

# Charge-Transfer Behavior of Conducting Polymers as Contact Electrode for Semiconductor Devices

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## Abstract

As a contact electrode material alternative to metals necessary for downsized semiconductor devices in 10 nm process generation, intrinsically conducting polymer was studied regarding its important charge-transfer behavior with inorganic semiconductor. Polypyrrole as the conducting polymer was formed using an electrochemical technique on the oxide semiconductor and its electronic properties were evaluated using scanning probe microscopy. The experimental results showed that ohmic contact behavior was observed dynamically in local site although the Schottky barrier was expected statically over the measurement areas. From this research, the conducting polymer was found to be available as a contact electrode.

## 1. Introduction

With progressive downsizing of semiconductor devices, the half-pitch size regarded as the processing state of the art is expected less than 10 nm around 2020. In the transistor, the ohmic contact electrode is used for the exchange of current between the semiconductor and the conductive path connected to the external circuit. Metals and alloys have been used as the contact electrode material while the present deposition technology is difficult to form the metals and alloys in a width less than 10 nm with the uniform grain size, leading to increase the electrical resistance of the contact electrode. Intrinsically conducting polymer is a promising candidate because of its size such as a molecular width of around 3 nm, its conductivity ( $\sim 10^5 \Omega^{-1}\cdot\text{cm}^{-1}$ ) as high as most metals and alloys and its controllable work function. In addition, the conducting polymers can be formed on a target area of the semiconductor by using the electrochemical technique under the atmosphere. Technological issues to apply the conducting polymer for the contact electrode are to control both its shape and electronic structure. In previous studies, morphology and Fermi level of conducting polymer joined with inorganic semiconductor was revealed by using scanning probe microscopic (SPM) measurements on polypyrrole as one of the conducting polymers, which was formed by photo electrochemical polymerization on titanium dioxide ( $\text{TiO}_2$ ) as the inorganic semiconductor [1,2]. The purpose of this study was to reveal charge-transfer behavior at the interface between the conducting polymer and the inorganic semiconductor.

## 2. Experimental

Three electrode electrochemical cell with a glass window was used to prepare polypyrrole on  $\text{TiO}_2$  [1]. A single crystal of rutile  $\text{TiO}_2$  with the exposure faces of (100), (001), etc. was used as the working electrode. The electrolyte contained  $0.1 \text{ mol}\cdot\text{dm}^{-3}$  of pyrrole as a monomer and *p*-toluene sulfonate (PTS) as a dopant in acetonitrile. The ultraviolet light was introduced to the working electrode through the window of the cell. The galvanostatic polarization was applied to the working electrode at a current density of  $5 \mu\text{A}\cdot\text{cm}^{-2}$  for 5.4 ks.

Scanning probe microscopy was used to evaluate electric properties of polypyrrole on the  $\text{TiO}_2$  substrate by applying different measurement modes, which were Kelvin probe force microscopy (KFM) and conductive atomic force microscopy (C-AFM) to obtain the Fermi level and the I-V characteristics, respectively. X-ray photo-electron spectroscopy (XPS) was used to evaluate the energy state of polypyrrole and  $\text{TiO}_2$ .

## 3. Results and discussion

Fig. 1 shows the surface potential image of polypyrrole formed on the crystal plane (100) of rutile  $\text{TiO}_2$  observed with the KFM mode of SPM. In this image, the surface potential was  $150 \text{ mV} \pm 8 \text{ mV}$  and its deviation was small around 5%.  $\text{TiO}_2$  with other crystal planes and polypyrrole formed on these  $\text{TiO}_2$  substrates also showed small distri-

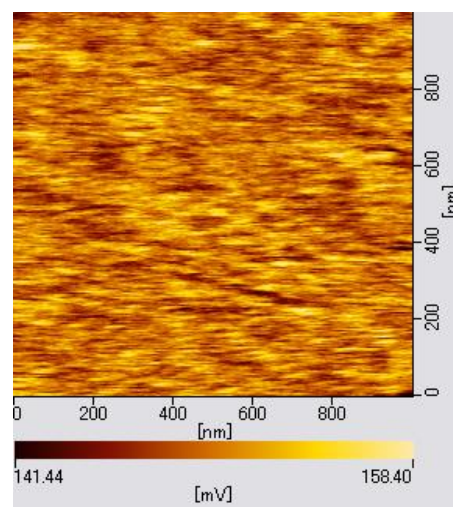


Fig. 1 Surface potential images of polypyrrole formed on single crystal of  $\text{TiO}_2$  (rutile phase, (100) face exposed).

bution of the surface potential, indicating that polypyrrole and the TiO<sub>2</sub> substrates showed the uniform electronic structure in this study. From distribution of specimen's surface potential, the mean and deviation values were calculated and converted to the Fermi level assuming that the work function of gold as a coating of probe for KFM was 5.1 eV. The Fermi level values of TiO<sub>2</sub> and polypyrrole formed on TiO<sub>2</sub> were shown on the different crystal plane of TiO<sub>2</sub> in Fig. 2. These values were almost comparable with the Fermi level estimated from the reported values regarding TiO<sub>2</sub> and polypyrrole. As seen from Fig. 2, the Fermi level of polypyrrole was lower than the value observed for TiO<sub>2</sub> on every crystal plane. In addition, TiO<sub>2</sub> and polypyrrole show different dependence of the Fermi level on the crystal plane of TiO<sub>2</sub>. This might be caused by differences in surface state among different crystal planes of TiO<sub>2</sub> and in polarization potential of the working electrode to form polypyrrole among them. The energy state of the electron in TiO<sub>2</sub> and polypyrrole was confirmed by XPS. These results about the static electronic state suggested that the interfacial structure between polypyrrole and TiO<sub>2</sub> was Schottky barrier junction.

An example of measurement points by C-AFM and resulting I-V curves are shown in Fig. 3. Current flow on the polarization to the negative direction was observed for the TiO<sub>2</sub> substrate corresponding to a rectifying action characteristic of n-type semiconductor. Similar curves were also obtained for every measurement point of TiO<sub>2</sub> with the different crystal planes. On the other hand, polypyrrole formed on TiO<sub>2</sub> showed current flow on the polarization to both the negative and positive directions, i.e. ohmic conduction, in some measurement points regardless from the crystal face of the TiO<sub>2</sub> substrate while the rectifying phenomenon was observed in the other measurement points, similarly to the TiO<sub>2</sub> substrates. These results suggested that polypyrrole in this study be conductive like metal and that ohmic characteristic of the polypyrrole appear locally and dynamically by changing the electronic structure when the electric field was applied into the polypyrrole.

#### 4. Conclusions

Polypyrrole as the intrinsically conducting polymer joined with titanium dioxide as the inorganic semiconductor showed ohmic contact behavior dynamically in local site although the static electronic state suggested Schottky barrier junction over the measurement areas. From this research, the conducting polymer was found to be available as a contact electrode.

#### References

- [1] J. Kawakita et al., J. Nanosci. Nanotechnol., 11 (2011) 2937.
- [2] J. Kawakita et al., Electrochim. Acta, 82 (2012) 378.

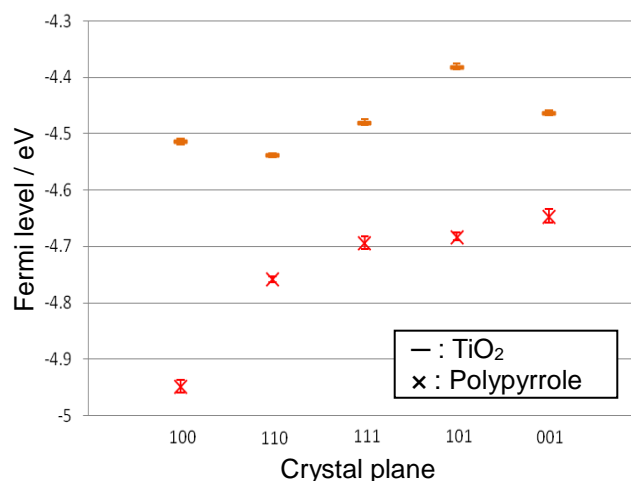


Fig. 2 Fermi level of TiO<sub>2</sub> and polypyrrole on different crystal plane of TiO<sub>2</sub>.

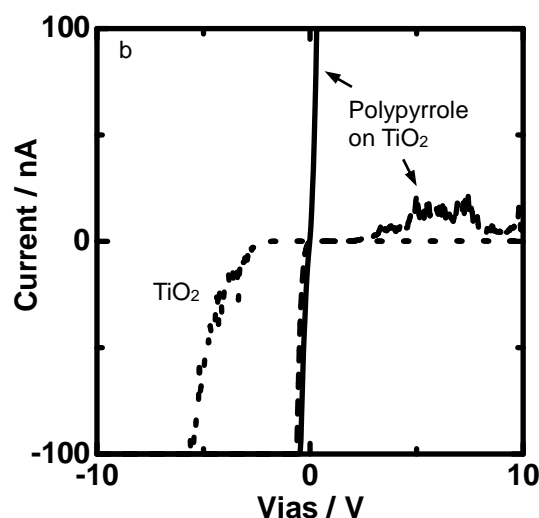
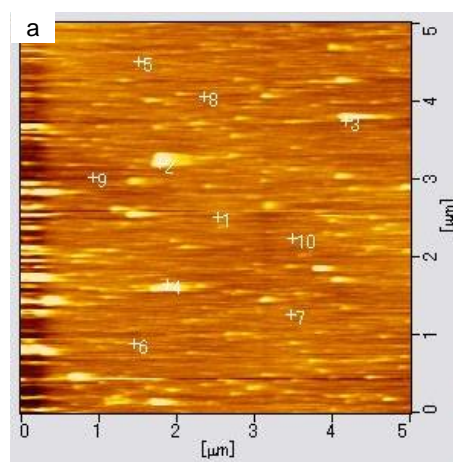


Fig. 3 (a) AFM image of polypyrrole formed on single crystal of TiO<sub>2</sub> (rutile phase, 001) face exposed) and (b) its I-V curves by conductive AFM in comparison of TiO<sub>2</sub>. Numbers stand for measurement points of conductive AFM.