The TiO$_2$/Ru(dcbpyH$_2$)$_2$(NCS)$_2$/Au Schottky junction

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Abstract

Ru(dcbpyH$_2$)$_2$(NCS)$_2$ molecules have specific binding sites for TiO$_2$ and Au surfaces and a large dipole moment what makes them attractive for engineering of Schottky junctions. The rectification of the junction conditioned with a monolayer of Ru(dcbpyH$_2$)$_2$(NCS)$_2$ molecules increased by several orders of magnitude in comparison to the bare TiO$_2$/Au junction. The influence of (i) trap-assisted tunneling, of (ii) specific interaction of Ru(dcbpyH$_2$)$_2$(NCS)$_2$ molecules with oxygen vacancies at the TiO$_2$ surface and of (iii) the dipole moment of the Ru(dcbpyH$_2$)$_2$(NCS)$_2$ molecules on the activation energy of the diode saturation current was demonstrated. The estimated projected dipole moment of one Ru(dcbpyH$_2$)$_2$(NCS)$_2$ molecule amounted to about 5 D.
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Keywords: Rectification; Dipole moment; Binding sites

1. Introduction

The transport properties of Schottky junctions are defined by the barrier height at the junction and by electronic states in the forbidden gap of the semiconductor. The barrier height depends on the surface work functions of the metal and semiconductor as well on dipoles in the interface region. Small organic molecules with a dipole moment can be adsorbed with defined orientation at semiconductor [1–3] or metal surfaces [4]. This opened new opportunities for engineering of Schottky junctions, for example at rectifying GaAs interfaces [5]. Moreover, asymmetric current–voltage characteristics can be realized even at a junction between a gold surface and a gold nanoparticle if they are linked by bipolar organic molecules to each other [4,6]. Metal oxides such as TiO$_2$ are semiconductors with a wide band gap. They have a large application potential, for example, TiO$_2$ can serve as a selective electron contact in dye-sensitized solar cells [7] or as an absorber in sensors for ultra violet light based on Pt/TiO$_2$ Schottky junctions [8]. Plasmon-induced charge separation has been demonstrated at TiO$_2$ films loaded with gold nanoparticles [9].

Ru(dcbpyH$_2$)$_2$(NCS)$_2$ molecules (N3) are widely used in dye sensitized solar cells for visible light absorption [10]. N3 molecules form a monolayer on TiO$_2$ surfaces [10]. It was shown recently that gold contacts can be used for regeneration of N3 dye molecules [11]. The N3 molecule has binding sites to both TiO$_2$ and Au via the carboxylic groups and cyanate groups, respectively. N3 molecules can interact also between each other through hydrogen bonding of the carboxylic groups. Fig. 1 shows a possible configuration of two neighbored N3 molecules. The N3 molecule can be linked to the TiO$_2$ surface by one, two or three bonds. The dipole moment of the N3 molecule is large. For example, a dipole moment of 10.9 D has been obtained in gaseous atmosphere by applying time dependent density functional theory [12]. Calculations by semi-empirical quantum mechanics at the MP3 level [13] resulted in a dipole moment of 19.4 D (Fig. 1). It has to be noted that the dipole moment of an adsorbed N3 molecule can be different to the calculated dipole moment of an isolated in vacuum. Further, the dipole moment is very sensitive to the ambience [12]. In addition, N3 molecules are very stable even at relatively high temperatures [14]. The (i) formation of an oriented monolayer at TiO$_2$ surfaces during adsorption in ethanol solution, (ii) large dipole moment and (iii) high stability favor N3 molecules for engineering of Schottky junctions. In this work we compare Au/TiO$_2$ Schottky junctions

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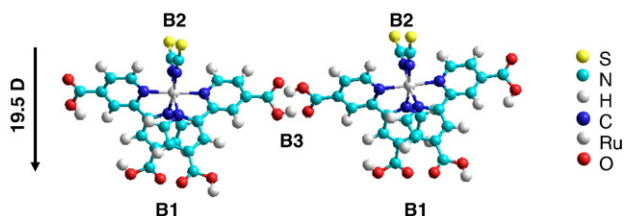
Fig. 1. Side view of two Ru(dcbpyH$_2$)$_2$(NCS)$_2$ molecules. B1, B2 and B3 denote the binding sites to the TiO$_2$ and Au surfaces and the intermolecular binding sites, respectively.

without and with an organic monolayer of N3 molecules at the interface. For this purpose spectral photocurrent and current–voltage (IU) measurements were performed. The specific action of oxygen vacancies at the TiO$_2$ surface has been studied by comparing IU characteristics measured in vacuum and oxygen atmosphere.

2. Experimental

Compact layers of TiO$_2$ (thickness 160 nm) were prepared by spray pyrolysis on glass coated with conductive oxide (SnO$_2$:F, TEC7). The compact TiO$_2$ layers were post-treated in TiCl$_4$ solution in order to close remaining pinholes. Afterwards the TiO$_2$ layers were fired at 500 °C in air for 30 min. N3 molecules were adsorbed overnight from ethanol solution. Gold contacts (thickness 100 nm) with a diameter of 3 mm were thermally evaporated in high vacuum (base pressure 10^{-7} mbar). The SnO$_2$:F contact was grounded. The gold was contacted with a carbon foil to the lead. Illumination was performed with chopped light (chopping frequency 8 Hz) through the transparent SnO$_2$:F contact. A quartz prism monochromator with a halogen lamp was used for illumination. The photocurrent spectra were detected with a lock-in amplifier (EG&G 5210) and normalized to the photon flux. IU characteristics were measured with a picoampere meter (HP 4140B) between room temperature and 125 °C in high vacuum (10^{-5} mbar) or oxygen atmosphere (800 mbar). The IU measurements started at the highest temperature after stabilization of the sample.

3. Results and discussion

3.1. Spectral photocurrent

Fig. 2 shows the photocurrent spectra of the Au/TiO$_2$ and Au/N3/TiO$_2$ junctions. The threshold for internal photoemission (Φ_B) from gold into TiO$_2$ is about 1 eV. For comparison, the value of Φ_B amounted to about 1.3 eV for the Pt/TiO$_2$ junction [8]. The photocurrent spectrum of the Au/TiO$_2$ junction shows a local maximum in the region of plasmon absorption in the gold layer. The photocurrent increases at energies above 3.2 eV due to fundamental absorption in the compact TiO$_2$ layer. The characteristic spectral feature of internal photoemission from the Au into TiO$_2$ disappears in the photocurrent spectrum of the Au/N3/TiO$_2$ junction and the characteristic absorption of the N3 dye molecules dominates the spectrum. The photocurrent from the monolayer of the N3
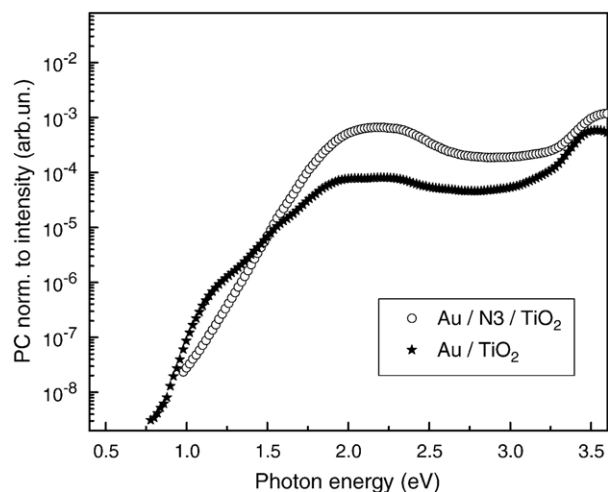

Fig. 2. Photocurrent spectra normalized to the photon flux for a Au/TiO$_2$ (stars) and for a Au/N3/TiO$_2$ (circles) junctions.

dye molecules is larger by about one order of magnitude than that induced by internal photoemission from Au. This demonstrates the high extinction coefficient of the N3 molecules and the efficient regeneration of the dye molecules by gold [11].

3.2. Current–voltage characteristics in vacuum

The rectification of the Au/TiO$_2$ junction in vacuum is less than 1 order of magnitude (Fig. 3(a)) and the activation energy (E_A which has the meaning of the barrier height for current flow) of the saturation current amounts to about 0.25 eV. This seems very low in comparison to the high value of Φ_B. However, one has to take into account the high density of states in the nanocrystalline compact TiO$_2$ layer which is of the order of 10^{20} cm^{-3} [15]. States closer to the SnO$_2$:F/TiO$_2$ contact are
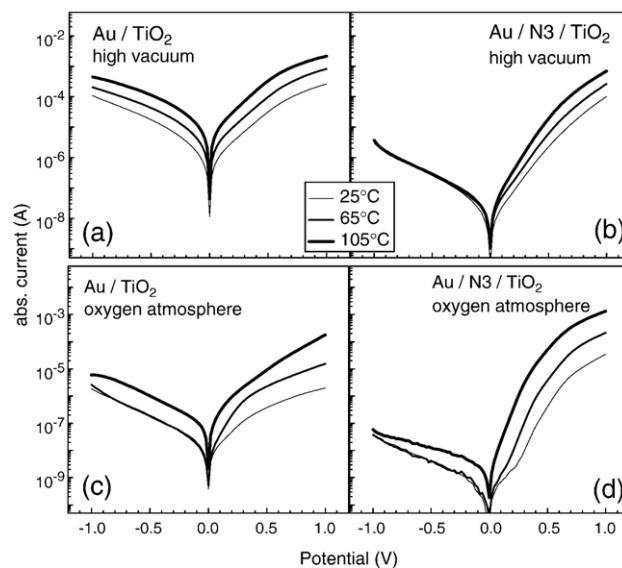

Fig. 3. Current–voltage characteristics of Au/TiO$_2$ ((a) and (c)) and Au/N3/TiO$_2$ ((b) and (d)) junctions measured in vacuum ((a) and (b)) and oxygen atmosphere ((c) and (d)) at various temperatures.

filled with electrons which results in an extremely inhomogeneous field distribution in the nanocrystalline compact TiO_2 layer. Therefore, the electrical field at the Au/TiO_2 junction can be locally very high so that tunneling becomes important. The local field distribution depends also on the temperature due to the temperature dependent occupation of states.

The diode saturation current in vacuum decreases by about two orders of magnitude at the $Au/N3/TiO_2$ junction in comparison to the Au/TiO_2 junction (Fig. 3(b)). Surprisingly the value of E_A decreases to about 0.12 eV at the same time. Regarding to the decrease of the saturation current, to the large value and to the direction of the dipole moment of N3 molecules at the $Au/N3/TiO_2$ interface one would expect just an *increase* of E_A. This behavior can be understood only if considering the specific interaction between N3 molecules and oxygen vacancies at TiO_2 surfaces. The onset of electron injection from N3 dye molecules into TiO_2 shifts to lower energies by about 0.4 eV in oxygen deficient ambience [16] which corresponds to a decrease of E_A being stronger than the increase due to the directed dipole moment.

3.3. Current voltage characteristics in oxygen atmosphere

The value of E_A of the Au/TiO_2 junction in oxygen atmosphere increased to about 0.43 eV while the saturation current decreased by about 2 orders of magnitude in comparison to the Au/TiO_2 junction in vacuum (Fig. 3(c)). This is explained by the disappearance of oxygen vacancies at the TiO_2 surface in oxygen atmosphere since oxygen vacancies support trap assisted tunneling. The highest value of E_A (about 0.65 eV) and the lowest saturation current (corresponded to a rectification by more than 4 orders of magnitude) were reached for the $Au/N3/TiO_2$ junction in oxygen atmosphere. As remark, the shunt resistance of the $Au/N3/TiO_2$ junction in oxygen atmosphere is of the order of 0.1 GΩ which is about 20 times larger than for the Au/TiO_2 junction in oxygen atmosphere. This gives evidence that pinholes in the N3 monolayer are not significant, i.e. the N3 monolayer can be assumed as a dense monolayer.

3.4. Barriers of current flow and dipole moment

The barrier heights for the current of the Au/TiO_2 junction are $\Phi_{Au}=0.43$ eV and $\Phi_{Au}^T=0.25$ eV in oxygen atmosphere and vacuum. The barrier height for the current of the $Au/N3/TiO_2$ junction in oxygen atmosphere is the sum of Φ_{Au} and $\Delta\chi$ where $\Delta\chi$ is the contribution of the dipole moment. The value of $\Delta\chi$ amounts to 0.22 eV since E_A is 0.65 eV for the $Au/N3/TiO_2$ junction in oxygen atmosphere. The area of one N3 molecule is 1.65 nm^2 [10]. If assuming a relative dielectric constant of 5 and a density of N3 molecules of $6\cdot10^{13}$ cm^{-2} one will get an averaged value of the projected dipole moment of roughly 5 D. This value is in very good agreement with those calculated for isolated molecules if considering uncertainties due to possible inclination of adsorbed molecules, the assumed dielectric constant and influence of the Au and TiO_2 contacts on the

charge distribution in the N3 molecule. The sum of Φ_{Au}^T and $\Delta\chi$ corresponds to the sum of $\Delta\Phi_{OvN3}$ (contribution of the interaction between oxygen vacancies and N3 molecules) and E_A obtained for the $Au/N3/TiO_2$ junction in vacuum. The resulting value of $\Delta\Phi_{OvN3}=0.34$ eV is in excellent agreement with the observed red shift of the onset of electron injection from N3 dye molecules into TiO_2 in oxygen deficient ambience [16].

4. Conclusions

A rectifying $Au/N3/TiO_2$ junction has been realized whereas the organic N3 monolayer with a large dipole was crucial for rectification. This seems surprising in comparison to Pt/TiO_2 junctions which show excellent rectification without any additional interface dipole layer. The reason for the striking difference between Au and Pt contacts on TiO_2 is, in our opinion, the different affinity to oxygen which is important for the formation of oxygen vacancies at the TiO_2 surface. In oxygen atmosphere, the barrier for the current flow at the Au/TiO_2 interface increased by 0.22 eV due to introduction of a monolayer of N3 molecules. For a deeper understanding of the mechanism of the barrier formation it will be important to deposit also other metals.

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