

Determination of Semiconductor Type and Optical Properties of SnO₂:F(FTO) and SnO₂:In(ITO)

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Abstract- Transparent and conducting oxide (TCO) glass electrode is the essential part of solar cell system. Fluorine-doped tin oxide (SnO₂:F) (FTO) and indium-doped tin oxide (SnO₂:In) (ITO) are TCO layers of glass electrode. In this work, type of semiconductor has been determined by hot point probe method and optical properties of FTO and ITO have been studied to improve the performance of solar cell efficiency by UV-VIS spectroscopy. The comparison of optical properties of FTO and ITO shows that ITO has low absorbance, high transmittance and low reflectance. The band-gap energy of FTO is 3.65 eV and that of ITO is 3.75 eV.

Index Terms- band-gap, FTO, ITO, SnO₂, TCO, UV-VIS spectroscopy

1. INTRODUCTION

The sun is a very abundant and democratic source of energy that can be freely and directly supplied to our home. The amount of solar energy reaching the earth surface is 120,000 terawatts (TW). The currently estimated energy consumption for seven billion people worldwide is about 13 TW. So, there would be no worry about the energy supply line even if a small fraction of sun light could be converted to alternative and usable energy forms. Solar energy is the perfect clean energy resource to solve the serious environmental problem such global warming. So, the searching for affordable solar energy technology is one of the hottest research fields all over the world^[1,2].

Tin (stannic) oxide (SnO₂), wide band-gap n-type semiconductor, thin film is one of the TCO layers on glass substrate. To get more conductivity of film, a few impurity atoms are added to SnO₂ solution, called doping. The effect of doping concentration during deposition reaction influences the crystal growth.

In this work, semiconductor type of FTO and ITO has been determined, and band-gap and optical properties of FTO and ITO thin films have been analyzed to increase the solar cell efficiency. They are very important factors on solar cell

efficiency. UV-VIS spectroscopy is the measurement of attenuation of beam of light after passing through the sample. Different molecules absorb radiations of different wavelengths. The perceived colours depend on the chemical involved. Ultraviolet and visible light is energetic enough to promote outer electrons to higher levels. The minimum required energy for electronic transition is known as band-gap energy of material. Fig 1.1 shows the schematic configuration of dye-sensitized solar cell (DSSC) with FTO. Two glass electrodes: working electrode and counter electrode, are TCO layers of DSSC.

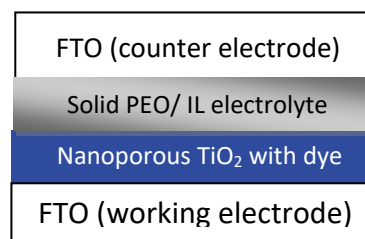


Fig 1.1 TiO₂ based dye-sensitized solar cell

DSSC consists of four main parts such as TiO₂, acts as electron acceptor, dye sensitizer, electrolyte as electron donor and carbon catalyst layer. FTO is the transparent conducting oxide (TCO) layer.

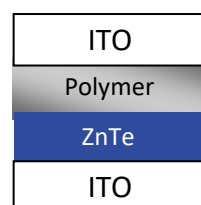


Fig 1.2 Solid state, photo-electrochemical solar cell. As shown in Fig 1.2, solid state photoelectrochemical solar cell contains polymer, ZnTe and ITO, used as TCO layer^[3-9].

II. BACKGROUND THEORY

2.1. UV-VIS Spectroscopy

Ultraviolet visible (UV-VIS) spectroscopy is the absorption spectroscopy in the ultraviolet-visible spectral region. The absorption in the visible range directly affects the perceived colour of the chemical involved. Absorption of UV-VIS radiation causes electronic transitions from the ground state to the excited state in atoms or molecules. The minimum energy required for electronic transition from the valence band to the conduction band is known as the band-gap energy. So, measuring the band-gap energies for the materials used in photovoltaic cell is important.

Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length.

$$A = \epsilon \cdot c \cdot L = \log_{10} \frac{I_0}{I}$$

A = absorbance

ϵ = molar absorptivity or extinction coefficient

c = concentration of the absorbing species

L = path-length

I_0 = intensity of light before passing through the sample

I = intensity of light after passing through the sample

$$\%T = \frac{I}{I_0} \times 100\%$$

T = transmittance

The reflectance (R) of the sample can be evaluated by the relation.

$$R + T + A = 1$$

R = reflectance

For direct band-gap semiconductors, the relation between the absorption coefficient and the photon energy is

$$\alpha = \frac{(h\nu - E_g)^{1/2}}{h\nu} \quad (\text{or}) \quad (\alpha h\nu)^2 = h\nu - E_g \quad E_g =$$

energy band-gap

α = absorption coefficient

$h\nu$ = photon energy

For the semiconductor thin film, the absorption coefficient can be calculated by the equation.

$$\alpha = \frac{1}{t} \ln \frac{1}{T} \quad (\text{or}) \quad \alpha = \frac{2.303A}{t}$$

α = absorption coefficient

t = film thickness

T = transmittance

A = absorbance

The point on the absorption spectrum of a solution which represents the minimum energy required for electronic transition from the valence band to the conduction band is the absorption edge of the solution. The wavelength at the absorption edge can be used to calculate the energy band-gap of the solution. Fig 2.1 shows visible spectrum of electromagnetic radiation.

The energy of the electromagnetic spectrum can be calculated by the formula, $E = \frac{hc}{\lambda}$, where E = energy of the wave, h = plank's constant, c = velocity of light in vacuum and λ = wavelength of the wave^[12].

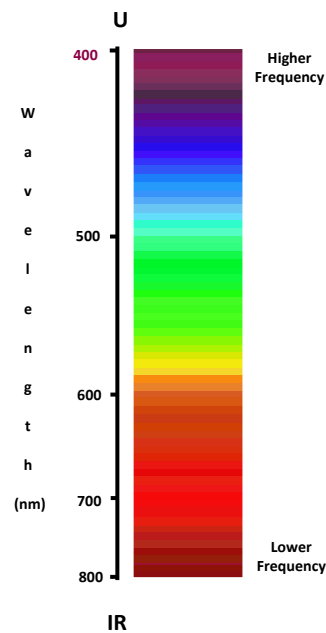


Fig 2.1 Visible spectrum

When white light passes through or is reflected by a coloured substance, some photons with certain wavelengths are absorbed. The remaining light will appear as the perceived colour as shown in Fig 2.2. Table 2.1 is the relationship between absorbed colour and perceived colour. UV-VIS spectrophotometer is shown in Fig 2.3.

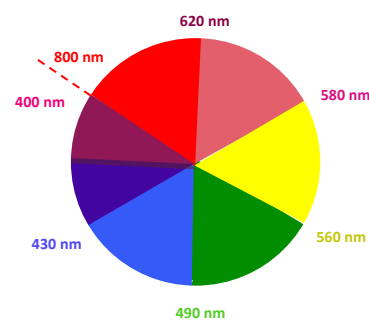


Fig 2.2 Colour wheel

Table 2.1 Relationship between absorbed and perceived colours

Absorbed wavelength	Absorbed colour	Perceived colour
380-420 nm	Violet	Yellow-green
420-440 nm	Violet-blue	Yellow
440-470 nm	Blue	Orange
470-500 nm	Blue-green	Red
500-520 nm	Green	Purple
520-550 nm	Yellow-green	Violet
550-580 nm	Yellow	Violet-blue
580-620 nm	Orange	Blue
620-680 nm	Red	Blue-green
680-780 nm	Purple	Green

and the polarity of the thermal voltage shows positive value. So, FTO and ITO in this work are n-type semiconductors.



Fig 2.3 Photograph of UV-Vis spectrophotometer



Fig 3.1 Positive polarity of FTO



Fig 3.1 Positive polarity of ITO

III. EXPERIMENTAL DETAILS

3.1. Determination of Semiconductor Type for FTO and ITO

Tin (stannic) oxide (SnO_2) is direct band-gap oxide semiconductor. According to the literature, FTO and ITO are wide band-gap n-type semiconductors with band-gap energy of 3.8 eV and 3.6 eV respectively. In this work, the hot point probe method has been used to determine the conductivity type of the semiconductor. Firstly, the hot soldering gun tip is connected to the positive probe of the multi-meter. And then the measurements can be made as shown in Fig 3.1 and Fig 3.2 for FTO and ITO respectively. The sign of the voltage polarity defines the type of the semiconductor whether n-type or p-type. According to Table 3.1, the polarities of the thermal voltages of FTO and ITO are positive. It means that the majority carriers (electrons in n-type) moves away from the point in which the high temperature probe of voltmeter exists

3.2. UV-VIS Spectroscopic Analysis

By using the formula, $\alpha = \frac{1}{t} \ln \frac{1}{T}$ (or) $\alpha = \frac{2.303A}{t}$,

absorption coefficient α for various wavelengths can be calculated. According to the ellipsometry measurement, film thickness of FTO and ITO are 848.11 nm and 231.75 nm respectively. This is because that different deposition method can cause different film thickness.

The equation $(ah\nu)^2 = h\nu - E_g$ is a straight-line equation for $(ah\nu)^2$ and $h\nu$. So, an extra-plotting line must be drawn on $(ah\nu)^2$ vs. $h\nu$ graph to get the energy band-gap (E_g) of the film. The point, cuts on X-axis, is the band-gap energy.

RESULTS AND DISCUSSION

4.1 Investigation of n-type Semiconductors

According to Table 4.1, the polarities of the thermal voltages of FTO and ITO are positive. It means that the majority carriers (electron in n-type) move away from the point of high temperature probe of voltmeter and the polarity of thermal voltage shows the positive value. So FTO and ITO in this work are n-type semiconductors.

Table 3.1 Hot point probe method whether n-type or p-type semiconductor

Sample	Thermal voltage (V _t)	Semiconductor type
FTO	+4 mV	n-type semiconductor
ITO	+2 mV	n-type semiconductor

4.2 Optical Properties of FTO and ITO Thin Films

Indium-doped tin oxide thin film (ITO) and fluorine-doped tin oxide thin film (FTO) are TCO layers for solar cell system. Low electrical resistivity and high visible transmittance are the key elements for TCO glass electrode. As shown in Fig 4.1, Fig 4.2 and Fig 4.3, ITO has low optical absorbance, high transmittance and low reflectance. So, ITO is the best TCO layer for a solar cell. But the conductivity of ITO decreases markedly at the deposition temperature of 450°C and the efficiency of DSSC also reduces.

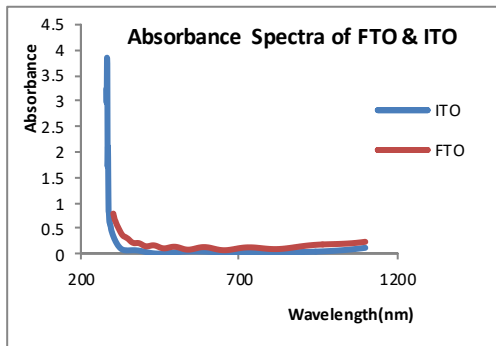


Fig 4.1 Absorbance spectra of FTO and ITO

From absorbance spectra, the wavelength at absorption edge for FTO is 351 nm. So the band-gap energy of FTO is 3.52 eV, and the wavelength for ITO is 310 nm and the band-gap is 3.98 eV.

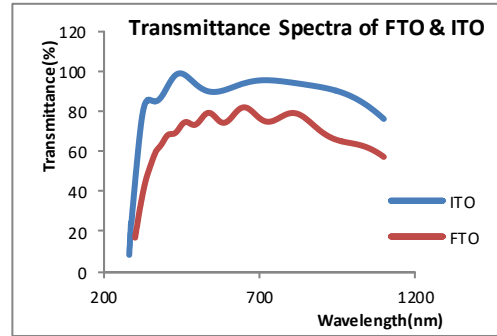


Fig 4.2 Transmittance spectra of FTO and ITO

As shown in transmittance spectra, the transmittance of ITO is 99% at the wavelength of 444 nm while that of FTO is 72% at that wavelength. And then 0% reflectance of ITO exists at 444 nm. But 14% FTO reflectance shows at that wavelength. So ITO has high visible transmittance and low reflectance^[11].

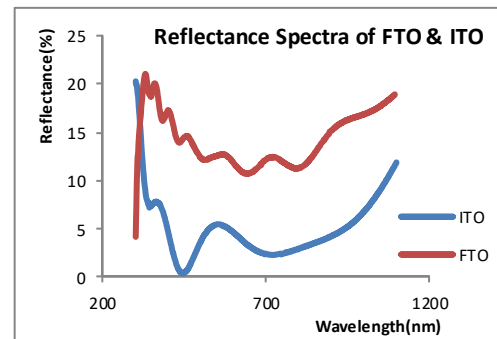


Fig 4.3 Reflectance spectra of FTO and ITO

As shown in Fig 4.4, the band-gap energy of FTO is about 3.65 eV and that of ITO is 3.75 eV. The values of the strong cut-off point are different from those of the extra-plotting. Therefore, the extra-plotting method is more convenient than the strong cut-off point for finding the band-gap energy. Because the absorbance depends on the film thickness. In this work, there is a difference between FTO thickness and ITO thickness. So the strong cut-off points on absorbance spectra can vary, and the optimum band-gap energy cannot be achieved. If the film thickness is known, the absorption coefficient can be calculated by the formula, $\alpha = \frac{2.303A}{t}$. And then the $(\alpha h\nu)^2$ vs. $h\nu$ graph does not depend on the film thickness. So the extra-plotting line on $(\alpha h\nu)^2$ vs. $h\nu$ should be used to get band-gap energy for thin films^[10].

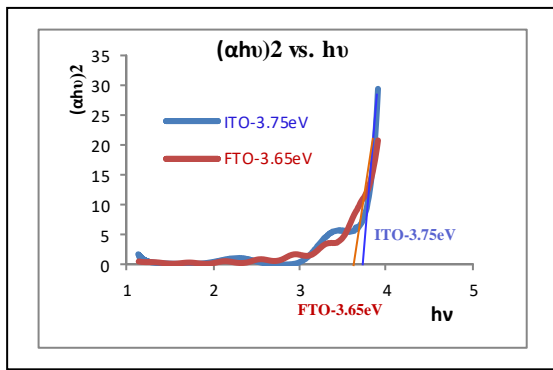


Fig 4.4 $(\alpha hv)^2$ vs. $h\nu$ graphs for ITO and FTO

CONCLUSION

Combustion of fossil fuel leads to serious environmental problem such global warming by large amount of carbon dioxide emission. In nuclear power stations, no viable method has been found to dispose of the dangerous nuclear fuel wastes yet. Therefore, solar energy becomes the perfect clean energy resource. If the small fraction of sun light is converted into usable energy form, the environmental problem has been solved automatically. So the clean and sustainable energy resource as substitute for the traditional fossil fuel and nuclear power plants, has become an urgent work for human beings.

In this work, band-gap energy and optical properties of FTO and ITO have been studied by UV-VIS spectroscopy. As shown in Fig 1.1 and Fig 1.2, TCO glass electrode is the essential part of solar cell. High visible transmittance is one of the key elements for TCO layer. According to UV-VIS data, ITO with low absorbance, high transmittance and low reflectance is the best TCO layer for solar cells.

The band-gap energy of FTO is 3.8 eV and that of ITO is 3.6 eV in literature. In the proposed work, FTO band-gap is 3.65 eV and ITO band-gap is 3.75 eV. There is a little difference between literature values and proposed work values due to the drawing of an extra-plotting line and the concentration of dopants.

The absorbance is directly proportional to the film thickness ($A = \epsilon c L$). So, FTO absorbance is about three times larger than ITO. Because FTO film thickness is 848.11 nm and ITO is 231.75 nm. Therefore, the same film deposition method should be used and the fabrication should be carefully prepared to get the same film thickness.

As shown in Fig 1.1 and Fig 1.2, FTO should be used in TiO_2 based dye-sensitized solar cell (DSSC). Because TiO_2 film sintering temperature on TCO layer is recommended at 450°C. If ITO is used in DSSC, the conductivity of ITO decreases markedly at 450°C and the efficiency of DSSC also reduces. To avoid the increase of ITO resistance, TiO_2 coated ITO glass electrode should be at 180°C. But the photo-current

of DSSC reaches in the range of μA . So ITO matches only with photo-electrochemical solar cell.

Solar cell technology is a limited use due to the relatively high manufacturing cost of silicon based technology and the low power efficiency of organic polymer based technology. So the searching for affordable clean solar energy technology is one of the hottest research fields all over the world. Among them, DSSC gives the high energy conversion efficiency. Therefore, the properties of FTO for DSSC should be analyzed from various points of view.

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