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The Fabrication of ZnO Thin Film by Sputter Deposition for the Core-shell Structure

コアーシェル構造のためのZn0薄膜のスパッタ蒸着

Min-Kyu Son[1], Hyunwoong Seo[1,2], Jin-Kyoung Kim[1], and Hee-Je Kim[1]
孫 珉圭, 徐 鉉雄, 金 珍暻, 金 熙濟

[1]*Department of Electrical Engineering, Pusan National University, Geumjeong, Busan, 609-735, Republic of Korea*
[2]*Graduate School of Information Science and Electrical Engineering, Kyushu University, Fukuoka, 819-0395, Japan*
[1]釜山大学校 電子電気工学科 〒609-735 釜山市 金井區 長箭二洞 山30
[2]九州大学 システム情報科学府 〒819-0395 福岡市 西区 元岡 744

Dye-sensitized solar cells have been considered as a potential alternative to current photovoltaic devices. However, its efficiency is limited by the electron recombination with the electrolyte. Therefore, a barrier layer called as the core-shell structure has attracted. Especially, ZnO is a significant candidate to the barrier layer with similar band gap energy of TiO_2. In this work, ZnO film was fabricated by sputter deposition not conventional wet process. The structural characteristics of deposited film, photovoltaic performance and electrochemical impedance of cells with a barrier layer were analyzed for the verification of its effect.

1. Introduction

Since dye-sensitized solar cell (DSC) was developed by Grätzel et al. in 1991, its efficiency reached over 11% through continuous researches [1]. The growth of fundamental components such as dye, TiO_2, and electrolyte played the most important role in the enhancement of performance but additional layers such as the compact, barrier, and light scattering layers also played a significant role [2,3]. Especially, the barrier layer made the photo current much increased by the prevention of recombination. ZnO has been widely used as the barrier layer because of its unique properties, i.e. high electrical stability, absence of toxicity, and similar energy level of TiO_2. ZnO barrier layer was generally fabricated by the wet process using aqueous zinc solution. However, the wet process has some disadvantages such as high cost, the consideration of cleanup, and a bad effect to TiO_2 structure. Therefore, we tried to fabricate ZnO barrier layer by sputter deposition as the dry process. General sputter deposition of ZnO film using ZnO target or Zn target with O_2 gas is already famous and has no novelty and specialty. However, there is no report about the sputter deposition using Zn target with only Ar gas because the oxidization of sputtered Zn film is too difficult. In this work, the insufficient oxidization of Zn was solved by the acid treatment. Zn was activated by the treatment and it was sufficiently oxidized. In order to verify the properties of deposited film as the barrier layer, the effects in terms of the structural characteristics, photovoltaic performance and electrochemical impedance were examined.

2. Experimental

Fluorine-doped tin oxide (FTO) substrates were used as the TCO to make the photo and counter electrodes. A uniform and nano-porous TiO_2 with a thickness of about 50μm was pasted on the FTO substrate by the doctor blade method. After sintering at 450°C for 30 min, Zn was sputtered on the FTO/TiO_2 electrode by DC sputter deposition. For the acid treatment, the deposited electrodes were treated by the hydrochloric acid solution. After that, the electrodes were sintered at 450°C for 30 min. The deposited films were characterized by X-ray diffraction (XRD). The FTO/TiO_2/ZnO electrodes were soaked in a 0.2mM N719 dye solution. The platinized counter electrode was sputtered by radio frquency sputtering. After that, the photo and counter electrodes were sealed and the sealed DSCs were completed by injecting a redox electrolyte. Another DSC was fabricated as a reference under identical conditions except for ZnO barrier layer.

The photovoltaic performance was measured under 1 sun (100mW/cm^2). The irradiated cell area was 0.25cm^2. I-V characteristic curve were used to calculate the short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF) and an overall efficiency (η). The internal impedance was measured by electrochemical impedance spectroscopy (EIS). The EIS spectra were measured over the frequency range from 10mHz to 1MHz and characterized using the Nyquist diagram.

3. Results and Discussion

Figure 1 shows XRD patterns of FTO/TiO_2/Zn electrodes before and after sintering. Most of phases came from SnO_2 and TiO_2 under Zn film. A diffraction peak at 70.3° was detected as the reflection of Zn. After sintering, more diffraction peaks were showed and the peak of ZnO was also detected at 31.7° so that the oxidization of Zn was confirmed. However, the peaks of Zn were still remained. It means that the insufficient oxidization of Zn film.

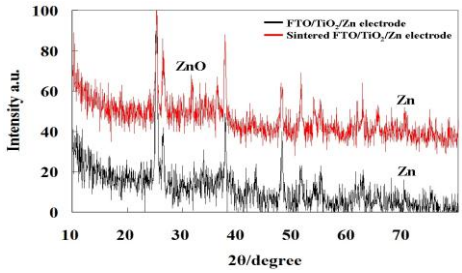

Fig.1. XRD of FTO/TiO_2/Zn electrode before and after sintering

Figure 2 shows I-V characteristic curves and EIS diagrams of DSCs according to Zn deposition time. All DSCs with sputtered barrier layers had worse performance than standard DSC because of too thick and insufficiently oxidized barrier layer. The performance was gradually increased with the decrease of deposition time although all results were too bad. It means that thick layer disturbed the electron injection from dye to TiO_2. And insufficiently oxidized film was not able to act as good barrier layer. Therefore, the sufficient oxidization and the deduction of proper thickness were essential for the good barrier layer.

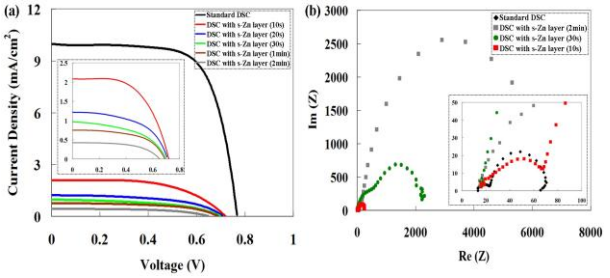

Fig.2. (a) I-V characteristic curves and (b) EIS diagrams of DSCs according to Zn deposition time

For the oxidization of Zn films, they were treated with acid reagent. In a previous report, hydrochloric acid was most effective as compared with other acid reagents such as sulfuric acid and acetic acid because it was strong and non-oxidative acid, and suitable active points were able to be formed on SnO_2 and TiO_2 [4]. ZnO diffraction peaks at 31.7°, 33.8°, and 36.3° were detected after the acid treatment. In other words, XRD patterns of sintered Zn electrodes with the acid treatment confirmed the enhancement on the oxidization of Zn.

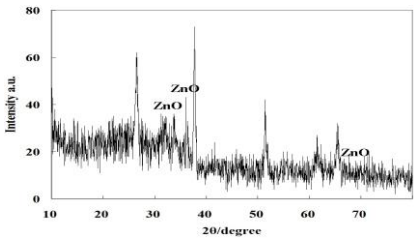

Fig.3. XRD of acid-treated FTO/TiO_2/Zn electrode

Figure 4 shows I-V characteristic curves and EIS diagrams of DSCs with ZnO barrier layer according to the acid treatment. The photovoltaic performance of DSC without the acid treatment deteriorated because of the insufficient oxidization of Zn film by sintering alone. However, that of DSC with the acid-treated barrier layer was overall improved by the barrier effect of sufficiently oxidized ZnO film. EIS diagram also confirmed the effect of the acid treatment. Total series resistance was much decreased from 250 to 53Ω so that the photo current was much increased.

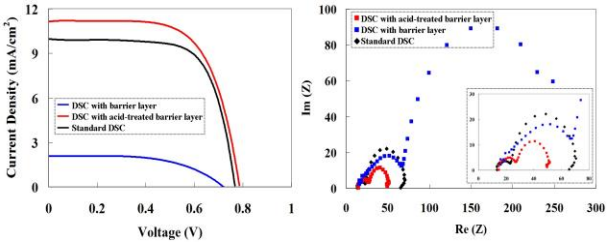

Fig.4. (a) I-V characteristic curves and (b) EIS diagrams of DSCs with and without the acid treatment

4. Conclusion

In a DSC, the barrier layer positioned between TiO_2 and dye prevents the recombination so that the photo current is increased. Especially, ZnO has been widely used as the barrier layer due to its unique properties. In this work, ZnO barrier layer was deposited by sputtering not conventional wet process. Zn film deposited using Zn target with only Ar gas is difficult to be oxidized. Therefore, the insufficient oxidization of Zn was solved by the acid treatment. XRD patterns of ZnO film with the acid treatment confirmed the oxidization of Zn and the improved photovoltaic performance confirmed the effect of the barrier layer. Consequently, the performance was much increased from 2.01% to 5.83% after the acid treatment.

References

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