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1/*f* Noise in dye-sensitized solar cells and NIR photon detectors

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Abstract

All electronic devices are plagued with 1/*f* noise originating from many causes. The most important factors contributing to 1/*f* noise in a semiconductor is believed to be recombination of carriers and their trapping at defects and impurity sites. Adsorption of moisture and electron acceptor molecules enhances the intensity of 1/*f* noise. Amazingly, some molecular species that strongly chelate to the semiconductor surface, suppress 1/*f* noise owing to passivation of the recombination sites. Thus in addition to sensitization, the dye adsorbed on the nanocrystallites plays a key role in mitigation of recombinations. For this reason dye-sensitized heterojunctions could also find application as low noise NIR photon detectors. Experiments conducted with oxide semiconductors (TiO_2, ZnO, SnO_2) indicate that the mode of binding of dyes at specific sites determines the extent to which the recombination and 1/*f* noise are suppressed. The transport of electrons in a nanocrystalline matrix is diffusive with a diffusion coefficient D depending on the trapping and detrapping processes. Thus passivation of trapping sites by the adsorbed dye is expected to increase the response time which can be expressed as $\tau \sim L^2/D$, where L = thickness of the nanocrystalline film. Measurement techniques and construction of a dye-sensitized NIR photon detector will be discussed.

1. Introduction

Dye-sensitized solar cells (DSSCs) based on nanocrystalline high bandgap oxide semiconductors receive much attention as cheap alternatives to the conventional solar cells made from low bandgap semiconductors. The functioning of these devices depends on dye-sensitization (DSN), i.e. process by which a photo-excited dye molecule anchored to a semiconductor surface injects an electron to the conduction band forming a dye cation [1,2]. Electron injection is energetically permitted if the band edges of the semiconductor and the ground (S) and excited (S^*) levels of the dye are located as in Fig. 1. The positive charge on the dye cation can be transferred to a suitable hole collecting medium in contact with the dyed nanocrystalline surface to form heterojunction of the configuration N/D/P, where N denote the nanocrystalline n-type semiconductor, D = dye and P = hole collecting medium (Fig. 2). In one version of DSSCs, the hole collecting medium is a redox electrolyte [1,2] which efficiently collects the positive charge on the dye cations formed during electron injection, whereas in the other version P is a hole collecting solid material [3,4] (i.e., a p-type semiconductor of appropriate band positions).

The electron injected into the n-type material and the dye cation on its surface undergoes recombination. However, the rate of recombination happens to be several orders of magnitude slower than the rate of injection and this is one of the reasons why the DSSCs function, converting light to electricity at reasonably high quantum efficiencies [2]. The dye coverage on the semiconductor surface needs to be maintained at monolayer level to avoid insulation by thick dye layers and to prevent rapid quenching of the excited molecules by mutual interaction. Although the dye coverage is at monolayer level, the large roughness factor (~1000) greatly increases the light absorption

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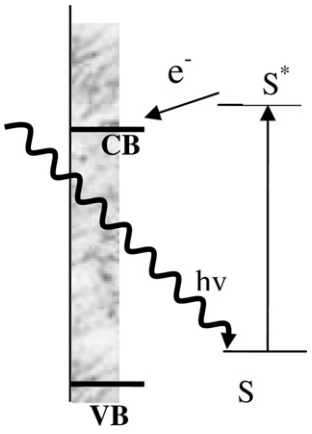

Fig. 1. Schematic diagram showing relative positions of the bands of semiconductor and ground (S) and excited (S*) levels of a dye molecule anchored to the semiconductor surface.

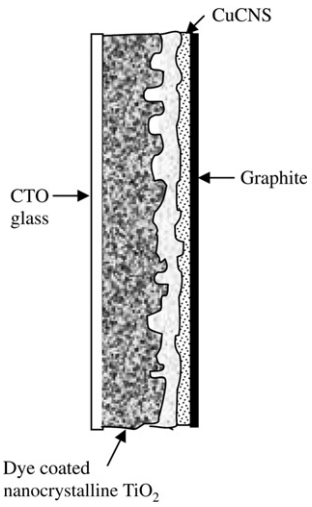

Fig. 2. Construction of the dye-sensitized photovoltaic heterojunction.

cross-section. As DSN involves carrier transfer to one band, bulk recombinations are absent, but the large effective area of the interface makes a DSSC susceptible to surface recombination. However, DSSCs deliver quantum efficiencies exceeding 85% and energy conversion efficiencies around 10% are readily achievable [1,2], indicating that recombination does not occur at the expected rate. Trapping and detrapping of carriers at the surface of semiconductors generate $1/f$ noise [5,6]. Both bulk and surface interactions of carriers contribute to $1/f$ noise. In nanocrystalline semiconductors where surface to bulk ratio is exceptionally large the trapping–detrapping of carriers at surface states makes the most significant contribution to $1/f$ noise. Nanocrystalline surface is heavily populated with defects and adsorbed species that act as trapping and recombination sites. Under thermostatic conditions the current passing through a nanocrystalline semiconductor films exhibits $1/f$ noise fitting into the Hooge's formula $S(f) = AI_0^2/f^\delta$ (I_0 = mean value of the fluctuating current, A = constant, δ = an exponent close to unity). Thus a electric current through nanocrystalline semiconductors where the surface to bulk ratio is exceptionally high, shows $1/f$ noise more conspicuously. Measurements indicate that current through nanocrystalline film of TiO_2 exhibits $1/f$ noise which is greatly enhanced on exposure of the surface to electron acceptor molecules. Amazingly this noise was found disappear almost completely when the nanocrystallites are coated with a dye. Observation suggests that dye adsorption passivates the trapping sites on the semiconductor surface. As trapping sites are also recombination centers, dye adsorption suppresses recombination as well. Because of the very low level of $1/f$ noise the heterojunction N/D/P could also serve as a sensitive photon detector. The directivity of a semiconductor based device depends on the bandgap of the material used. Low bandgap semiconductors show high sensitivity to thermal noise. Thus the use of high bandgap semiconductors is a tremendous advantage for NIR detection because of the low level $1/f$ as well as thermal noise.

2. Experimental

Nanocrystalline n-TiO_2 films of type required for fabrication of solid-state DSSCs were deposited on conducting fluorine doped tin oxide glass plates (FTO) by the method reported previously [4]. Briefly, the method adopted involve painting of a colloidal suspension of TiO_2 on the FTO surface followed by sintering at 150 °C and repetition of the process until the film grows to a thickness of about 10 μm. Finally the film is heated to 430 °C for 30 min to sinter together TiO_2 nanocrystallites. Dyes used in this investigation are Ru-bipyridyl complex (N3 dye, Solaronix), bromopyrogallol red and IR dyes (IR 783, IR 820, IR 1040, Aldrich).

The hole-collector used was CuSCN (p-type semiconductor of bandgap 3.6 eV). CuSCN was coated on the dyed nanocrystalline surface from a solution in n-propyl sulfide. The outer CuSCN surface was painted with graphite to improve the ohmic contact and gold plated FTO glass plate pressed onto graphite served as the back contact. The photocurrent spectral responses were recorded using a monochromator, light chopper, lock-in amplifier system. Light intensities were measured with a calibrated silicon diode.

Nanocrystalline films used for measuring the noise in the electrical current were prepared as described below. A scribe (~8 μm thick) is drawn on the surface of a FTO glass plate (1.5×2 cm^2, sheet resistance 12 Ω cm^{-2}) with a fine diamond point to break the electrical connectivity. A layer of colloidal TiO_2 (thickness ~10 μm) was screen printed above the scribe and the plate is sintered at 430 °C for 25 min (sample geometry indicated in Fig. 3). Fig. 4 shows the experimental set up used for noise measurements. The sample housed in an enclosure provided with facilities for evacuation and heating is connected in series with a resister and a Ni–Cd battery. A low noise preamplifier amplified the voltage fluctuations across the sample and power spectrum analyzer (Stanford Research SR785 Fourier

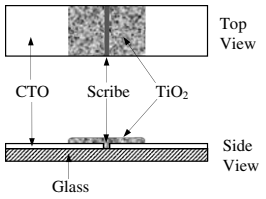

Fig. 3. Schematic diagram showing the sample preparation for measurement of $1/f$ noise in the current through the nanocrystalline semiconductor film (CTO – conducting tin oxide glass).

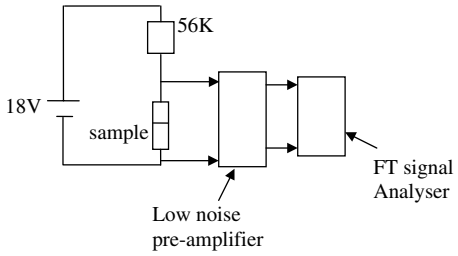

Fig. 4. The experimental set-up used for recording power intensity of the $1/f$ noise.

Transform Dynamic Signal Analyser) was used to obtain the spectral power intensity $S(f)$ as a function of frequency.

3. Results and discussion

When the chamber is filled with air, frequency dependent noise (FDN) was readily noticeable in the power spectrum. The observed FDN power spectrum fits into the Hooge's formula [7] $S(f) = AI^2/f^{\delta}$, here $I =$ mean value of the fluctuating current, $f =$ frequency and δ an exponent close to unity [8]. On evacuation of the chamber, FDN persisted but at a lower intensity. However, if sample is heated about 90 °C during evacuation FDN did not appear even after the sample cooled to the room temperature. Again, FDN remained undetectable after flushing the chamber with dry nitrogen. However, introduction of trace amounts of water renewed generation of FDN [8]. Above observations clearly indicate that the moistures adsorbed on the semiconductor surface has been the cause of FDN. Even under vacuum conditions, water adsorbed on the nanocrystalline surface is not readily released until the sample is heated. Water molecules adsorbed on TiO_2 and other oxide surfaces dissociate into protons and hydroxyl radicals [9] and the latter acts as a strong electron acceptor. The cause of FDN noise induced by moisture seems to originate from trapping of the electrons by the hydroxyl radicals adsorbed onto the TiO_2 surface. The effect of electron acceptors in generating FDN noise in the current through a nanocrystalline film is more glaringly seen when a small amount of iodine is introduced to the nitrogen atmosphere (Fig. 5). As iodine happens to be powerful electron acceptor iodine adsorbed on the TiO_2 surface readily traps electrons creating FDN. It is amazing to note that iodine induced FDN gets completely suppressed when the nanocrystalline surface is bonded with a dye. Here the dye passivates iodine absorption sites on the TiO_2 surface preventing electron transfer to iodine. An alternative possibility not ruled out completely could be transient trapping of electrons in the surface states of TiO_2 and these acting as intermediates in transfer of electrons to iodine. In this case, it is those surface states that get passivated by bonding of the dye to the TiO_2 surface. An observation that supports the second point of view is the following. The electron transport in the nanocrystalline film is diffusive with an effective diffusion coefficient depending on the rate of trapping and detrapping of the nanocrystalline surface. Measurements indicate that the diffusion coefficient of electrons in dye coated nanocrystalline TiO_2 is larger than that in bare TiO_2. If the surface states that induce electron trapping are passivated by the adsorbed dye we naturally expect a higher electron diffusion coefficient in dye coated TiO_2.

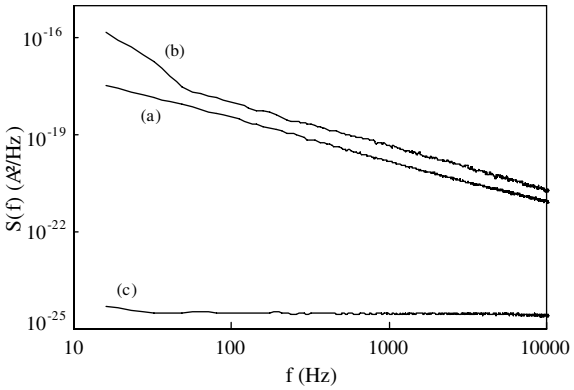

Fig. 5. Noise power spectrum of (a) TiO_2 in moist air, (b) TiO_2 in N_2 atmosphere containing iodine, (c) TiO_2/dye in N_2 atmosphere containing iodine.

The effect of moisture on generation of $1/f$ noise in dyed samples was also examined by varying the humidity of the chamber. Until the relative humidity of the nitrogen atmosphere is about 10–15%, the dye coating effectively prevented suppressed $1/f$ noise. On further increase of humidity signs of $1/f$ noise appeared and progressively enhanced as the humidity was further increased. The reason seems to be the desorption of dye into from the TiO_2 surface as dyes have an affinity for water. Dye-sensitized photoelectrochemical cells use an electrolyte based on acetonitrile. Therefore we examined effect of acetonitrile on noise in dye samples and found that unlike water, acetonitrile does not influence creation of $1/f$ noise.

When the dark current noise of heterojunctions of the form n-TiO_2/dye/p-CuSCN were examined by plotting $S(f)$ vs f, beyond a frequency the noise level was found to low ($\sim 10^{-28}$ A^2/Hz) and largely independent of frequency. The specific detectivities of the dyes having absorption peaks in the region 750–1000 nm was in the range 10^{11}–10^{10} cm $Hz^{-1/2}$ W^{-1}. The responsivities measured from the observation of photocurrent transients were nearly two orders of magnitude smaller than of silicon detectors

[10]. The response time of the detector is of the order L^2/D where L = film thickness, D = diffusion coefficient of carriers in the nanocrystalline matrix. Thus the response time is quite sensitive to the film thickness. However, the reduction of the film thickness would also weaken the light absorption cross-section, which depends on the amount of dye adsorbed and therefore on the thickness of the film. A possibility is to reduce the crystallites size and as effective surface area of the film varies as L/r (r = crystallite radius), the reduction of crystallite size by one order of magnitude will increase the responsivity by two orders of magnitude. This is practically realizable because the median crystallite size of film we have fabricated is about 30–50 nm and techniques are available to prepare TiO_2 particles of dimensions of the order 3 nm. Diffusion coefficient depends of the nature of the material (i.e., the effective electron mass) and to some extent the crystallite size. The effective electron mass in SnO_2 is nearly two orders of magnitude smaller than that in TiO_2. Hence, in principle responsivities of dye-sensitized detectors can be further increased, possibly even above that of silicon detectors.

4. Conclusion

The above investigation on the measurements of $1/f$ noise in bare and dye coated nanocrystalline films of TiO_2 clearly shows that the bonding of the dye to the nanocrystalline surface largely suppresses the generation of $1/f$ noise. The mechanism involved seems to be the passivation of the semiconductor surface by the adsorbed dye. Passivation is also the cause that suppresses recombination in the dye-sensitized solar cells. There is room for improvement of the responsivities of the photon detectors based on dye-sensitization using films composed of smaller crystallites and/or materials where the intrinsic diffusion coefficient is higher. Problem that needs to be resolved is stability of the detector. The characteristics of the model detectors we have tested did not remain constant during storage. The problem seems to be the insecurity of the contact between the dye and the hole collector. Methods need to found to bond the dye both n- and p-semiconductors to avoid weakening of the contacts.

References

[1] B. O' Regan, M. Gratzel, Nature 353 (1991) 737.
[2] M. Gratzel, J. Photochem. Photobiol. A 164 (2004).
[3] K. Tennakone, G.R.A.A. Kumara, I.R.M. Kottegoda, K.G.U. Wijeyantha, V.P.S. Perera, J. Phys. D: Appl. Phys. 80 (1996) 4749.
[4] K. Tennakone, G.R.R.A. Kumara, A.R. Kumarasinghe, K.G.U. Wijayantha, P.M. Sirimanne, Semicond. Sci. Technol. 10 (1995) 1689.
[5] M.B. Weissman, Rev. Mod. Phys. 60 (1988) 537.
[6] A.K. Raychaudhuri, Curr. Opin. Solid State Mater. Sci. 6 (2002) 67.
[7] F.N. Hooge, Phys. Lett. A 29 (1969) 139.
[8] P.V.V. Jayaweera, P.K.D.D.P. Pitigala, A.G.U. Perera, K. Tennakone, Semicond. Sci. Technol. 20 (2005), L1.
[9] S. Wendts, J. Maththisen, R. Schub, E.K. Vestegaard, E. Laegsgaard, B. Besenbacher, R. Hammer, Phys. Rev. Lett. 96 (2006) 66107.
[10] P.V.V. Jayaweera, A.G.U. Perera, M.K.I. Senevirathne, P.K.D.D.P. Pitigala, K. Tennakone, Appl. Phys. Lett. 85 (2004) 5754.