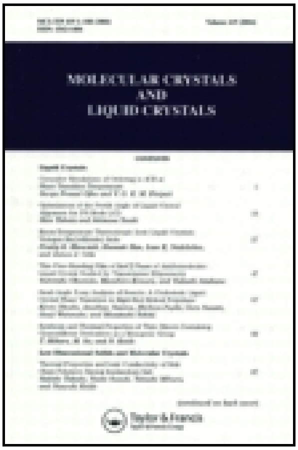

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Dye-sensitized anatase TiO_2 *(001) surface was prepared in the solution directly connected with an ultrahigh vacuum analysis chamber. We measured the ultraviolet photoelectron spectroscopy (UPS) and low energy electron transmission (LEET) of the dye-sensitized surfaces with and without illumination. The highest occupied molecular orbital (HOMO) and other levels showed different peak shifts in UPS when illuminated. The observations were discussed in relation to the device characteristics of a half photocell.*

Keywords: anatase; dye-sensitized solar cells; low energy electron transmission spectroscopy; organic semiconductors; ultraviolet photoelectron spectroscopy

INTRODUCTION

Electronic devices made of organic materials have a promising future in environment-friendly, wearable and low-weight applications. They may also lead to "molecular devices" which utilize quantum processes in a single molecule. The mechanism of device operation, however, has not been understood in detail compared with the devices made of

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conventional semiconductors. Although the organic materials and their static device structures have been studied by various surface science techniques, few results on the organic devices in operation have been reported. Electron spectroscopy such as ultraviolet photoelectron spectroscopy (UPS) and electron energy loss spectroscopy (EELS) will be very useful to identify molecular energy levels, local carrier dynamics and electronic structure in the devices. The application area of these techniques will be from fundamental study of the materials to the fault analysis of actual devices [1–3]. In this paper, we will present the results of electron spectroscopy of an organic-inorganic interface used in dye-sensitized solar cell ("Grätzel-cell" [4]) under illumination.

Due to the possibility of high-efficiency and low-cost solar cells, the dye-sensitized surfaces of sintered oxide nanoparticles are gathering much attention recently. In particular, TiO_2 nano-particles with an anatase-type crystal structure have given high efficiency and high stability. The fundamental questions include what determines the high efficiency of these systems and the possible route to remove redox solutions to improve the stability [5]. Surface-scientific characterization of the dye-sensitized oxide semiconductors will be useful to study those issues. Although there have been many studies of the dye-sensitized anatase surfaces [6], there have been no reports of the dye-sensitized surfaces under illumination. We have prepared dye-sensitized single-crystalline anatase TiO_2 (001) and measured ultraviolet photoelectron spectroscopy (UPS) and low energy electron transmission (LEET) [7] of dye-sensitized solar cell. We have developed an ultrahigh vacuum compatible solution chemistry system, which was used to chemically attach the dye molecules from the solution on anatase TiO_2 (001) surfaces prepared by plasma assisted molecular beam epitaxy.

EXPERIMENTAL

We have developed an UHV-compatible solution process equipment as shown in Figure 1. It has two vessels to contain solutions that are isolated from the UHV components by gate valves. One of the solutions was a distilled ethanol solution of Ruthenium dye for sensitization and the other was pure distilled ethanol for rinsing. We have used a sample holder that can be separated to two parts. The bottom part is to manipulate the sample in the UHV spectrometer and the top part can be separated from the bottom part and immersed in the solution. By keeping the bottom part out of the solution, it is possible to avoid

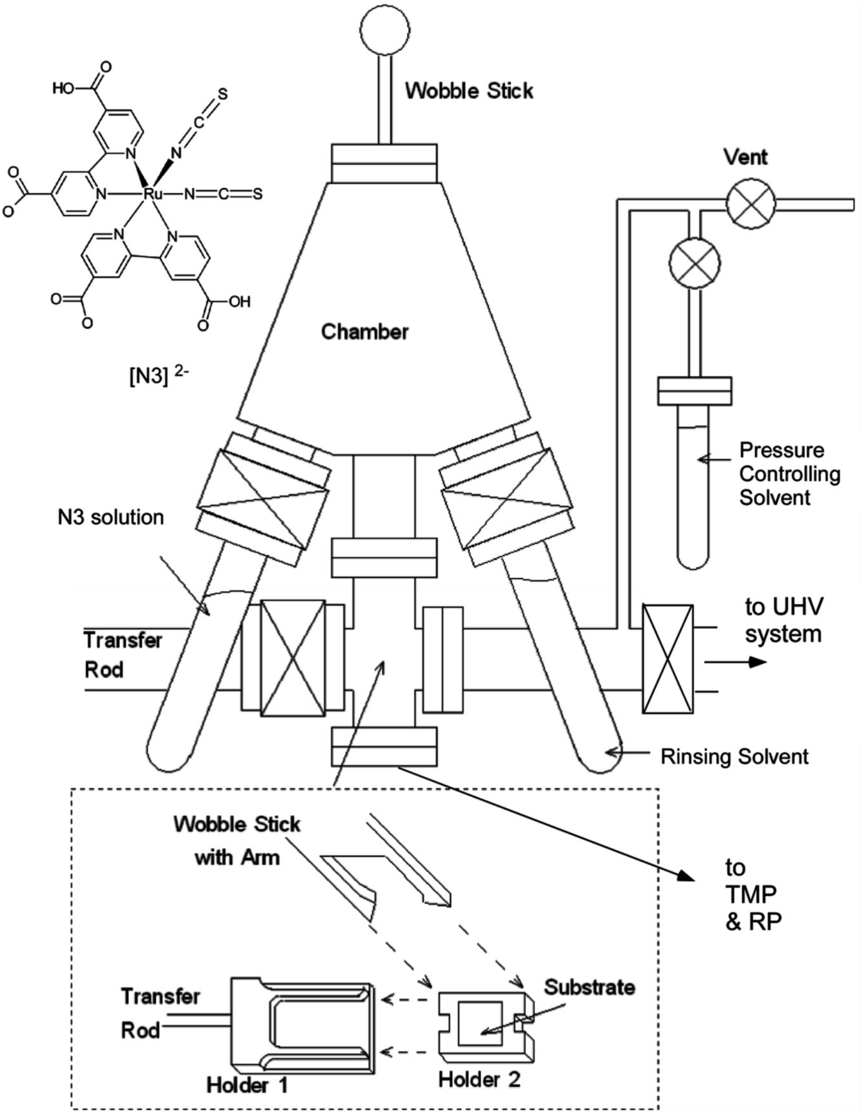

FIGURE 1 Setup for the preparation of dye-sensitized surfaces and the structure of the dye molecule.

unnecessary contamination in UHV systems. The solutions were purified by suck-and-saw processes using liquid nitrogen and turbo molecular pump for three times.

The dye used in the present experiment was "N3" (cis-bis(isothiocyanato) bis(2,2′-bipyridyl-4,4′-dicarboxilato)-ruthenium(II)bis-tetrabutylammonium,used as purchased from Solaronix Inc. (Fig. 1 inset)), which was chosen because the adsorbed structure is neutral and we can avoid the inclusion of the counter cation. We have found that the charge in the ionic clusters can affect the electron spectroscopy results [8].

The anatase (001) surface was prepared by plasma assisted molecular beam epitaxy on conductive Nb-doped (0.05%) $SrTiO_3$(001) substrate in UHV. The substrate was "Step-and-terrace" grade purchased from Shinkosha (Tokyo) and used without further chemical cleaning.

After the preparation of anatase (001) surface, the sample was transferred to the solution chamber with keeping vacuum condition and immersed in the dye solution for 24 hours, and then rinsed 1 hour in ethanol. It was then retrieved into the vacuum condition, which was quickly pumped by a turbo molecular pump to the UHV region. It was then transferred to the analysis chamber.

The analysis chamber was equipped with Vacuum Generators ADES400 angle resolved electron spectrometer, EMU-50 monochromatized electron gun for low electron energy beams, EG-3000 focused electron gun for AES and He-discharge UV lamp. The sample can be biased for the electron transmission measurement. Atomic force microscopy (AFM, SPI-3700) was used in air to analyze the morphology of the sample surface.

RESULTS AND DISCUSSIONS

A. Sample Preparation

Anatase TiO_2 (001) was epitaxially grown on $SrTiO_3$ as reported [9] and atomic-level flatness was achieved by carefully tuning the growth condition. The epitaxial films were characterized by RHEED, AFM and TEM. The total grown thickness of anatase was 10 nm. After immersing the substrate in the N3-solution followed by the rinsing in ethanol, RHEED and AFM were measured. RHEED image was halo that means there is no long-range order in the films, although the AFM gave atomic-level root-mean-square roughness (0.5 nm). AES was measured and the existence of the ruthenium dye was confirmed. It was concluded from the angle-resolved AES and the reported escape depth of Auger electrons that the thickness of the adsorbate was $\sim$1 nm, which coincides with the size of the adsorbate dye molecule. The precise analysis of the adsorbate structure will be given elsewhere.

B. UPS

We have measured UPS spectra of the dye-adsorbed epitaxial anatase in both of the dark and illuminated conditions. In the illuminated condition, a Xe discharge lamp (150 W) was used with a focusing lens and a filter to remove the ultraviolet photons which might excite the substrate directly.

Figure 2 shows a UPS spectra of the dye-adsorbed sample taken under illuminated and dark conditions. Since radiation damage was observed as the broadening of the spectra, the position of the measurement was frequently moved by carefully observing the spectra. The overall structure of the spectra of the dye-adsorbed sample in the dark condition agrees well with those reported in the previous studies on dye-adsorbed nanocrystalline surfaces [6]. In the measurement using He-II ($h\nu = 40.8\,\mathrm{eV}$), all peaks other than HOMO shifted to the higher binding energy side by 0.26 eV when illuminated. However, the HOMO position only moved slightly ($\sim 0.05\,\mathrm{eV}$) to the lower binding energy side. On the other hand, the shift is not significant in the measurement using He-I ($h\nu = 21.2\,\mathrm{eV}$) while the HOMO peak is shifted very slightly to the lower binding energy side.

The mechanism of the peak shifts induced by the illumination is considered as follows. In principle, photo-illumination in the present setup corresponds to the open circuit condition of the photocell. It should induce the open-circuit photovoltage by the holes transferred from the photoexcited molecules to the substrate. This hole transfer is completed in the timescale of picosecond in the solution [4] and the electrostatic field will become balanced by the suppression of the

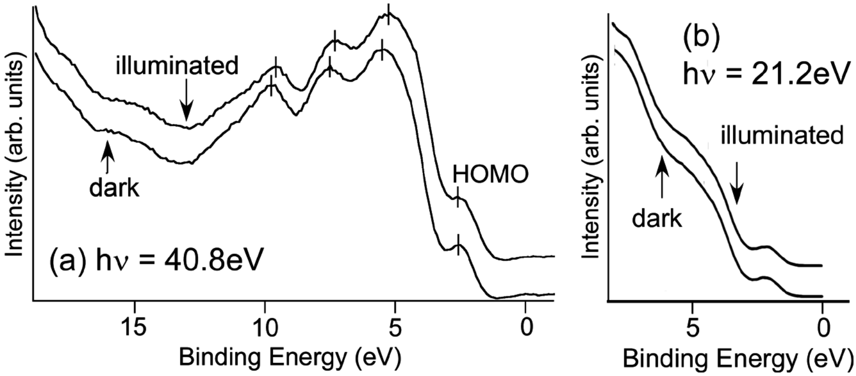

FIGURE 2 UPS of a dye-sensitized anatase TiO_2 (001) surface with and without illumination. (a) He-II ($h\nu = 40.8\,\mathrm{eV}$), (b) He-I ($h\nu = 21.2\,\mathrm{eV}$).

hole transfer by the open-circuit voltage. The photovoltage will make the surface positive compared to the substrate bulk Fermi level and this effect reasonably accounts for the peak shift of the valence band to the higher binding energy site. The reason why HOMO shifted to the opposite side by illumination can be explained if we assume that the HOMO band is located in the center of the photoexcitation and the site becomes negatively charged by the removal of the holes from the site. If we assume the above, this result gives information on the time scale of photo-induced charge transfer. If the time scale of the charge transfer is much longer than that of photoelectron emission process in UPS, the spectrum shape will be determined by the superposition of those of the neutral molecules shifted by photovoltaic effect and those of the molecules in the charge-transferred state. Since the peak shift is much smaller than the energy gap between HOMO and the Fermi level in the spectrum, only a small number of molecules are in the charge-transferred state. In this case, the spectrum will be dominated by the major part, that is, the spectrum without illumination uniformly shifted in one direction by photovoltage. However, the observation is that the HOMO was shifted to opposite direction. It is thus concluded that the time scale of the photo-induced charge transfer is smaller than the time scale of UPS process.

The difference between He-II and He-I can be explained by the different intensity in the ultraviolet photons, in which He-I is stronger than He-II by two orders of magnitudes in our measurement system. The results can be reasonably explained by assuming He-I spectra in the dark are actually in the illuminated condition by strong He-I photons.

C. LEET

The dye-adsorbed anatase in a vacuum can be regarded as a half-cell. Although it is possible to measure the open circuit photovoltage of the half-cell by above-mentioned technique, characterization of the performance as a full photocell is important for the materials searching. We have thus examined the possibility to use an electron beam as the redox reagent to measure the characteristics of the photocell. In this concept, electrons in vacuum and electron gun correspond to I^- and Pt cathode in the Grätzel solar cell [4], respectively. The problem is that not all of the electrons emitted from the cathode are absorbed by the anode when the potential difference is set small to mimic the full photocell. Instead, we measured the current absorbed by the dye-sensitized anatase surface with applying a bias voltage between the photocell and the electron gun, which emits a certain flux of electrons. The electrons that are not absorbed by the sample was refracted and absorbed by the surrounding components in the measurement chamber.

We measured the electron current absorbed in the sample around the threshold. We have to deal with the very small electron kinetic energy. The kinetic energy from the electron gun was set to 15.0 eV which is determined by the potential difference between the emitter filament and the surrounding chamber which is set to ground level. The sample bias was changed by applying a sweeping bias voltage to the floating pA-meter. The bias supply circuit was made of high-precision operational amplifier powered by a battery. The voltage was controlled by rotating a potentiometer using a stepping motor controlled by a microprocessor. The electron beam was irradiated vertically to the sample surface. In the ordinary measurement without biasing the sample, the beam diameter was ~2 mm and much smaller than the sample area (1 cm × 1 cm). The FWHM of the electron beam energy from the gun was 0.8 eV as determined by measuring the electron energy distribution without biasing the sample.

It was found that the resulting current-voltage curve was extremely sensitive to the geometry of the measurement and reproducible results were only observed when the sample was not moved during the measurement. The data shown below were obtained under this condition.

Figure 3(a) shows the sample current vs. bias voltage characteristics of dye-sensitized anatase formed on Nb-doped $SrTiO_3$ measured without and with photo-illumination. It was found that the overall curve structure is shifted to the lower bias voltage side when illuminated, while the threshold voltage for the appearance of the current is not shifted. The appearance of the sample current is used to measure the work functions of ordinary surfaces in the "diode method". However, we consider that the results of this technique to the half photocell can be related to the device characteristics as follows. As illustrated in Figure 3(b), the half-cell is in the reversed bias condition when the current is observed. The upper limit in the negative current is determined by the initial electron beam from the electron gun, while the shift of the threshold voltage correspond to the open circuit voltage. Therefore, the redox cycle of the dye-sensitized half-cell is closed by using the electron beam in the vacuum as the redox reagent. The behavior just above the current appearance (positive bias side) contains important information about the tunneling of electrons beyond the photo-generated potential barrier. In the present result, the little shift of the threshold voltage strongly suggests that there is a path of back transfer of the photo-separated charges, whereas the current

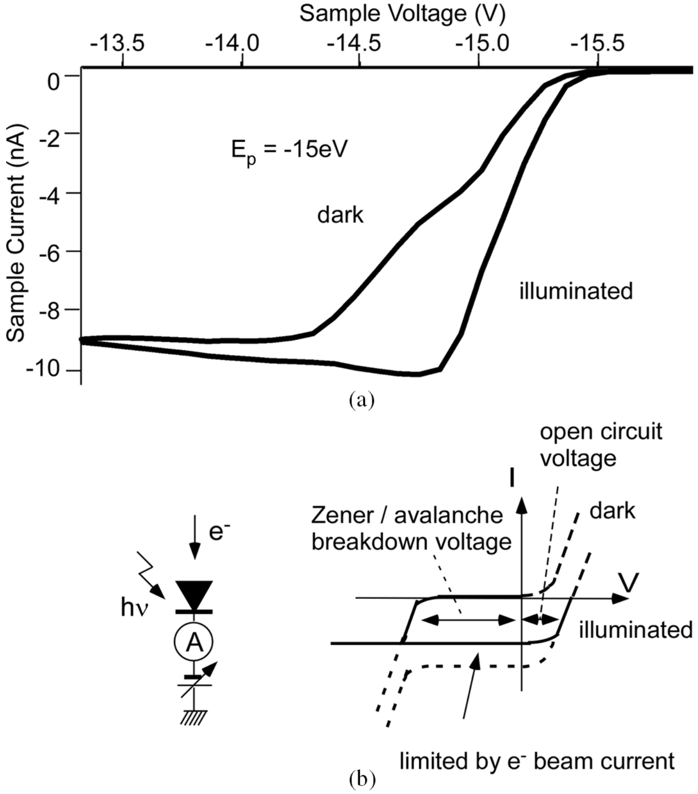

FIGURE 3 (a) LEET of a dye-sensitized anatase TiO_2 (001) surface with and without illumination. (b) Comparison with ordinary photocell characteristics.

that can go through the path is limited because the curve is shifted above the threshold. Since the back transfer of the photo separated charges is critically important for the efficiency of the photocell, the present technique will be useful to evaluate the half cell itself in the clean and controlled conditions without complicated chemical environment in the solution.

CONCLUSION

We prepared dye-sensitized anatase TiO_2 (001) surface in the solution directly connected with an UHV analysis chamber. We measured the UPS and LEET of the dye-sensitized surfaces with and without the illumination. The observed characteristics were discussed in relation to the device characteristics of the half photocell.

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