

Degradation of Dye-sensitized Solar Cells due to Formation of Surface States in the Semiconductor Film

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ABSTRACT

With prolong illumination efficiency of dye sensitized solar cells decline which is a general scenario that occurs due to drop in photo voltage and photocurrent. Generally, the semiconductor materials used to fabricate dye sensitized solar cells are polycrystalline metal oxides so that traps originated at the grain boundaries could lead to recombination of charge carriers degrading photocurrent and photovoltage. Flat band potential of the semiconductor is a determination factor of the photovoltage of the cell and formation of trap states moves the flat band potential to a lower energy level in the energy scale where flat band potential of TiO₂ films can be measured with Mott-Schottky measurements.

In this study we have measured flat band potential of TiO₂ films, TiO₂ films coated with ruthenium bipyridyle dye and dye coated TiO₂ films of degraded solar cells. The flat band potential of the TiO₂ film increased after coating the dye and decreased after used them in dye sensitized solar cells. The increment in the flat band potential after coating the dye is explained as a result of passivation of surface states and reduction of flat band potential is ascribed due to formation of surface states again in the semiconductor film.

1. INTRODUCTION

The degradation of the photo voltage followed by the photocurrent is general scenario in dye sensitized solar cells with prolong illumination where the efficiency decreases to a lower value as a consequence. The life time of dye-sensitized solar cell may vary depending on the type of the dye and the semiconductor material used to fabricate a solar cell which is comparably short with the life time of single crystalline solar cells. Generally the semiconductor materials used to fabricate dye sensitized solar cells are polycrystalline metal oxides [1] so that the traps originated at the grain boundaries could lead to recombination of charge carriers. In this study we have investigated whether trap states originated at the surface or grain boundaries lead to degradation of photocurrent and photovoltage by measuring the flat band potential of the semiconductor film before and after the degradation of the solar cell. Due to the formation of trap states on the surface, the flat band potential moves to low energy levels in the energy scale following the quasi Fermi level of the semiconductor material where, flat band potential of TiO₂ films were measured with Mott-Schottky measurements [2].

2. EXPERIMENTAL

TiO₂ films were deposited on CTO glass by doctor blade method using a past made grinding Degussa powder with acetic acid and ethanol. Then the film was sintered at 450

°C in a furnace. The films were coated with ruthenium bipyridyl dye by immersing the films in a dye solution. The fabrication of the electrochemical cell is done by placing a Pt coated CTO glass on the dye coated surface of the film and filling the capillary space with an electrolyte containing I/I^{3-} redox couple. Then the films were illuminated with white light with the intensity of 100 mW/cm^2 . The flat band potential of (a) TiO_2 films as deposited on CTO glass, (b) TiO_2 films coated with ruthenium bipyridyl dye and (c) dye coated films after degradation of the solar cell were measured using Mott-Schottky measurement. The capacitance of the films was measured using a HP LCZ meter coupled to a computer at the frequencies 1.5 kHz and 1.0 kHz. Electrolyte used in the Mott-Schottky measurement was 0.5 M Na_2SO_4 solution.

3. RESULTS AND DISCUSSION

Figure 1 shows the Mott-Schottky plot of TiO_2 film deposited on CTO glass plate. The curve (a) and curve (b) refers to measurements taken at 1.5 kHz and 1.0 kHz respectively. The point at which the extrapolated lines meet the voltage axis gives the flat band potential with respect to the reference electrode. The reference electrode used was a standard calomel electrode (SCE) in this experiment. Therefore from these curves it can be seen that the flat band potential of TiO_2 film lies around -0.3 V with respect to the SCE.

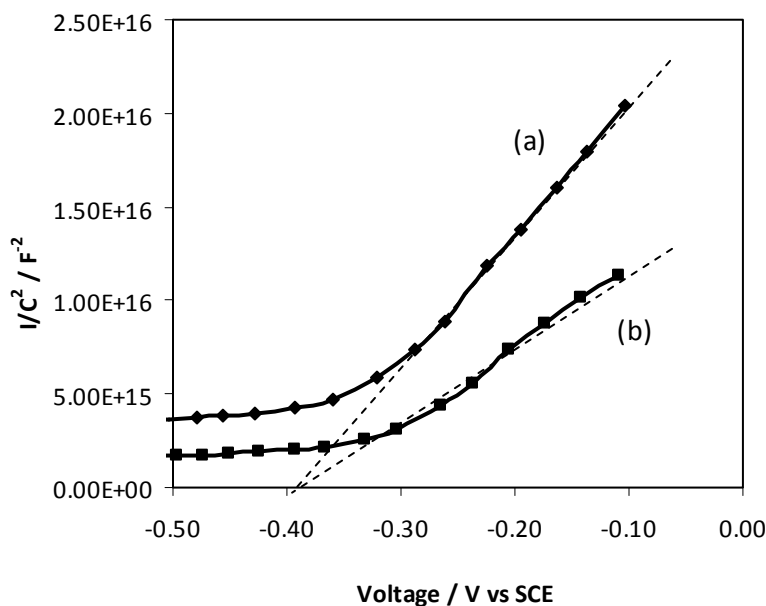


Figure 1: Mott-Schottky plot of TiO_2 film measured at (a) 1.5 kHz and (b) 1.0 kHz.

Figure 2 shows the Mott-Schottky measurements taken for TiO_2 film coated with ruthenium bipyridyl dye. The flat band potential shifted to a higher level (-0.4 V vs SCE) after coating the dye on the TiO_2 film.

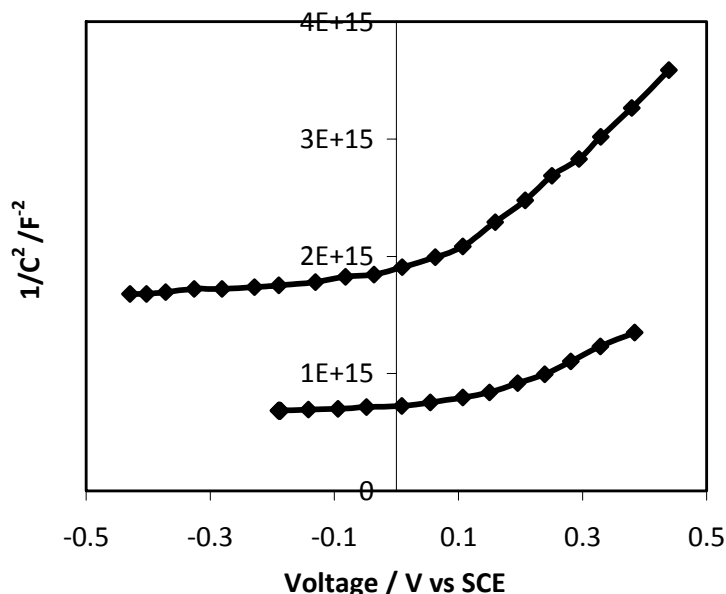


Figure 2: Mott-Schottky plot of TiO₂ film coated with ruthenium bipyridyle dye measured at (a) 1.5 kHz and (b) 1.0 kHz.

Solar cells were fabricated using these dye coated films and they were illuminated with white light for several days. Initially, photovoltage and photocurrent of those cells were ~ 650 mV and 10 mA/cm² respectively. The photovoltage and photocurrent remain the same for the first few days but after that the photovoltage started to decay followed by the photocurrent. The photovoltage decreased to 250 mV and photocurrent decreased to 6 mA/cm² in 5 days of consecutive illumination of the cell. At this stage the cell was dismantled and TiO₂ plate coated with dye was taken for the Mott-Schottky measurement after washing out the electrolyte. Figure 3 shows the Mott-Schottky plots of this film taken at 1.5 kHz and 1.0 kHz. It can be seen that the flat band potential has decreased to 0 V with respect to the SCE.

According to the above results it can be seen that flat band potential of TiO₂ film moves to a higher energy level by coating the dye on the surface. This is attributed due to the passivation of surface states of TiO₂ by chelation of dye molecules on the surface [3]. But according to the figure 3 it is very clear that photovoltage and photocurrent of dye-sensitized solar cells decreases because of the lowering of flat band potential of dye coated TiO₂ electrode. This can happen due to the formation of surface states on the film. The formation of trap states could originate in two ways. One way is reopening of the passivated trap states on prolonged illumination due to loosening or removal of dye chelated with the semiconductor film.

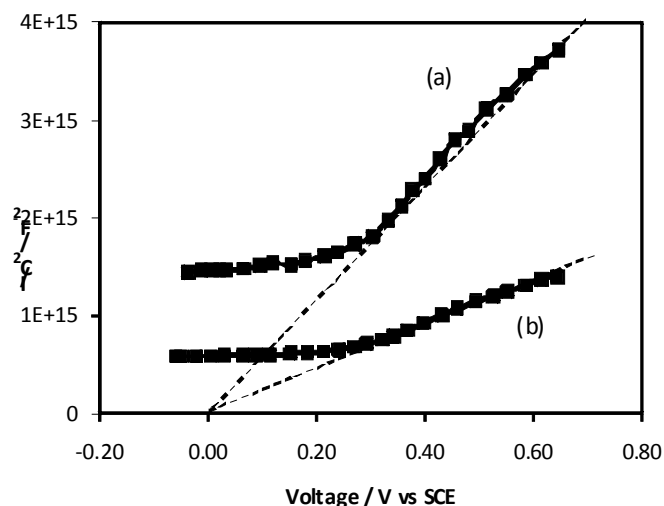


Figure 3: Mott-Schottky plot of TiO_2 film coated with ruthenium bipyridyle dye measured after degradation of the solar cell at (a) 1.5 kHz and (b) 1.0 kHz.

The other possibility is formation of new surface states on the semiconductor due to exposure to high energy rays such as UV radiation. Anyway it can be concluded that trap states are formed on the surface of the semiconductor film with prolong illumination of the cells leading to lowering the efficiency of the dye sensitized solar cells.

4. CONCLUSION

Degradation of dye sensitized solar cells with prolong illumination is investigated and formation of surface states on the semiconductor film is clearly noticed as the reason. Since the photovoltage of a solar cell is determined by the flat band potential, Mott-Schottky measurements were used to measure the flat band potential of TiO_2 films as deposited, TiO_2 films coated with ruthenium bipyridyle dye and dye coated TiO_2 film after using in a dye sensitized photoelectrochemical solar cell. The flat band potential of TiO_2 film increased after coating with the dye which is attributed due to passivation of surface states and prolong illumination of cells lead to formation of surface states again in the semiconductor film that identified as the fact leads to degradation of the solar cells. Further investigations are under way.

5. ACKNOWLEDGEMENT

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