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Abstract. The dye-sensitized nanocrystalline solar cell (DSC) offers potential opportunities in the area of renewable energy sources mainly due to its simple fabrication procedure and use of low cost materials. A theoretical model based on the thermionic emission theory was developed to determine the interfacial effect of ZnO/TCO on the performance of DSC. It was found that under conditions where thermionic emission is valid, photoelectric outputs are affected by temperature and Schottky barrier height (ϕ_b). The model can be used to facilitate better selection of suitable TCO material. © *2012 Society of Photo-Optical Instrumentation Engineers (SPIE).* [DOI: 10.1117/1.JPE.2.027003]

Keywords: dye-sensitized solar cells; Schottky barrier; ZnO/TCO interface.

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1 Introduction

Dye-sensitized solar cells (DSC) are basically photo electrochemical solar cells that are currently being subject to intense research in the framework of renewable energies as low cost photovoltaic devices. The DSC is composed of photoactive electrode, which is generally made of mesoporous, nanostructured metal oxide film (TiO_2, ZnO, SnO_2, etc). The photoelectrode is sensitized to visible light by adsorbing a molecular dye. When the photon is absorbed, dye gets to the excited state. This leads to the injection of electrons into the metal oxide substrate. The injected electrons move through the nanostructured film to the transparent conducting oxide (TCO). The electron donor in the electrolyte solution regenerates the dye, which in turn gets regenerated by accepting the electron coming from the counter electrode. The power conversion efficiency of the DSC has reached up to 11.5%.[1] The movement of electrons through nanostructured network is a complicated process because of the large surface-area-to-volume ratio of the concerned nanomaterial. Efficient electron injection from excited dye to nanostructured metal oxide film plays a crucial role in the performance of DSC.[2,3] The injected electron gets transported through nanostructured film mainly due to diffusion.[4,5] The transport kinetics of flow of injected electrons is influenced by the incident intensity and trapping-detrapping mechanism.[6,7] The electric potential distribution plays a vital role in the functioning of dye-sensitized solar cells. Ruhle et al. proposed a model based on a built-in electric field and the possibility of a Schottky barrier at the interface of the mesoporous semiconductor (TiO_2) and the TCO (usually *F*-doped tin oxide, FTO).[8] Kron et al. investigated the influence of front contact barrier by using different front contact materials to the nanoporous TiO_2 layer.[9] Most of the research in DSC has been centered on TiO_2 as a nanostructured film as a photo electrode. The best-suited alternative material to TiO_2 is ZnO,[10–12] which has a similar band gap (3.2 eV) and band edge position to TiO_2.[13] ZnO nanoparticles and nanowires are repeatedly used to fabricate DSC electrodes.[14,15] Branched ZnO nanowire structure has recently been used in DSC.[16] In this study, a theoretical model was developed by taking a thermionic emission model into consideration and investigating the ZnO/TCO interfacial effects on the performance of DSC. TCO substrate can be considered to be metal as it is heavily doped (e.g., doped SnO_2) and has high electrical conductivity.[8] A Schottky barrier model can then be used for simulation of ZnO/TCO interface.[17–19] The details of theoretical modeling are discussed in the following sections.

2 Theoretical Modeling

There is a flow of injected electrons through the porous nanostructured ZnO thin film toward the TCO. Subsequently the electrons reach the counter electrode by the external circuit. There is a regeneration of oxidized dye by redox madiators followed by the transportation of the oxidized redox mediators (I_{3^-}) to the counter electrode where they are regenerated to complete the cycle.

The electron density inside mesoporous layer rises with the injection of electrons in which the quasi-Fermi level (E_F) comes near to conduction band edge (E_c). The difference between E_F and the electrolyte redox potential is considered to be the photovoltage.[20,21] However, under maximum power operating conditions the potential differences due to two interfaces should also come into the picture (i.e., photoelectrode/TCO and electrolyte/counter electrode interface). There has been various efforts to study the influence of counter electrode,[22–24] but the effect of ZnO/TCO interface has not been effectively studied.

Under irradiation, photo injection of electrons results in a rise in quasi-Fermi levels of ZnO and TCO as shown in Fig. 1. As the ZnO/TCO interface effect is under study, the loss of voltage due to counter electrode/electrolyte interface in not considered. The photovoltage can be rewritten as

$$V = V_0 - V_1, \tag{1}$$

where V_0 is the potential difference between the ZnO Fermi level (E_F) and redox potential of electrolyte (E_{redox}), and V_1 is the voltage loss at the ZnO/TCO interface. This voltage loss, derived from the Schottky barrier height, appears at the ZnO/TCO interface, resulting in the internal resistance.

Two mechanisms that control electron transfer at the interface are thermionic emission and electron tunneling as described by metal semiconductor contact theory.[17,18] But electron tunneling can be neglected as ZnO is lightly doped,[19,20] and cell operates at a high temperature (300 K); under such circumstances thermionic emission dominates the electron transfer. It should be mentioned here that when ZnO is heavily doped or the operating temperature is low, electron tunneling becomes significant, which minimizes the interfacial effect. It should be noted that due to small size of ZnO particles (~15 nm) as well as the strong screening effect of electrolyte, there is negligible macroscopic electric field in the porous ZnO thin film. Therefore, under such conditions, the proposed thermionic emission model may not be valid.

However, here we treat DSC as a series connection of a Schottky diode with a certain barrier height representing the metal/n-type semiconductor interface and the main diode, which corresponds with the injection of electrons from semiconductor film into the electrolyte. J is the current density corresponding to the applied voltage V, including the voltage loss V_1 at the ZnO/TCO interface.

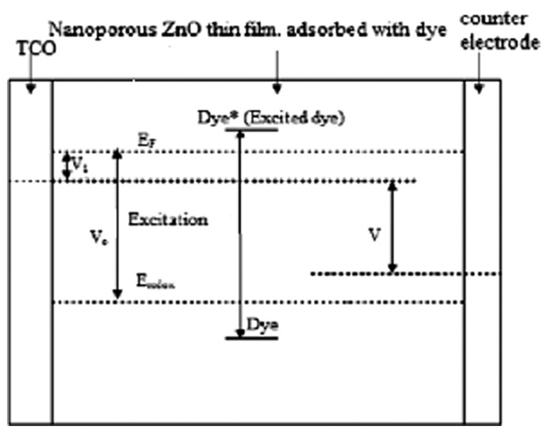

Fig. 1 Potential diagram of DSC under illumination.

The following expression correlates the voltage loss at the ZnO/TCO interface with reference to thermionic emission theory.[18,25]

$$J = AT^2 \exp(-q\phi_b/kT)[\exp(qV_1/kT) - 1] \tag{2}$$

where A is the effective Richardson constant equal to $3.2 \times 10^6\, A\, m^{-2}\, K^{-2}$ for ZnO, T is the temperature, k is the Boltzmann constant equal to $1.38066 \times 10^{-23}\, JK^{-1}$ and q is the charge of an electron equal to $1.60218 \times 10^{-19}\, C$. Equation (2) can be rearranged to

$$V_1 = (kT/q) \ln[1 + J/\{AT^2 \exp(-q\phi_b/kT)\}]. \tag{3}$$

3 Results and Discussion

According to Eq. (3), the voltage loss V_1 due to ZnO/TCO interface depends upon Schottky barrier height, temperature, and recombination current at the TCO/electrolyte interface.

Cameron et al. estimated that the current density due to recombination of electrons with electrolyte via TCO substrate lie in the range from 10^{-5} to 10^{-4} A m^{-2} (Ref. 26). Figure 2 shows the variation of V_1 with ϕ_b, for different values of J. There exists a critical value of ϕ_b below V_1. An increase in J results in decrease in this critical ϕ_b.

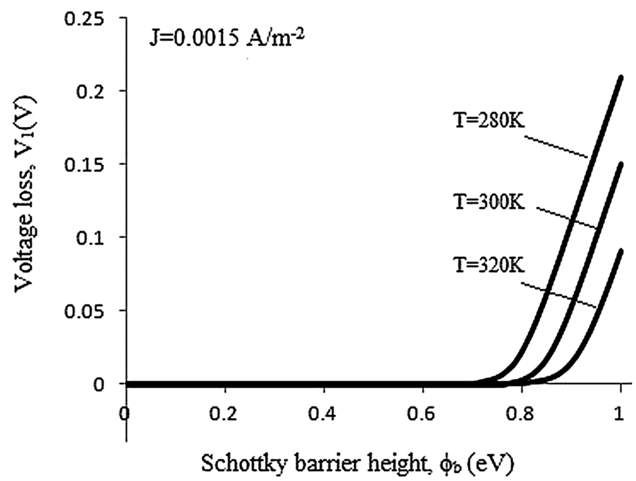

Fig. 2 Variation of voltage loss at ZnO/TCO interface with Schottky barrier height and temperature.

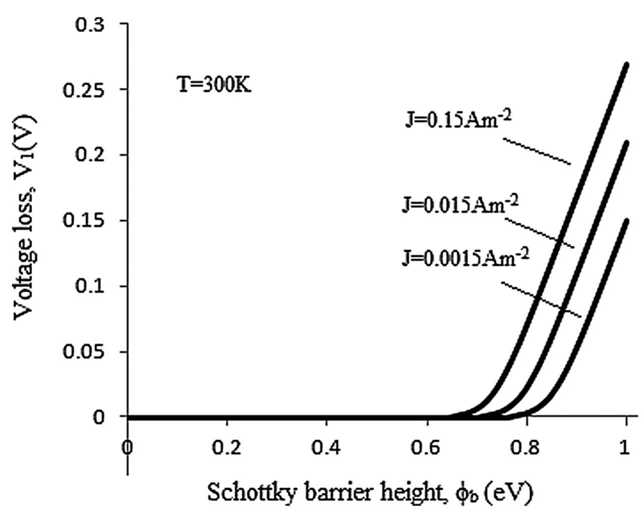

Fig. 3 Variation of voltage loss at ZnO/TCO interface with Schottky barrier height and current density.

Taking current density to be 0.0015 $\mathrm{A\,m^{-2}}$, the theoretical analysis was done, and the result showing the effect of ϕ_b, on V_1 at different T are plotted in Fig. 3. Again there exists a critical value of ϕ_b below, which V_1 is negligible. Above this critical value, V_1 increases with increase in Schottky barrier height. As temperature increases there is a rise in the critical value. It is evident that for values of $\phi_b \leq 0.6$, the voltage loss V_1 is negligible. It can be predicted that FTO and Al can be good candidates for TCO material.

4 Conclusions

Investigation of ZnO/TCO interfacial effect on DSC was done on the basis of a Schottky barrier model derived from thermionic emission theory. The effect of the interface depends on the current density, temperature, and Schottky barrier height. At low Schottky barrier height, there is negligible voltage loss that leads to almost unaffected DSC performance. The interfacial effect becomes significant as the Schottky barrier height increases beyond critical value. The results are important: by considering the voltage loss at the ZnO/TCO interface, the accuracy in the prediction of *J-V* characteristics of the DSC can also be improved. The modeling can be used to assist selection of appropriate TCO material for high ZnO-based DSC efficiency.

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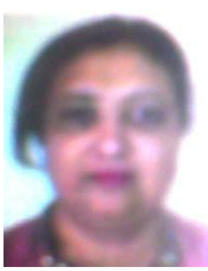

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