatively new conducting polymer groups with good thermal stability, electrochemical, and photoactive characteristics, and its conducting form can be easily obtained by electrochemical polymerization.[5–7] Polycarbazole and its derivatives have

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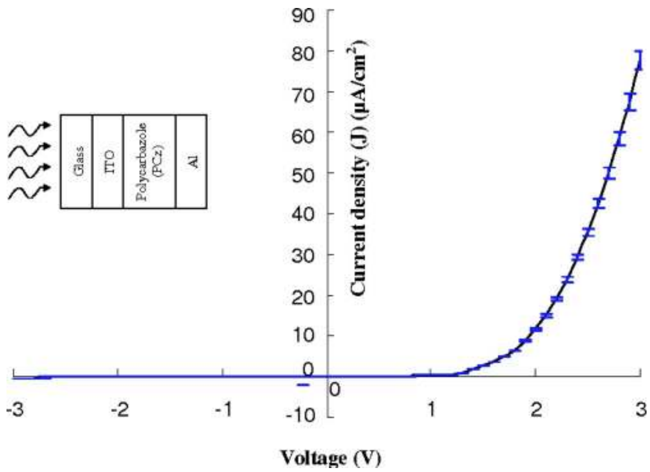

FIG. 1. (Color online) *J-V* characteristic of Al/PCz/ITO showing standard deviation in measurements on random samples along with device configuration shown as inset.

been widely synthesized and used for a variety of applications such as sensors, light-emitting diodes, and photovoltaic devices.[8–11]

Metal/semiconductor Schottky junction is a very useful device for evaluating electronic properties of semiconductors. A thorough understanding of these properties are essential in order to explain the fundamental mechanism of charge injection from metal electrode to π-conjugated polymeric system, which is the key to the design and operation of electronic and optoelectronic devices.[12,13] The metal/organic semiconductor junctions have been tried as a substitute of the metal/inorganic semiconductor junctions in order to provide low-cost flexible electronic devices and systems. This success has been phenomenal over the past decade opening up new avenues and possibilities of replacing conventional inorganic devices by plastic ones. The absorption of light energy in thin films of π-conjugated and conducting polymers in the UV and visible range is an added advantage of these material systems which can be exploited for conversion of electrical signal to optical one and vice-versa leading to some interesting applications such as solar cell, luminescence devices, storage devices, and photodetectors.[14–17]

In this paper we report an organic Schottky diode based on polycarbazole semiconducting conjugated polymer with a configuration of indium tin oxide (ITO) coated glass/PCz/Al. Four sets of devices fabricated in separate batches have been characterized for electrical and optical properties.

II. EXPERIMENTAL

The schematic cross sectional view of fabricated device ITO/PCz/Al Schottky junction is shown in the inset of Fig. 1. The metal Al was deposited with area of 16 mm^2 using a mask on different samples of PCz/ITO by vacuum evaporation method by using vacuum coating system from HIND HIVAC (model 12A4D). The devices Al/PCz/ITO were not sealed up from attack of moisture and oxygen, but kept in vacuum desiccator for further characterizations. The thickness of polymer was of the order of 400 nm as estimated from atomic force microscope (AFM) measurement and thickness of metals on top of the polymer film was preadjusted to 80 nm in each case. Current-voltage (*I-V*) and capacitance-voltage (*C-V*) measurements of devices Al/PCz/ITO structure was carried out with HP Semiconductor Parameter Analyzer (SPA) of Hewlett-Packard, USA make, model 4145B and *LCR* meter from the Hewlett-Packard, model HP4284A, respectively, at room temperature (27 °C) in air under dark condition.

The polycarbazole films were electrochemically polymerized under ambient condition by using Electrochemical Work Station (CH Instrument Inc., USA) at constant potential (1.3 V) in three electrodes equipped cell having conducting ITO glass substrate (with surface resistance of 12 $\Omega\ cm^2$) as working electrode, Pt plate as counter electrode, and Ag/AgCl as reference electrode.[8] The reaction solution consists of 60 mM carbazole, 0.1M tetrabutyl ammonium perchlorate (TBAP) in dichloromethane. After polymerization, ITO coated glass electrode was washed by dichloromethane to remove extra monomer, dried, and preserved for the various characterization. Surface morphology of electropolymerized PCz film on ITO coated glass plate was studied by using AFM (NT-MDT, Russia made, model PRO 47). The semiconducting polymer PCz was characterized for optical and electrical properties. UV-visible study was done by using the spectrophotometer from Perkin Elmer, Germany (model Lamda 25). Electrochemical studies were done using Electrochemical Work Station of CH Instrument Inc., USA. For optical characterization the device was tested under illumination of red light ($\lambda = 650$ nm, optical power $= 10\ mW/cm^2$) through the rear glass side using an injection laser diode (ILD) unit with drive circuit from Benchmark (model FOSM-D 600).

III. RESULTS AND DISCUSSION

The band gap of polymer is evaluated from the absorbance spectra of the PCz polymer coated on optically transparent ITO glass. The substrate absorbance was corrected by introducing an uncoated ITO glass of the same size as the reference. The optical bandgap of polymer was estimated by fundamental relation given by[18]

$$\alpha h\nu = B(h\nu - E_g)^n, \tag{1}$$

where α is the absorption coefficient, $h\nu$ is the energy of absorbed light, $n=1/2$ for direct allowed transition, and B is the proportionality constant. Energy gap (E_g) was obtained by plotting $(\alpha h\nu)^2$ versus $h\nu$ and extrapolating the linear portion of $(\alpha h\nu)^2$ versus $h\nu$ to zero, as shown in Fig. 2. The absorbance versus wavelength plot is shown in Fig. 3. The band gap of PCz was estimated to be 2.88 eV by using this method. The electroactivity and stability of PCz film was supported by cyclic voltammetry in the 0.1M tetrabutyl ammonium perchlorate and dichloromethane solution in the range of −0.4 to 1.6 V, as shown in Fig. 4. The redox behavior of electropolymerized polycarbazole is associated with doping (*p*-type) and dedoping of the ClO_4^- anion within the polymer interstices. The surface morphology of the electropolymerized polycarbazole on ITO coated glass plate was studied using AFM under semicontact mode ($8\times 8\ \mu m^2$

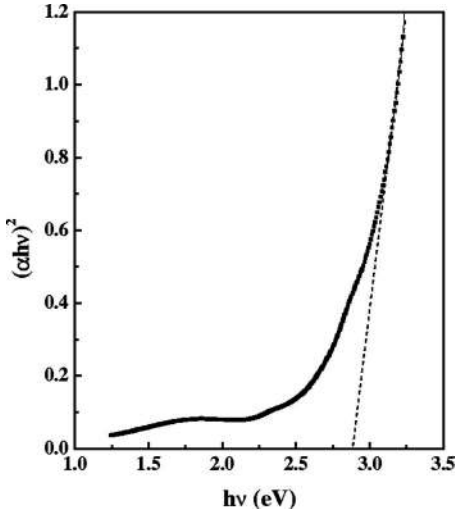

FIG. 2. $(\alpha h\nu)^2$ vs $h\nu$ plot for bandgap estimation of PCz.

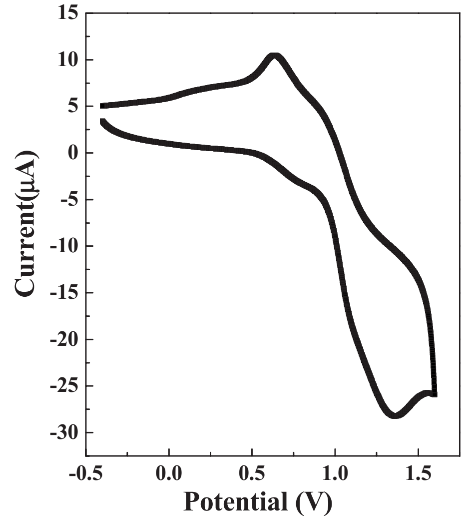

FIG. 4. Cyclic voltammogram of PCz/ITO at 50 mV/s scan rate.

scan size), as shown in the Fig. 5. The surface of polymer film looks like a uniformly organized globular structure, which is made up of polycarbazole chains bundles.

The rectifying nature of the devices is confirmed by the measured *J-V* characteristics. The *J-V* characteristics under dark condition of a sample ITO/PCz/Al device taken from the four sets of devices fabricated in the laboratory is illustrated in Fig. 1. Also shown in the figure are the departures in the current values at different applied voltages for random samples taken from the four sets in terms of standard deviation shown by vertical lines in the *J-V* characteristics shown in Fig. 1. The metal-semiconductor rectifying contacts can be described by thermionic emission-diffusion theory and/or field emission theory in the case of heavily doped semiconductor.[19] As the semiconducting polymer behaves as a lightly doped *p*-type material,[20] the electrical characteristics of ITO/PCz/Al junction have been analyzed by assuming the standard emission-diffusion theory. According to this theory, the *J-V* relationship is expressed as

$$J = J_0\left[\exp\left(\frac{qV}{\eta kT}\right) - 1\right], \tag{2}$$

where J $(=I/A)$ is the current per unit area, J_0 is the saturation current density in absence of external bias, q is the electronic charge, V is the applied voltage, T is the absolute temperature, η is the diode quality factor (ideality factor), and k is the Boltzmann constant. Further J_0 is related to the Schottky barrier height, ϕ_B as

$$J_0 = A^* T^2 \exp\left(\frac{-q\phi_B}{kT}\right), \tag{3}$$

where A^* is the effective Richardson constant. The value of A^* is calculated by using effective mass of charge carrier in polycarbazole thin film and found to be 1.2 A cm^{-2} K^{-2}.[21]

Under the condition $qV/\eta kT \gg 1$, Eq. (2) can be approximated as

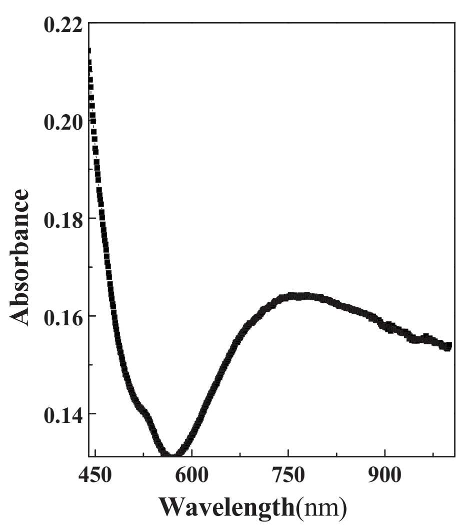

FIG. 3. UV-visible spectrum of PCz.

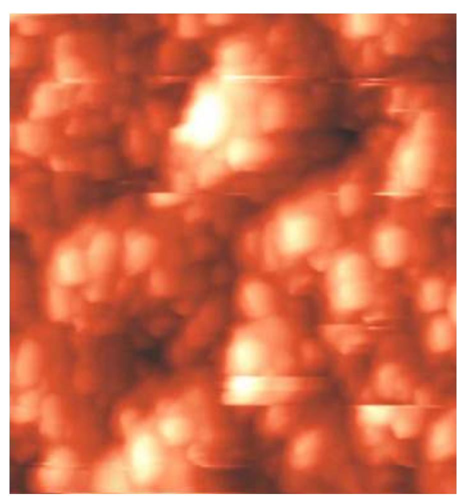

FIG. 5. (Color online) AFM image of electropolymerized PCz film on ITO coated glass substrate.

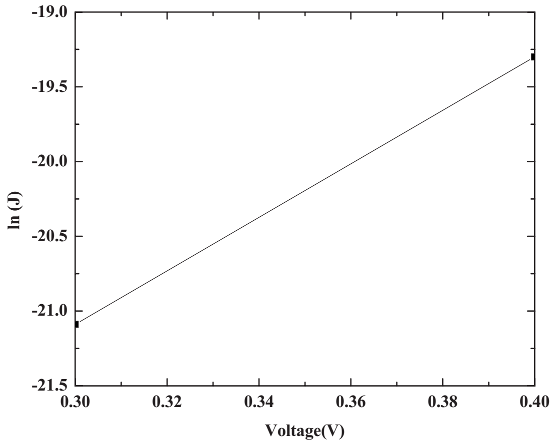

FIG. 6. $\ln(j)$ vs V.

$$\ln(J) = \ln(J_0) + \frac{q}{\eta kT}V. \tag{4}$$

The value of ideality factor at 27 °C for the device was determined from the slope of the plot $\ln(J)$ versus V, as shown in Fig. 6, and found to be 1.9 (Table I). The reverse saturation current was determined by putting above the value of ideality factor in Eq. (2) at $V=0.2$ V and is found to be 5.32×10^{-10} A/cm^2. The barrier height ϕ_B evaluated from Jo at room temperature was found to be 0.85 eV. The departure of the ideality factor from unity is attributed to the barrier inhomogeneity. The smaller value of J_0 accounted for larger depletion width (as confirmed from C-V measurements discussed later in this section), which reduces the possibility of tunneling at the interface. An extremely low value of reverse saturation current density of the device would make it especially attractive for low noise application in the detection of optical signal in visible region.

Capacitance-voltage (C-V) measurements were carried out for determination of built-in potential V_{bi} and depletion width W_d and carrier concentration in depletion layer of diode.[19] The capacitance-voltage relationship of the Schottky junction under bias can be expressed as

$$C = \left[\frac{q\varepsilon_0\varepsilon_s N_A}{2(V_{bi}-V)}\right]^{1/2}, \tag{5}$$

where C is the junction capacitance of the Schottky diode per unit area, V_{bi} is the built-in potential, V is the applied voltage, ε_0 is the free space permittivity, ε_s is the dielectric constant of PCz (=4.8) (Ref. 21), and N_A is the acceptor concentration in the depletion layer.

Equation (5) can be expressed as

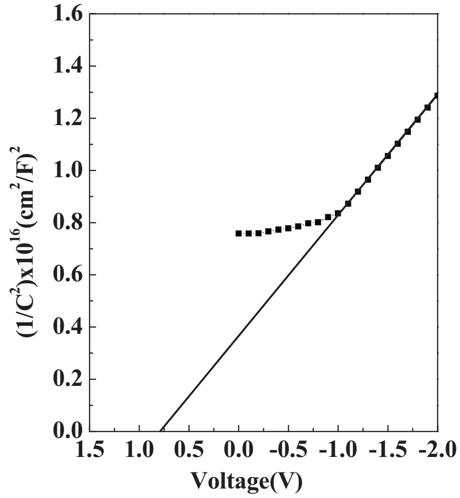

FIG. 7. $1/C^2$ vs V characteristic of Al/PCz/ITO.

$$\frac{1}{C^2} = \frac{2V_{bi}}{q\varepsilon_0\varepsilon_s N_A} - \frac{2V}{q\varepsilon_0\varepsilon_s N_A}. \tag{6}$$

From Eq. (6) it is seen that the variation in $1/C^2$ versus voltage will be a straight line and is independent of measuring frequency. However, the results of experimental measurements reveal that the slope of the $1/C^2$-V line varies slightly with the measuring frequency as observed and reported by others.[22–24] The $1/C^2$-V characteristics of the device measured experimentally at 100 kHz by LCR meter is shown in Fig. 7.

Further, the depletion layer width is expressed as

$$W_d = \left[\frac{2\varepsilon_0\varepsilon_s(V_{bi}-V)}{qN_A}\right]^{1/2}. \tag{7}$$

The built-in potential $V_{bi}=0.80$ V is determined by extrapolating the linear region of $1/C^2$ versus V to cut the V-axis and the acceptor concentration is calculated from slope of $1/C^2$ versus V. The nonlinearity observed in $1/C^2$ versus V plot may account for the interface states across the band gap and/or the surface irregularities which cause the variation in effective area of diode with bias. The variation in the depletion layer width with the applied voltage as estimated on the basis of Eq. (5) is shown in Fig. 8. The value of barrier height obtained from C-V measurement is found to be 0.78 eV. The deviation of barrier height from J-V and C-V measurement may be due to the presence of interfacial dipole ($\Delta=0.07$ eV).[25] The work function of polymer can be calculated using the value of the metal work function and measured built-in potential by relation.[26]

TABLE I. Device electrical parameters.

Device	Φ_S (eV)	η	ϕ_B (eV)	J_0 (A/cm^2)	V_{bi} (V)	N_A (cm^3)	W_d (nm) for applied voltage of 0 V	−3 V
ITO/PCz/Al	5.08	1.9	0.85	5.23×10^{-10}	0.80	4.0×10^{16}	103	224.6

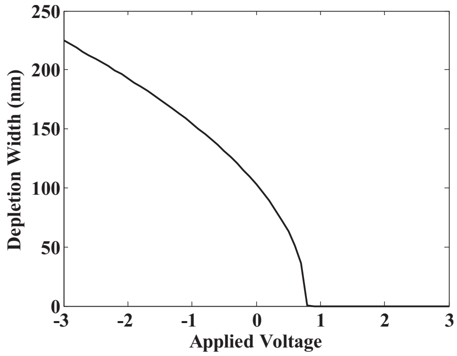

FIG. 8. Variation in depletion width (W_d) vs applied voltage (v).

$$\varphi_{sc} = qV_{bi} + \varphi_M, \tag{8}$$

where φ_{sc} and φ_M are the work function of semiconducting polymer (PCz) and metal (Al), respectively. Figure 9 shows the reverse bias characteristics of this Schottky diode in dark and under illumination of wavelength 650 nm and power density of 10 mW/cm^2. The device was illuminated by a 650 nm Fabry-Perot (FP) laser source from the rear side (glass substrate). The current-voltage characteristic in the illuminated condition was measured by using HP SPA. The incident optical power was measured by an optical power meter from Benchmark (model FOPM-101E). The quantum efficiency is estimated using the relationship[19]

$$\eta_i = \frac{I_p}{P_{opt}}\left(\frac{hc}{\lambda q}\right), \tag{9}$$

where I_p is the measured photocurrent, P_{opt} is the measured optical power, h is Planck's constant, c is the velocity of light, λ is the operating wavelength (650 nm), and q is the electronic charge.

The variation in photocurrent density of the device with the applied voltage varying from 0 to −6 V is shown in Fig. 10. The voltage dependent detectivity (D) of the device was estimated using following expression[27]

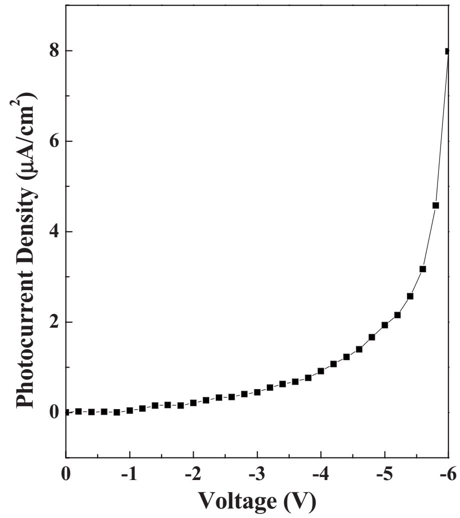

FIG. 10. Photocurrent density vs reverse bias applied voltage.

$$D = \frac{\lambda \eta_i q}{hc}\sqrt{\frac{RA}{4kT}}, \tag{10}$$

where η_i is internal quantum efficiency, k is the Boltzmann constant, T is the temperature, and RA is resistance-area-product of the device extracted from J-V characteristics as[19]

$$RA = \left(\frac{\partial J}{\partial V}\right)^{-1}. \tag{11}$$

Variation in RA product with applied voltage is shown in Fig. 11. It is clear from this figure that zero bias resistance-area-product (R_0A) is nearly 7 $\Omega\,cm^2$ and near zero bias RA product is 14 $\Omega\,cm^2$. This indicates that device may be used at some reverse bias for better performance. The detectivity of the ITO/PCz/Al Schottky diode is estimated of the order of 10^7 cm $Hz^{1/2}$ W^{-1} near zero bias and 10^9 cm $Hz^{1/2}$ W^{-1} for an applied reverse bias of −6 V, as shown in Fig. 12. Such a high value of detectivity along with extremely low dark current of the fabricated device is satisfactory enough to

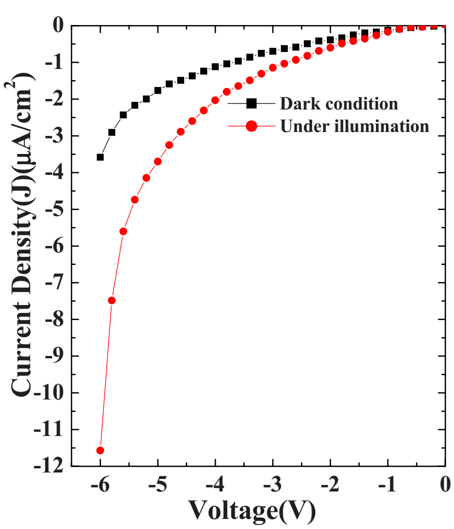

FIG. 9. (Color online) Reverse bias J-V characteristics of Al/PCz/ITO under illumination of light.

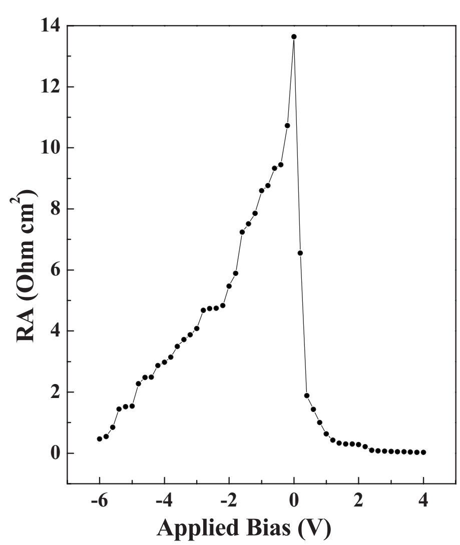

FIG. 11. Variation in RA product of the device with applied bias voltage.

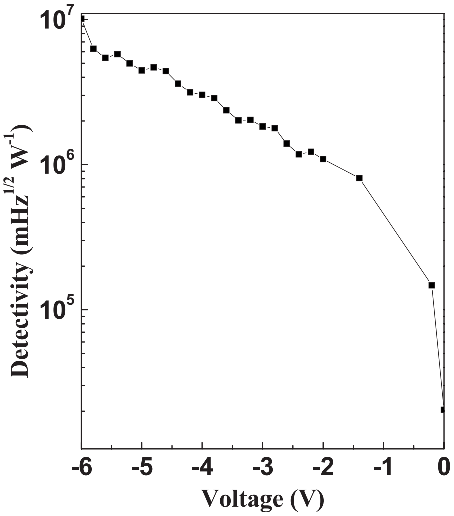

FIG. 12. Variation in detectivity of the Al/PCz/ITO with applied bias voltage.

be used as a photodetector in optical communication system operating in the visible region at 650 nm.

IV. CONCLUSION

The electrochemically polymerized polycarbazole films were used as semiconductor material for formation of Schottky junctions with a low-cost metal such as Al. The current-voltage (J-V) and capacitance-voltage (C-V) measurements were used for extraction of the diode performance parameters under dark condition. The electrical and optical measurements confirmed that the Schottky diode can be used as a flexible electronic and optoelectronic device. The reported Schottky diode is expected to find application as cost effective low noise photodetector for free space optical communication in the visible region at 650 nm using ILD source with high modulation capability. Further optical characterization of the devices is currently underway.

[1]T. A. Skotheim, R. L. Elsenbaumer, and J. R. Reynolds, *Handbook of Conducting Polymer*, 2nd ed. (Dekker, New York, 1998).
[2]A. Tusumura, H. Koeguka, and T. Ando, Appl. Phys. Lett. **49**, 18 (1986).
[3]R. H. Baughman, Synth. Met. **78**, 339 (1996).
[4]H. Ye, J. Huang, J. J. Xu, A. Khalfan, and S. G. Greenbaum, J. Electrochem. Soc. **154**, A1048 (2007).
[5]H. Macıt, S. Sen, and M. Sacak, J. Appl. Polym. Sci. **96**, 894 (2005).
[6]V. Saxena and R. Prakash, J. Solid State Electrochem. **4**, 234 (2000).
[7]S. Y. Abe, J. C. Bernede, L. Ugalde, Y. Tregouet, and M. A. del Valle, J. Appl. Polym. Sci. **106**, 1568 (2007).
[8]P. C. Pandey, R. Prakash, G. Singh, I. Tiwari, and V. S. Tripathi, J. Appl. Polym. Sci. **75**, 1749 (2000).
[9]N. Kobayashi and M. Kijima, Appl. Phys. Lett. **91**, 081113 (2007).
[10]J. Y. Lim, H. C. Ko, and H. Lee, Synth. Met. **156**, 695 (2006).
[11]N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. N. Plesu, M. Belletete, G. Durocher, Y. Tao, and M. Leclerc, J. Am. Chem. Soc. **130**, 732 (2008).
[12]J. C. Scott, J. Vac. Sci. Technol. A **21**, 521 (2003).
[13]W. R. Silveira and J. A. Marohn, Phys. Rev. Lett. **93**, 116104 (2004).
[14]E. Ahlswede, W. Mühleisen, M. W. bin Moh Wahi, J. Hanisch, and M. Powalla, Appl. Phys. Lett. **92**, 143307 (2008).
[15]C. W. Tang and S. A. Vanslyke, Appl. Phys. Lett. **51**, 913 (1987).
[16]M. Ujimoto, W. Takashima, and K. Kaneto, Thin Solid Films **499**, 313 (2006).
[17]D. Ray and K. L. Narasimhan, Appl. Phys. Lett. **91**, 093516 (2007).
[18]J. Tauc, *Amorphous and Liquid Semiconductors* (Plenum, London, 1974).
[19]S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. (Wiley, New York, 1981).
[20]A. K. Singh, R. Prakash, A. D. D. Dwivedi, and P. Chakrabarti, IEEE Electron Device Lett. **29**, 571 (2008).
[21]R. Clergereaux, I. Seguy, P. Jolinat, J. Farenc, and P. Destruel, J. Phys. D: Appl. Phys. **33**, 1947 (2000).
[22]P. Syed Abthagir and R. Saraswathi, Org. Electron. **5**, 299 (2004).
[23]M. N. Latto, D. Jason Riley, and P. W. May, Diamond Relat. Mater. **9**, 1181 (2000).
[24]W. P. Gomes and F. Cardon, Prog. Surf. Sci. **12**, 155 (1982).
[25]Y. J. Lin, Appl. Phys. Lett. **92**, 046101 (2008).
[26]A. Turut and F. Koleli, J. Appl. Phys. **72**, 818 (1992).
[27]R. K. Lal and P. Chakrabarti, Opt. Quantum Electron. **36**, 935 (2004).