자기중성방전 스퍼터에 의한 DSCs용 ITiO 박막제작

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ITiO films prepared by magnetic null discharge sputtering for DSCs application

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Abstract - Titanium-doped indium oxide (ITiO) films were prepared on soda-lime glass substrate using a magnetic null discharge (MND) sputter source. The ITiO thin films containing 10 wt.% Ti showed the minimum resistivity of $\rho=5.5\times10^{-3}\Omega$cm. The optical transmittance increases from 70% at 450 nm to 80% at 700 nm in visible spectrum. The surface roughness of the sample showed a change from 10 nm to 50 nm. The ITiO film used for TCO layer of DSCs exhibited an energy conversion efficiency of about 3.8 % at light intensity of 100 mW/cm^2.

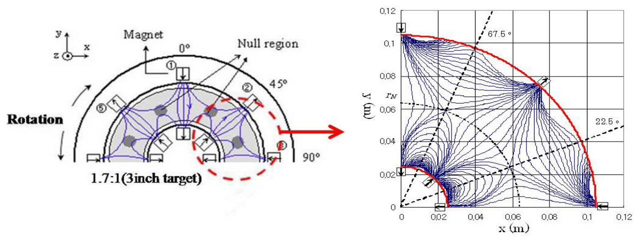
1. INTRODUCTION

The recent advances in photovoltaic (PV) technology [1] have triggered considerable interests in the fields of solar power as an alternative and renewable source of electricity. Also, solar cells now allow applications for various electronic equipment, including satellites, calculators, remote radiotelephones, and advertising signs. The dye-sensitized solar cells (DSCs) devised by Prof. M.Grätzel in 1991[1, 2] have been characterized by its electrochemical cell structure through the use of iodine solution, and not silicon semiconductors. Due to its low cost and low burden on the environment, it has gathered attention and hope worldwide as the next generation in solar cells [3, 4]. Typically, DSCs consist of a transparent conducting oxide (TCO) layer and dye-sensitized TiO_2 electrode in contact with electrolyte and is completed by an inert counter electrode. The TCO materials most commonly used for DSCs are F-doped tin-oxide (FTO) and indium-tin-oxide (ITO). However, the CVD process is costly and somewhat complicated for the application of mass production. Also, the FTO/ITO films have limitations in their infrared ray (IR) transmission and thermal resistance as a transparent conductor. Thus, more studies are still required to enhance these defects. The potential advantage of a titanium-doped indium oxide (ITiO) relative to the FTO/ITO of comparable sheet resistance resides in its high mobility and near-IR transmittance [4]. The properties of ITiO layer show that the long-wavelength fall off in transmittance does not occur until 1500nm compared to about 1000nm for an 8Ω/sq. In this work, the properties of ITiO films prepared by a magnetic null discharge (MND) sputter source [5-8] were studied. The MND sputter source realizes the uniform processing as well as the successful reduction of plasma localization from the wall effect by controlling the position and the diameter of the MN region. And various electrical, optical properties and surface structure the films were measured by the 4-point probe, and atomic force microscopy (AFM), respectively. Finally, the photovoltaic performance of the prepared DSCs made by the ITiO film was evaluated.

2. EXPERIMENTAL

2.1 preparation of ITiO films

The experimental magnetic null discharge (MND) sputter source has been described in our previous reports [5-7], and can be briefly described as follows. Fig. 1 shows the target of the MND sputter source with the magnetic field formed by the permanent magnets and the calculated magnetic field line distribution on the target surface, respectively. The target was in doughnut shape 70 mm in width. The distance between the target and a substrate was 150 mm. Cooling water was circulated through the target to prevent overheating.



<Fig. 1> Schematic arrangement of the experimental apparatus.

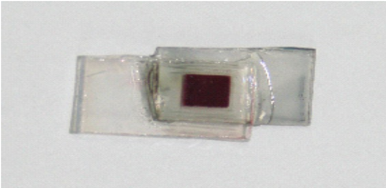
As shown in Fig. 1 with the arrangement of permanent magnet (of 120 mT), the resulting magnetic field is in a sector of 90° (from 0° to 90°). When the high frequency electric field is applied to the null field region via the target by a 13.56 MHz RF generator, electrons move in the electric and magnetic fields. From the calculation results involving the energy of electrons, the mean energy around the MNregion was found to be more than twice as much compared with other regions by the effective electron heating [5-8]. Therefore, in the application of MND sputter source, controlling the position and the diameter of the MN region can be easily achieved, which realizes the uniform processing as well as the successful reduction of plasma localization from the wall effect. The process conditions for the ITiO film preparation can be briefly summarized as shown in Table 1. At first, the chamber was exhausted vacuum to 2×10^{-6} Torr or less. The working gas of Ar(95%) and O_2(5%) was introduced to the chamber, and the total pressure was maintained at 5 mTorr during deposition. The RF power (P_{RF}) of 500 W was supplied to a sintered ITiO target (90 wt.% In_2O_3 and 10 wt.% TiO_2). The distance between the target and a soda-lime glass substrate with sectional area of 2540 mm was 150 mm. During deposition, pure Ar/O_2(5%) gas was introduced into the chamber, by adjusting Ar/O_2 inlet to maintain an Ar/O_2(5%) pressure of 5 mTorr for ITiO film preparation. Post-annealing in vacuum was performed at 300°C for three consecutives hours. This step is necessary to promote the formation of best ITiO film. The deposited ITiO films were taken out of the chamber to confirm the properties of the films.

<Table. 1> Summary of the ITiO film depositions.

RF power	500 W
Working pressure	5 mTorr
Operating gas(Partial pressure)	Ar-O_2 (5%)
Target-substrate distance (d_s)	150 mm
Deposition time	60 min.
Annealing temperature	300 °C

2.2 Preparation of DSCs and Evaluation

The fabrication process of DSCs sample has been described in our previous report [9], and can be briefly described as follows. The prepared ITiO/TiO_2 films were dye-sensitized by soaking the films for 22h at 25°C in a N719 dye solution. Fig. 2 shows an image of the prepared DSCs sample. Pt counter electrodes were prepared on ITO coated glass substrates. The solar cells were assembled by placing the dye-sensitized ITiO/TiO_2 electrode and the Pt counter

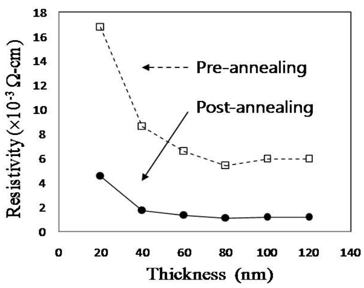


<Fig. 2> Image of the prepared DSCs sample.(size:5cm×5cm)

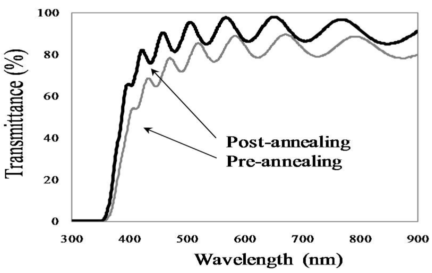
electrode together in a sandwich structure using 60 mm thick Surlyns film (DuPont) as spacer and edge sealant. The short-circuit photocurrent (J_{sc}) and the open-circuit voltage (V_{oc}) were measured using a solar simulator (Yamashita Denso YSH-80).

3. RESULT AND DISCUSSION

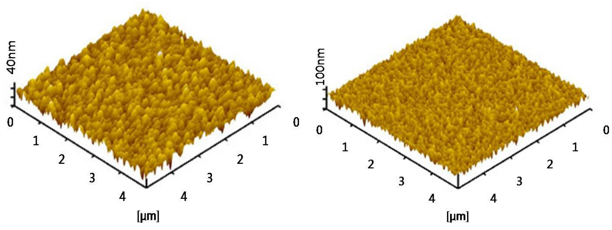
Fig. 3 shows the resistivity of the ITiO films prepared by MND sputter source with/without annealing as a parameter of the film thickness. The resistivity decreased with increasing film thickness for both cases. In the case of annealing at 300°C, the resistivity became constant at $1.4\times10^{-3}\Omega$cm for thickness of 100 nm, while resistivity of the film without annealing became constant at $6.1\times10^{-3}\Omega$cm at same thickness. Fig. 4 shows the optical transmittance spectrum of ITiO thin films (100nm) deposited on glass with/without annealing. Information concerning optical transmittance is important in evaluating the optical performance of TCO films. A high transparency for the ITiO thin film is required in applications with TCO electrode for optoelectronic devices. As shown in this figure, the transparency increases from 70% at 450 nm to 80% at 700 nm which is sufficiently high for use as a TCO electrode. The increase in optical transmittance with temperature can be attributed to the increase of structural homogeneity and crystallinity [10].



<Fig. 3> Dependence of the resistivity of the ITiO filmson the thickness



<Fig. 4> Optical transmittance spectra for theITiO films with/without annealing.



(a) without annealing (b) with annealing

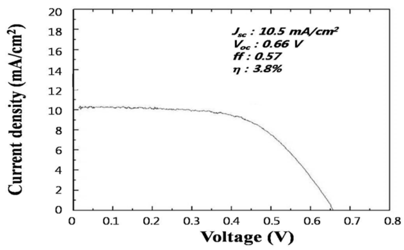
<Fig. 5> AFM images of theITiO films with/without annealing.

The AFM measurement confirmed the annealing effect on the ITiO films shown in Fig. 5. After annealing, the surface roughness of the sample showed a change from 10 nm to 50 nm. This can be explained by the fact that the heat treatment promotes the crystal nucleation of the films. One can conclude that more crystalline ITiO films can grow on the glass substrate by an appropriate post-heat treatment.

Finally, the prepared DSC was irradiated with a Light Drive 1000 lamp through an infrared-blocking filter. The current-voltage characteristics were recorded by varying an external potential compensating the photo-voltage. The integral photocurrent (short-circuit current) was obtained without the external potential. The photoelectric efficiency was calculated with respect to the solar spectra through a calibration of the Light Drive 1000 lamp with direct sunlight. The overall efficiency η of a photovoltaic cell can be calculated from the expression:

$$\eta(\%) = \frac{J_{sc} V_{oc} FF}{P_s}$$

where J_{sc} is the integral photocurrent density (current obtained at the short-circuit condition, divided by the area of the cell), V_{oc} is the open-circuit voltage, FF is the fill factor (related to the series resistance for a practical solar cell), and P_s is the intensity of the incident light. Fig. 6 illustrates the current-voltage-power characteristics of the prepared DSC. It exhibited an energy conversion efficiency of 3.8% at 100mW/cm^2 light intensity. Considering a maximum conversion efficiency of 7.2% for a conventionally prepared nanocrystalline solar cell, it is probable that our technique is feasible and effective.



<Fig. 6> *I-V* characteristics of a DSC based on ITiO/TiO$_2$ films.

4. CONCLUSION

In this work, titanium-doped indium oxide (ITiO) films were prepared on soda-lime glass substrate using a magnetic null discharge (MND) sputter source. The electrical and optical properties of the transparent conductive ITiO film and the photovoltaic performance of the prepared DSCs were examined. The ITiO thin films containing 10 wt.% Ti showed the minimum resistivity of =$5.5\times10^{-3}\Omega$cm. The optical transmittance increases from 70% at 450 nm to 80% at 700 nm in visible spectrum. In addition, AFM measurements were performed to investigate the surface structural properties of the films. Finally, the ITiO film used for TCO layer of dye-sensitized solar cells (DSCs) exhibited an energy conversion efficiency of about 3.8 % at light intensity of 100 mW/cm^2. It can be therefore seen that the ITiO films obtained by MND sputter system exhibited good transparent conductive properties, well suited for DSCs application.

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