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Pentacene/n$^-$-Si heterojunction diodes and photovoltaic devices investigated by *I–V* and *C–V* measurements

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ABSTRACT

The forward and reverse current density–voltage (*J–V*) and capacitance–voltage (*C–V*) characteristics of pentacene/n$^-$-silicon heterojunction diodes were investigated to clarify the carrier conduction mechanism at the organic/inorganic heterojunction. Current rectification characteristics of the pentacene/n$^-$-Si junctions can be explained by a Schottky diode model with an interfacial layer. The diode parameters such as Schottky barrier height and ideality factor were estimated to be 0.79–1.0 eV and 2.4–2.7, respectively. The *C–V* analysis suggests that the depletion layer appears selectively in the n$^-$-Si layer with a thickness of 1.47 μm from the junction with zero bias and the diffusion potential was estimated at 0.30 eV at the open-circuit condition. The present heterojunction allows the photovoltaic operation with power conversion efficiencies up to 0.044% with a simulated solar light exposure of 100 mW/cm^2.

1. Introduction

Organic electronic devices have advantages of their low production costs and mechanical flexibilities. Especially organic thin film transistors (OTFT) [1–3], photo sensors [4] and solar cells [5] have attracted much interest for recent years. The dramatic improvements seen in organic devices were undoubtedly achieved by the progress of high-mobility organic semiconductors. Most organic semiconductor materials such as thiophene and pentacene are p-type materials, while n-type materials such as C60 and fullerene derivatives are deficient in terms of molecular stability in air. In our laboratory, we examined heterojunctions with relatively stable p-type organic and very stable n-type inorganic oxide semiconductor materials using P3HT and TiO_2, where the junctions were found to have rectification characteristics and have as high photo sensitivity as Si based solar cells. However, the carrier conduction mechanism has not been elucidated yet. In this study, apart from the P3HT/TiO_2 junction, we investigated a simple junction of pentacene and n$^-$-Si to clarify the carrier conduction mechanism and the reason why the diffusion potential is generated. Using Cheung method [6] for current density–voltage (*J–V*) analysis, we found that the junction has a current rectification characteristic explained by a Schottky junction model with an interfacial layer.

As for the analysis on the inorganic and organic heterojunctions, Yakuphanoglu et al. investigated a junction of fluorescing sodium salt (FSS) and n$^-$-Si [7,8]. They proved with Richardson analysis that the FSS/Si heterojunction also has Schottky rectification characteristic. They also found that the ideality factor of the junction was very high, in range from 4.56 to 6.3, though the reason has not been discussed well. In the field of the inorganic heterojunction diodes, Cheung method has been utilized as an analysis method of the Schottky parameters [9–11] since it allows the analysis with minimized effect caused from the series resistance in the Schottky diodes. The high ideality factor has been explained by metal–insulator–semiconductor (MIS) junction model [9–11], while relatively few attempts have been made for analyzing organic/inorganic interfaces. In our laboratory, we investigated the current rectification mechanism of sexthiophene/n-Si heterojunctions with Cheung method, where it was found that the heterojunction can be also explained with the Schottky junction mechanism with an interfacial layer [12]. However, we believe that further investigation with a variety of organic/inorganic heterojunctions is required to discuss the band diagram and the carrier conduction at the interface of the heterojunction.

In this study, we investigated *J–V* characteristics of pentacene/n$^-$-Si heterojunction diodes and attempted to determine if the forward current conduction can be explained with the thermionic emission model inherent in the Schottky diodes by Richardson analysis of the diode. The Schottky barrier height and ideality factor were estimated by Cheung method. As pentacene is well-known to be one of high-mobility p-type organic materials with a relatively high optical transparency when the thickness is as much as less than 100 nm, it is expected that the junction of pentacene and n$^-$-Si has potential abilities in not only rectifiers but also

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photovoltaic devices. To obtain the diffusion potential, we measured *C–V* characteristics. We propose a band diagram to explain the mechanism of the current conduction and the photovoltaic operation in this paper.

2. Experimental

All the heterojunction diodes were fabricated on the n^{-}-Si epitaxially grown n^{+}-Si substrates. The substrate was cut from a 6 in. Si wafer. The n^{+}-Si substrate has a resistivity of 0.001 Ω cm and it was doped with As. The P doped n^{-}-Si epitaxial layer was fabricated on the n^{+}-Si substrate with a resistivity of 35 Ω cm by chemical vapor deposition(CVD). The thickness of the epitaxial layer was 50 μm. Before the deposition of the organic layer, all the substrates were cleaned with RCA method [13], followed by being rinsed with HF acid which leaves hydrogen passivated Si surfaces [14].

The schematic of the pentacene/n^{-}-Si heterojunction diodes was depicted in Fig. 1. Pentacene was deposited on the n^{-}-Si film by vacuum evaporation with a thickness of 50 nm at room temperature. As anode electrodes, Au films were fabricated with an area of 0.07 cm^2 on the pentacene film. The Au electrodes worked as Ohmic ones since the work functions of Au and pentacene are very closed to each other, which equal 4.7 and 5.0 eV, respectively. The Al back electrode also worked as Ohmic ones since the backside of the substrate was heavily doped with As. The *I–V* measurements were performed with an Advantest pA meter/voltage source in nitrogen ambient. We obtained the capacitance–voltage (*C–V*) relation of the pentacene/n^{-}-Si heterojunction in the reversed biased condition. The *C–V* measurement was carried out with a frequency of 100 kHz by a HIOKI 3532-50 LCR meter in nitrogen ambient.

To fabricate solar cells with the pentacene/n^{-}-Si heterojunction, diced Si substrates with an area of 1 cm^2 were prepared. The Si substrates were the same as the n^{-}-Si epitaxially grown n^{+}-Si substrates mentioned above. We deposited pentacene films with a thickness of 30 nm on the Si substrates. Then we deposited Au finger electrodes as anodes on the pentacene film. The distance between the finger electrodes was 0.17 mm. On the backside of the Si substrates Al electrodes as cathodes were fabricated. All the fabrication processes of the solar cells were made at room temperature. The photovoltaic properties of the solar cells were measured by using an *I–V* measurement system and a simulated solar light source with AM1.5 100 mW/cm^2 produced by Peccell Technologies.

3. Results and discussion

3.1. Schottky analysis

Fig. 2 represents the current density–voltage characteristics of the pentacene/n^{-}-Si heterojunction diodes. The measurement temperature ranged from 300 to 373 K. We can see a clear current

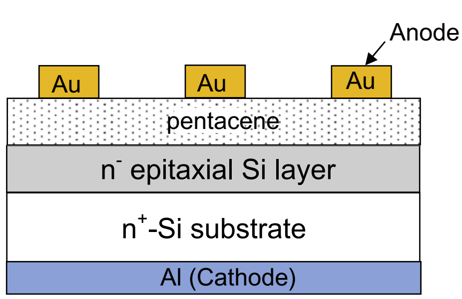

Fig. 1. Schematic of pentacene/n^{-}-Si heterojunction diode.

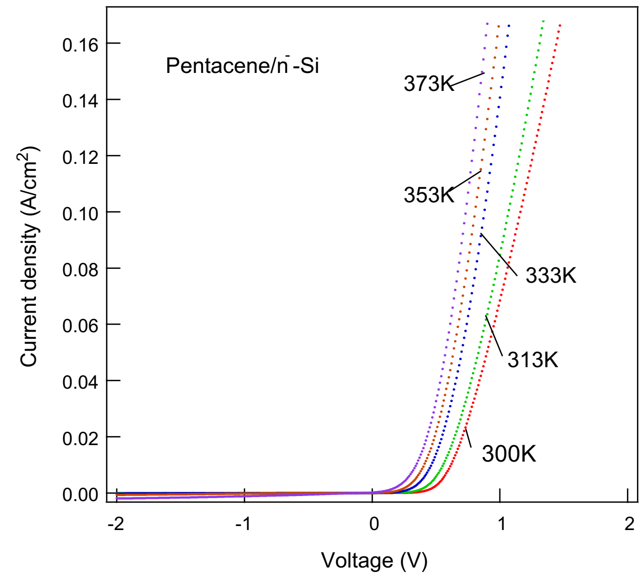

Fig. 2. Current density–voltage characteristics of pentacene/n^{-}-Si heterojunction diode.

rectification in the plot. The enhancement of the forward current by the sample annealing can be explained by the current rectification equation of a Schottky diode [6,15]. The Schottky rectification equation is given as,

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

where q is the unit charge, n is the ideality factor, R_s is the series resistance at unit area, k is the Boltzmann constant, T is the absolute temperature, S is the device area and I_s is the saturation current defined by

$$I_s = SA^{**}T^2\exp\left(-\frac{q\phi_B}{kT}\right) \tag{2}$$

where φ_B is the Schottky barrier height, A^{**} is the Richardson constant and equals to

$$A^{**} = \frac{4\pi mk^2q}{h^3} \tag{3}$$

In case of Si, A^{**} equals to 112 A/cm^2 K^2. To prove that the heterojunction is expressed with the Schottky relation, we obtained the Richardson relation expressed as

$$\ln\left(\frac{I_s}{T^2}\right) = \ln(SA^{**}) - \frac{q\phi_B}{kT} \tag{4}$$

This equation can be obtained from Eq. (2). The saturation current was measured by linear fitting of the ln(*J*)–*V* plot shown in Fig. 3, where the linear fitting was made in the forward bias range from 0.2 to 0.4 V, since the linearity was lacking around zero bias and in excess of 0.4 V which are due to noise and space charge limited conduction (SCLC), respectively. The Richardson plot was shown in Fig. 4. The linear relation of $\ln(\frac{I_s}{T^2}) - 1/T$ suggests that the carrier conduction at the forward bias is explained by thermionic emission inherent in the Schottky junction. We estimated ΦB as 0.59 eV. This estimation includes some errors due the series resistance of the heterojunction, which is discussed later.

To extract the Schottky parameters of ΦB and n while minimizing the effect of R_s, we utilized Cheung method [6]. From Eq. (1), the following equation is given,

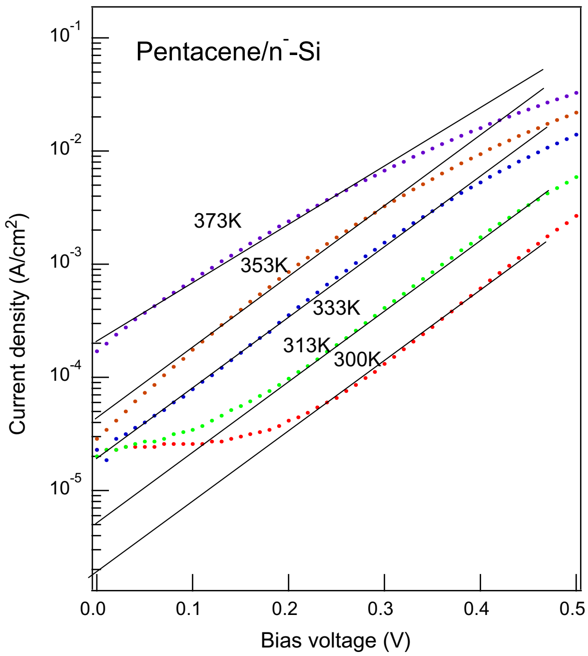

Fig. 3. Logarithmic plot of current density–voltage characteristics of pentacene/n$^-$-Si heterojunction diode in the forward bias region.

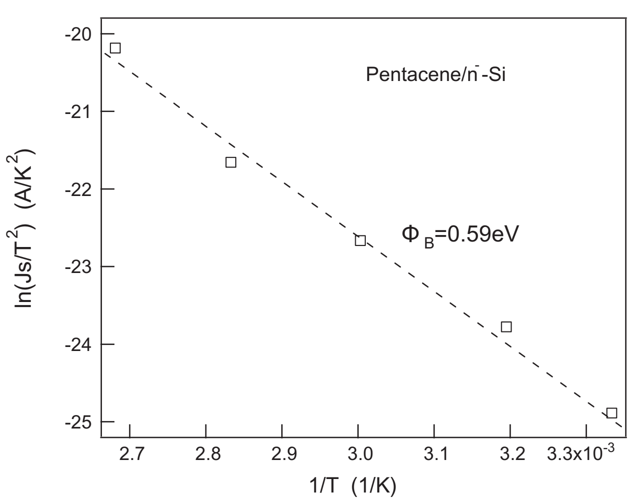

Fig. 4. Richardson plot of pentacene/n$^-$-Si heterojunction diode.

$$\log\left(\frac{I}{I_s}\right) = \frac{q}{nkT}V - \frac{qI}{nkT}\frac{R_s}{S} \tag{5}$$

If J is the current density and equals I/S, Eq. (5) is written as,

$$\log\left(\frac{J}{A^{**}T^2}\right) + \frac{q\phi_B}{kT} = \frac{q}{nkT}V - \frac{qJ}{nkT}R_s \tag{6}$$

If β is defined q/kT, Eq. (6) is changed to

$$V = R_sJ + n\phi_B + \frac{n}{\beta}\log\left(\frac{J}{A^{**}T^2}\right) \tag{7}$$

If V is differentiated by $\ln(J)$, we can obtain a simple linear equation as

$$\frac{dV}{d(\ln J)} = R_sJ + \frac{n}{\beta} \tag{8}$$

This means that the slope and the intercept of y-axis in the linear fitting of $\frac{dV}{d(\ln J)} - J$ indicate R_s and n/β, respectively. $dV/d(\ln J)$ was calculated numerically from the experimental data shown in Fig. 2. The $\frac{dV}{d(\ln J)} - J$ relation at 300 K is shown in Fig. 5(a). The series resistance at unit area and the ideality factor n were estimated at 4.3 Ω cm^2 and 2.4, respectively. The ideality factors estimated from I–V curves with temperatures from 313 to 373 K were also in range from 2.3 to 2.7. The presence of the ideality factor in excess of 1.0 indicates the generation of an interfacial layer and interface states at the heterojunction [16,17], which will be discussed later. If we define the function $H(J)$ as

$$H(J) = V - \frac{n}{\beta}\log\left(\frac{J}{A^{**}T^2}\right) \tag{9}$$

Eq. (7) was changed to a simple form as

$$H(J) = R_sJ + n\phi_B \tag{10}$$

From the intercept of $H(J)$ at y-axis as shown in Fig. 5(b), we estimated the Schottky barrier height ϕ_B at 0.79 eV. The Schottky barrier heights estimated from I–V curves with temperatures from 313 to 375 K were also in range from 0.79 to 1.0 eV. The slight difference of ϕ_B measured from the Richardson plot and the Cheung method must be caused from the effect of the series resistance. As the Cheung method is effective in removing the effect of the series resistance on the analysis, we use ϕ_B measured from the Cheung method for the discussion of the band diagram in the present paper.

To analyze the diffusion potential, we measured the capacitance–voltage characteristics of the pentacene/n$^-$-Si heterojunction diodes. The C^{-2}–V plot of the pentacene/n$^-$-Si heterojunction diode is shown in Fig. 6. The C^{-2}–V relation of the Schottky diodes is written as

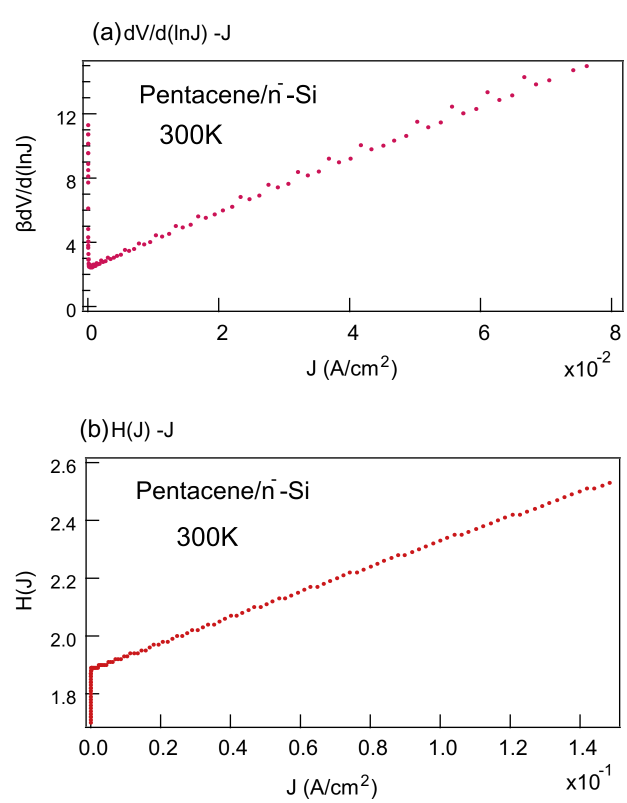

Fig. 5. $dV/d(\ln J)$–J and $H(J)$–J plots of pentacene/n$^-$-Si heterojunction diode.

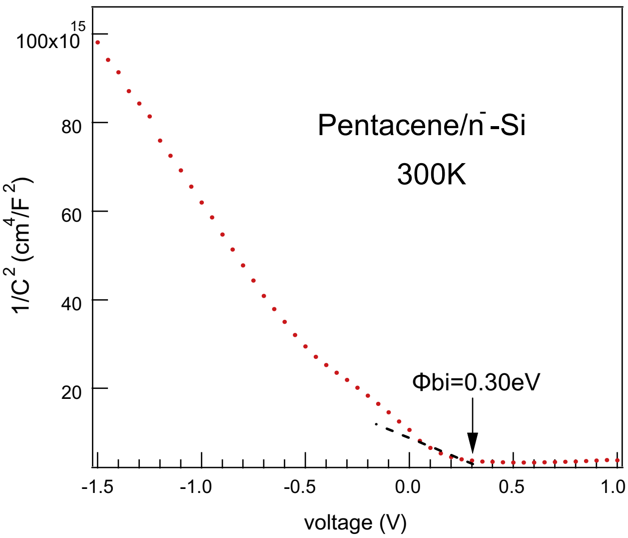

Fig. 6. $1/C^2$–V plot of pentacene/n$^-$-Si heterojunction diode.

$$C^{-2} = \frac{2}{q\varepsilon_o\varepsilon_s N}(\phi_{bi} - V) \tag{11}$$

where N is the carrier concentration, ε_o is the vacuum dielectric constant, ε_s is the relative permittivity of the semiconductor layer, and ϕ_{bi} is the diffusion potential. In the present study, we estimated the carrier concentration of order of 10^{14} cm^{-3} from the slope of the C^{-2}–V relation. This suggests that the pentacene film induces a depeletion layer in Si since the carrier concentration of the pentacene is estimated as much as 10^{16} cm^{-3} from the resistivity and field effect mobility measurements. The diffusion potential was measured 0.30 eV from intercept of x-axis. We summerized a band diagram as shown in Fig. 7. It is assumed here that the pentacene film acts as a metal layer and induces a depeletion layer in an n$^-$-Si film. The presence of the interfacial layer was assumed since the high ideality factor of 2.4 can be explained by metal–insulator–semicondcutors model [16–18]. We found that the maximum capacitance per unit area at the forward bias region was 1.8×10^{-8} F/cm^2, which corresponds to the interfacial layer of SiO_2 with a thickness of 290 nm. However, we assume that interfacial layer must be thinner as the leakage current may affect the maximum capacitance at the C–V measurement. We tentatively assume that the interfacial layer consists of both SiO_2 and the disordered surface layer of pentacene at the interface. As the potential difference of the Fermi level and the top of conduction band in the Si epitaxial layer is estimated as 0.33 eV, the Schottky barrier height ϕ_B and the diffusion (built-in) potential ϕ_{bi} can be consistently explained by the following equation,

$$\phi_B = E_C - E_f + \phi_{bi} \tag{12}$$

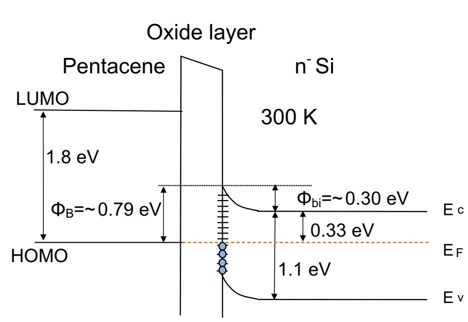

Fig. 7. Band diagram of pentacene/n$^-$-Si heterojunction diode.

According to Eq. (12), the Schottky barrier height ϕ_B is estimated to be 0.63 eV, which agrees with the ϕ_B of 0.79 eV measured by the Cheung method. If the heterojunction works as an ideal Schottky diode, the Schottky barrier height is expected to be the difference of the work functions of pentacene and n-Si. It is possible that the present heterojunction has an ideal Schottky barrier height. However we still assume the presence of pinning effect caused by interface states as shown in Fig. 7.

3.2. Photovoltaic characteristics

The present Schottky analysis suggests that the pentacene/n$^-$-Si heterojunction works as a Schottky diode and the pentacene film induces a depletion layer in the Si layer with the diffusion potential of 0.30 eV. We fabricated the pentacene/n$^-$-Si solar cells made with the pentacene/n$^-$-Si heterojunction. The J–V characteristics with a light exposure of 100 mW/cm^2 are shown in Fig. 8. The power conversion efficiency and the related parameters of the solar cells are summarized in Table 1. From the J–V characteristic, the open-circuit voltages (V_{oc}) were measured 0.22 V. It is possible that the V_{oc} was limited by the diffusion potential. The power conversion efficiency was measured as 0.044% as shown in Table 1. The experimental results mentioned above clearly indicate that the present organic/inorganic heterojunction has a photovoltaic ability. To enhance J_{sc}, we need further investigation on the optimized pentacene thickness since too thin pentacene has better transparency for the visible light and might rather deteriorate the diffusion potential. The improvement of J_{sc} must be also strongly related to the enhancement of the diffusion potential and V_{oc}. In this junction, the diffusion potential of 0.30 eV is expected to generate the depletion layer with a thickness of 1.47 μm. To absorb all the visible light in the simulated solar light with the Si layer, we consider the thickness of the depletion layer should be extended to more than 3 μm by increasing the diffusion potential. The diffusion potential must be enhanced by increasing the potential difference of work functions of Si and the pentacene. Increasing the doping level of Si must be effective, though we need to optimize the doping

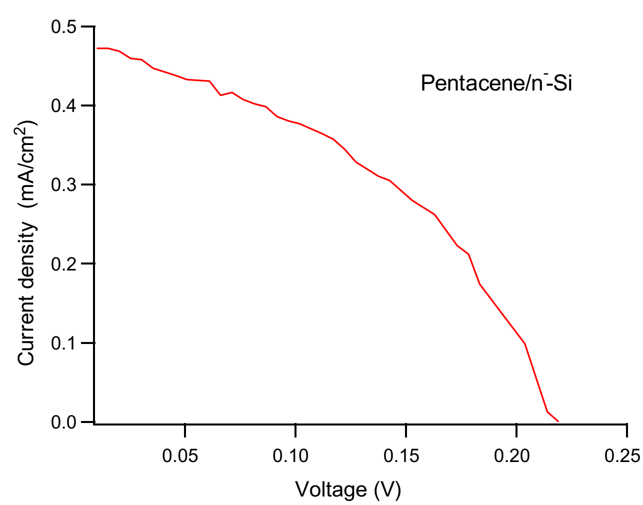

Fig. 8. J–V characteristic of pentacene/n$^-$-Si heterojunction photovoltaic device.

Table 1
Power conversion performances of pentacene/n-Si photovoltaic device.

Short-circuit current density, J_{sc} (mA/cm^2)	Open-circuit voltage, V_{oc} (V)	FF	Power conversion efficiency (%)
0.471	0.22	0.42	0.044

level. The fill factor of 0.42 suggests that it is necessary to decrease the series resistance. We have not optimized the fabrication process of the finger electrodes attached to the pentacene film. If we simply increase the density of the finger electrodes, the ff may be improved. In the present device, we should also consider that a recombination current during the photovoltaic operation might suppress the power conversion efficiency since the ideality factor of 2.3 suggests the presence of the interface states and the interfacial oxide layer. In our laboratory, we examined surface treatments and found that a β SiC treatment before the deposition of organic semiconductor is effective in decreasing both the ideality factor and series resistance. The related studies are to be released elsewhere [19]. Hoshino et al. Also reported that intentional formation SiC bond at the interface is resulted in the lower ideality factor [20].

Despite that the power conversion performance of the organic/inorganic heterojunction was not as good as the conventional Si or organic solar cell, we recognized a notable feature in the present cell; we can construct photovoltaic devices with a Si layer without doping. The activation of doping requires the high temperature process in excess of 500 °C. By using the pentacene film in place of doping, we can easily fabricate Si photovoltaic devices, or photo detectors at room temperature. This low temperature process must pave a way to realize Si based photosensors on flexible pet films as we just simply put the pentacene film on the n-type Si film. The present heterojunction may be considered as a candidate for the flexible image sensors. We should note that the present device has a big merit of cheap fabrication cost. In the field of portable electronics like solar cell attached calculators, the cheap solar cell with an efficiency less than 0.1% is used as the cost rather than the power generation performance is made much of. The present device can be a candidate for the micro power source for the portable electronics.

3.3. Discussion

Looking back at the previous studies related to the organic/inorganic heterojunction must give an insight to discuss the carrier conduction mechanism of the heterojunction. Yakuphanoglu has reported the current–voltage characteristics of the FSS/n^--Si heterojunction, where the carrier conduction was also explained by the Schottky model [8]. The high ideality factor in range from 4.56 to 6.3 was reported and its deviation from unity was tried to be explained by either recombination of electrons and holes at depletion layer or increasing the diffusion current with increasing the applied voltage. Despite the difference in the explained mechanism in the ideality factor, the paper suggests that the Schottky model was available in the organic and n-Si heterojunction. Hoshino et al. reported the current rectification of polythiophene/n-Si heterojunctions explained by the Schottky junction model. They also reported high ideality factors in excess of 1.7 and attributed it to the generation of interfacial layer like SiO_2 [20]. Their study may support the present explanation using MIS model. More recently, Kavasoglu et al. also applied the Schottky analysis using the MIS model on the poly(4-vinyl phenol)/p-Si heterojunction [21]. In most cases in the organic/inorganic heterojunction, the Schottky model has been successfully adopted for the explanation of current rectification.

In our previous work, we fabricated sexthiophene (6T)/n^--Si heterojunction diodes and solar cells and investigated their *J*–*V* characteristics and photovoltaic characteristics [12]. 6T is also well-known to be one of high-mobility p-type organic oligomers with a high optical transparency. In the study of 6T/n^--Si heterojunction, it was found that the 6T/n^--Si solar cells have a power conversion efficiency of 0.4% and a V_{oc} of 0.4 V. The V_{oc} was corresponded to the diffusion potential of 0.4 eV measured from the *C*–*V* analysis. Both the 6T/n^--Si and pentacene/n^--Si heterojunctions work as Schottky diodes and photovoltaic cells. The ideality factor of 6T/n^--Si, being measured 2.5, was very close to that of the pentacene/n^--Si heterojunction. The ideality factor in excess of unity was also explained by the MIS Schottky model. We consider that MIS Schottky model is widely available to explain the current conduction and photovoltaic operation at the heterojunction of Si and organic semiconductors.

In this study, it was assumed that the pentacene film worked like metal since the carrier concentration of pentacene was higher than that of n^--Si. However, we should note here that the present pentacene was not deteriorated by contamination but was preserved in the organic semiconductor device grade because we confirmed that thin film transistors (TFTs) made with the present pentacene film have relatively high hole mobilities around 10^{-3}–10^{-2} cm^2/V s and their ON/OFF ratios were in excess of 10^2. In case of heterojunction diodes, one of two junction layers with a relatively lower carrier concentration works as a semiconductor layer and the other does as metal. Thus, it is highly possible that even organic device grade pentacene behaves like metal when it is attached to high-resistance, low-doped Si. We consider that the carrier in the pentacene film was introduced by a small amount of impurity and molecular defects even though it was carefully formed in vacuum and nitrogen ambient.

4. Conclusion

We investigated *J*–*V* and *C*–*V* characteristics of pentacene/n^--silicon heterojunction diodes. It was indicated that the pentacene/n^--Si junction has a current rectification characteristic explained by a Schottky junction model with an interfacial layer. The *C*–*V* analysis suggests that the depletion layer is generated selectively in the n^--Si layer with a thickness of 1.47 μm from the junction and the diffusion potential was estimated 0.30 eV. The present heterojunction allows the power generation with power conversion efficiencies up to 0.044% with a light exposure of 100 mW/cm^2. The present results suggest a new method to fabricate Si photovoltaic devices without doping at very low temperatures at near room temperature.

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