INVESTIGATION OF SOLUTION PH EFFECT ON SURFACE MODIFICATION OF TiO_2 THIN FILMS

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Abstract

Thin film solar technology is used in various devices that convert the sun light into electrical energy. These applications have been crucial for human life since they supply us clean and alternative energy sources. For this application many components can be used such as Cu_2S, CdTe, CIGS, CNTS, and TiO_2, etc. TiO_2 is one of them and preferable for this technology because of its good electrical and physical properties.

TiO_2 based solutions that are completely transparent are coated on Indium Tin Oxide (ITO) coated glass with different pH values, by using sol gel dip coating method. This coated glass are annealed with the same temperature and the same holding time. Previous research shows that pH factor has significant effect on the surface morphology of films. Surface area and surface roughness are pH dependent parameters that are very important for light conversion efficiency.

In this study, the effect of pH on thin film surface morphology is investigated. Five different pH value sols are coated on ITO glass. These glasses annealed in the furnace with the same temperatures and the same holding times. The results are determined with several methods. Chemical properties are determined by X-ray photoelectron scanning (XPS), X ray diffraction scanning (XRD) surface properties and roughness values are investigated by atomic force microscopy (AFM), and scanning electron microscopy (SEM)-focused ion beam technique (FIB). The XPS and XRD results show that, because of the low working temperatures there is not any change in the chemical structure of TiO_2. The material that we study is glass. Above 600°C chemical structure of the glass can be deteriorated. We carried out our experiments below this temperature. According to the results of AFM, pH is an important factor on the film morphology. The results showed that if the pH increases, the surface roughness parameter (Ra) also increases.

Keywords: TiO_2, thin film, pH, surface area, surface roughness

1. INTRODUCTION

Increasing human population causes increasing energy demand. Energy sources in our world are becoming more and more insufficient. For this reason, alternative resources attract researchers and various devices have been developed to take an advantage of our natural power. Photovoltaic and solar cell technology provided us obtaining alternative energy from the sun. Solar cell technology is used to convert solar energy into electrical energy which can be used to power electrical devices. Solar cells are already used to supplement energy and decreased dependence on conventional energy sources. The importance of this technology is undeniable [1].

There are different solar cells such as single-crystal and polycrystalline silicon solar cells; thin film solar cell; III-V Semiconductors and photo electrochemical solar cells, etc. [2]. Thin film solar cell is a second generation solar cell, made by depositing one or more thin layers, or thin film of photovoltaic material on a substrate, such as glass, plastic or metal [3]. Thin film technology offers us high production capacity with using less material and energy input in the fabrication process and integrated module structures by the deposition process [4]. The thin film semiconductor materials have also much higher absorption coefficients than silicon, as the direct band gap semiconductors, and therefore typically less than 1 mm thickness semiconductor layer is required, which is 100-1000 times less than for Si [5].

Titanium dioxide is usually used in two forms; powder and thin film. The use of titania powders caused someproblems in the practical use. Especially high concentration powder particles tend to aggregate. The immobilization of the TiO_2 in the form of a thin film affords an advantage over the drawbacks encountered with the powder suspension and endows the surface with photo-induced hydrophilicity [6].In our study, we coat TiO_2 thin film for a hybrid solar cell by using sol-gel dip-coating. We prepared Ti containing solutions. Indium thin oxide glass is coated with that solution. This coated glass equipped as an n-type layer for the purpose of a hybrid solar cell. As shown in the **Figure 1**, our typical hybrid solar cells consist of different layers. TiO_2 thin film is coated on transparent conductive oxide coated glass with sol-gel dip coating method.

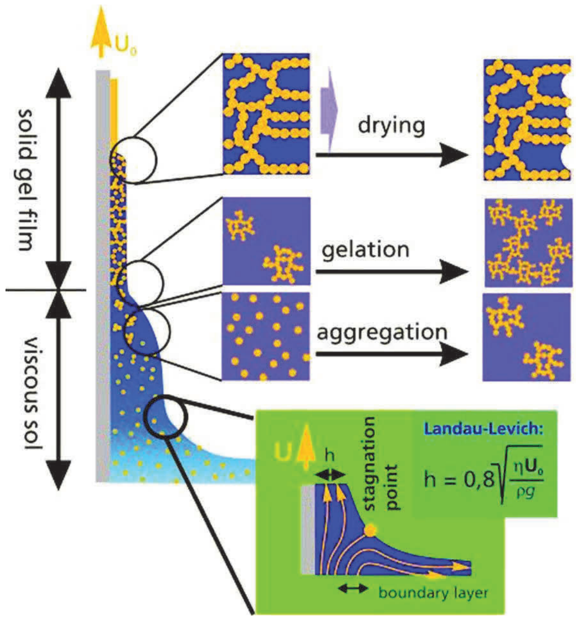

Figure 1 Schematic representation of sol-gel dip coating method

2. EXPERIMENTAL STUDIES

2.1. Materials and Methods

Indium tin oxide (ITO) is a ternary composition of indium, tin and oxygen in varying proportions. Depending on the oxygen content, it can either be described as a ceramic or alloy. Indium tin oxide is typically encountered as an oxygen saturated composition with a formulation of 74% In, 18% O_2, and 8% Sn by weight. Oxygen saturated compositions are so typical, that unsaturated compositions are termed oxygen deficient ITO. It is transparent and colorless in thin layers, while in bulk form it is yellowish to grey. In the infrared region of the spectrum it acts as a metal-like mirror [7]. ITO coated glasses are provided from Sigma Aldrich and Chemical precursors of Ti are supplied from Alfa-Aesar.

2.1.1. Solution

Solutions are prepared with Ti containing chemicals, acetyl acetone (chelating agent) and methanol (solvent). According to solubility properties of the mixing components, amount of acetyl acetone can be increased with little amount. Solution is mixed with the magnetic stirrer between 2 to 24 hours, according to solubility properties of the components. At the end of the stirring process, solution must be completely transparent. Because of the good solubility properties, titanium methoxide is chosen. Five different solutions were prepared with different pH values. The pH of the solution is achieved by adding acetic acid. The pH values of solution vary between 3 and 5. For dense and non-porous film coating, pH value of the solution must be kept in the acidic range [9]. After the acid addition process, the solution is stirred for 24 hours.

2.1.2. Drying/Firing and etching the coating

After the solution preparation, the coating step is performed. The coating was carried out by sol gel dip coating method. ITO coated glasses with 25*25 mm size are cleaned. The glass was dipped into the solution, then pulled into the vertical furnace which is heated at 450 ºC for 15 second.

Coated films are used in solar cell so that efficiency measurement is carried out for achieving a precise measurement. The ITO substrates are etched in the corner with HCl+Zn mixture. By etching the ITO layer on the corners of the substrate, indium tin oxide layer on the glass is removed.

2.1.3. Annealing process

After forming a solid and homogenous oxide thin film on the surface, samples are put in horizontal tube furnace for the final annealing to crystallize the thin film. Since the substrate is glass and annealing temperature is chosen not higher than the 500 °C which is the temperature that glass starts to soften or cracks form. The temperature profile of the annealing procedure is given in **Figure 2**.

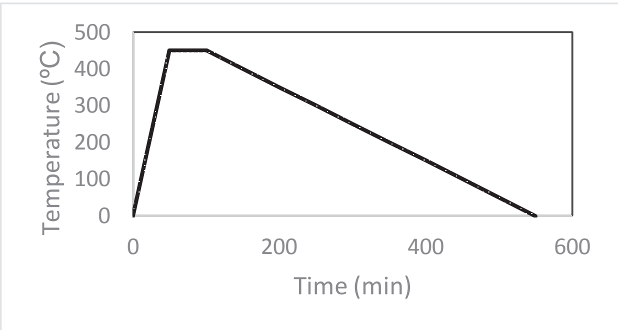

Figure 2 Temperature profile applied for annealing for crystallization

All the samples which are coated with different solutions having different pH values are heat treated at 450 ºC for 60 mins.

2.1.4. Characterization methods

Surface properties and surface roughness of TiO_2 thin films were characterized by AFM (PSIA XE-100). Chemical properties and crystalline structures are determined by X-ray photoelectron scanning (XPS, Thermo K-Alpha), and X-ray diffraction (XRD, PANalyticalXpert Pro MPD) respectively.

3. RESULT AND DISCUSSION

3.1. Characterization of XPS

XPS scanning is performed to evaluate the surface of the samples for chemical properties and analysis. Some pictures belonging to the carbon contaminant come out. These peaks can be distinguished from sharpen C peaks in the **Figure 4**. For removing the C layer on the surface, argon etching is applied. According to the scanning data, the Ti-TiO_2 bonds were observed significantly. As it is shown in the **Figure 3**, TiO_2 were formed noticeably but the crystallization process and transformation of anatase- rutil has not been occurred. The crystallization from amorphous to anatase and from anatase to rutile usually occurs in the temperature ranges of 450~550 °C and 600~700 °C, respectively [10]. The reason for that is, the phase transformation does not occur at the operating temperature which is lower than the phase formation temperature. Due to the heating limitation of glass substrate crystallization temperature must be kept under 550 °C. As can be seen in the figure, the XPS scanning of the TiO_2 thin film, there are only the peaks of titanium and oxygen. Therefore, the structure of the film contains only titanium and oxygen atoms. To determine the stoichiometry of the film, the data obtained from the XPS results are examined and the areas are divided into appropriate Atomic Sensitivity Factor (ASF) values, then the ratio of the O_2 to Ti is obtained.

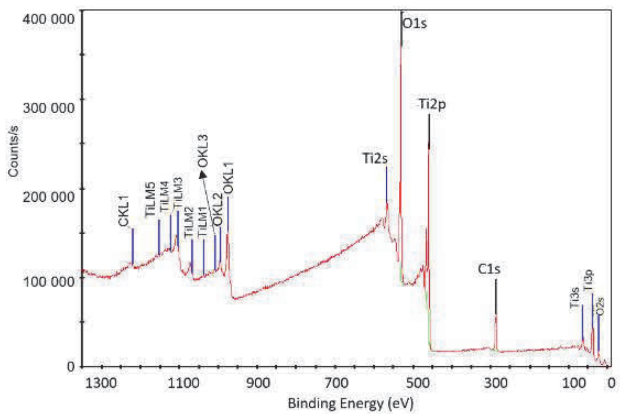

Figure 3 XPS characterization before Ar etching

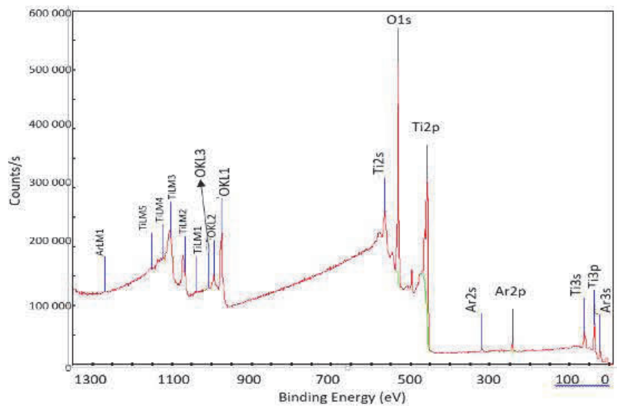

Figure 4 XPS characterization after Ar etching

Ti = (1618887.29/1.8) = 899391.83 (1)

O = (1247272.85/0.66) = 1889807.35 (2)

O/Ti = (1889807.35/899381.83) = 2.101 (3)

3.2. XRD Characterization

For XRD scanning, Al plate was used as substrate material. Before XRD scanning, the Al substrate was coated with titanium butoxide solution under the same condition. Since it is not possible to get a XRD peak from thin film on glass substrate, TiO_2 thin film is coated on Al plate to get the same conditions. Al plates were first grinded and polished then coated. **Figure 5** shows X-ray diffraction pattern of TiO_2 thin films prepared at pH values of 4 and 5. The peaks corresponding to the 38°, 45°, 65° and 83° 2ϴ all belong to Al substrate. The peak observed 78°belongs to TiO_2. Thus, TiO_2 formation is observed successfully.

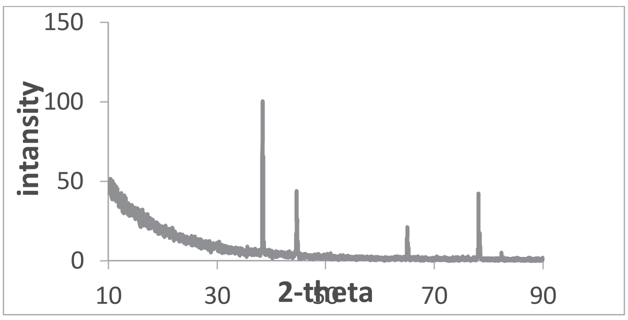

Figure 5 XRD scanning of TiO_2 thin films coated on Al substrate

3.3. Surface Characterization- AFM

The pH effects on the surface morphology are determined by AFM characterization. AFM characterization was performed to examine the changes in morphology. The images of AFM results show that the surface properties and structures of grains vary with different pH values. Previous research shows that the pH change of sol is directly affect the grain morphology [12]. Decreasing the pH values caused increase in the surface area. The profilometer images to be obtained from AFM were characterized with the software named Gwyddion-2.36.win32.pro. This software makes possible to examine the images from different angles. By using Gwyddion-2.36.win32.pro, average heights of the grains in the structure of the thin film are calculated approximately. After the processing of the scanned images by Gwyddion-2.36.win32.pro., average heights of grains are calculated. From these calculations, it is clearly seen that pH change is a key effect on surface morphology of tin film. According to the profilometer results, it is the reality that pH is an effective factor on film surface roughness; increasing pH leads to increasing in average surface area. Our pH values of sols are all in acidic range so the pH values are quite low. Due to the low pH values, the grain structure of thin film surface is small and the boundaries can be seen clearly. The difference between each pH value is 0.5 and so roughness values of each samples are very close to one another (each other). Low pH values caused smaller and specific grain structure. Small and specific grain structure provides the increasing of surface area. Increase in the surface roughness yields increase in the surface area (**Figure 6**). By using this property, an increase of the efficiency of thin films used in solar cells could be succeeded.

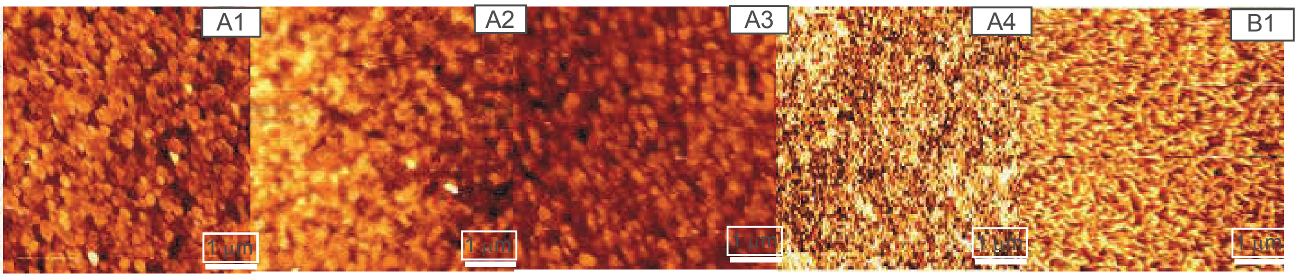

Figure 6 AFM images of TiO_2 samples with different pH values. (A1, A2, A3, A4 and B1)

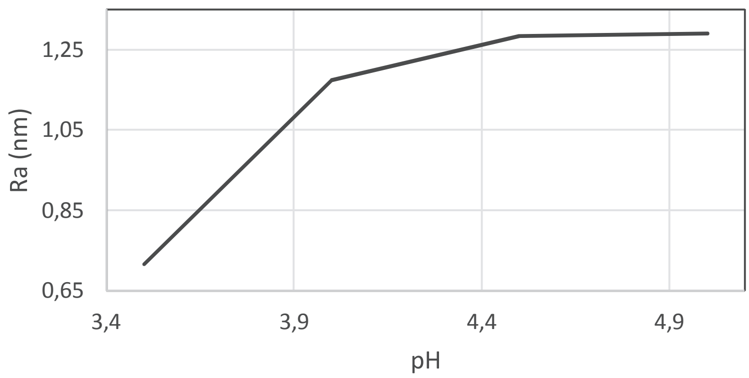

Figure 7 Average roughness versus pH

Table 1 Effect of pH on surface Ra values of samples (Gwyddion-2.36.win32.pro)

PRECURSOR	pH	CODE	Ra (nm) (average roughness)
Titanium Methoxide	pH =4.0	A1	1.175
Titanium Methoxide	pH =4.5	A2	1.285
Titanium Methoxide	pH =5.0	A3	1.290
Titanium Methoxide	pH =3.5	A4	0.715
Titanium Butoxide	pH =4.5	B1	1.27

Different solutions are prepared by using different precursors for investigation of the precursor effect on film roughness parameter. It is clearly seen in **Table 1** that, the precursor material also has an effect on film morphology. Roughness results are calculated and so the precursor effects can be analyzed. It is possible to say that the methoxide on at the same pH increased the roughness of sample surface. It is known from a previous research that, each dip gives a thickness of 60-70 nm [13].

4. CONCLUSION

Coating and formation of TiO_2 observed successfully on ITO substrates. The thickness of tin films is about 60 nm for per dipping. The pH effect on film surface is investigated intensively. The results show that increasing pH caused increase in roughness values of film surface. Also it is clearly observed that the roughness of surface value is a pH dependent factor. On the other hand, used precursor, is also effective on the surface properties of thin films. By means of precursor affect, the roughness parameter of titanium methoxide is higher than the roughness parameter of titanium butoxide.TiO_2 was formed noticeably but the crystallization process and transformation of anatase to rutil has not been occurred since the operating temperature is lower than the phase formation temperature.

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