Effect of wet etching process on the morphology and transmittance of fluorine doped tin oxide (FTO)

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Abstract. Wet etching process was performed on the surface of FTO. The FTO coated glasses substrates with size of 2x2 cm covered by screen were patterned using zinc powder and concentrated hydrochloric acid (1 M). The substrates were then cleaned in ultrasonic baths of special detergent(helmanex) diluted in deionized water and isopropanol in sequence. The screens with various of hole size denotes by T32, T49 and T55 were used in order to create a pattern of surface textured. The atomic force microscopy (AFM) image revealed that wet etching process changes the morphology of FTO. It indicates that texturization occured. Moreover, from the UV-Vis Spectrophotometer measurement, the transmittance of FTO increase after wet etching process. The time of etching and pattern of screen were affect to the morphology and the transmittance of FTO.

1. Introduction
Dye sensitized solar cell (DSSC) as a candidate of renewable generation solar cells has advantages relatively to silicon-based solar cells such as it can be fabricated at low cost and it does not require material with high purity. However, it’s lower efficiency and stability still being a big problem to overcome. In many recent years, researchers work to improve efficiency of DSSC through modifies some component of DSSC. Kilic et al. was observed that band gap engineering and modifying surface of TiO2 nanostructure by Fe2O3 succesfully increase the solar cell efficiency to 7.27% [1]. Also, various of natural dye as a sensitizer of DSSC have been investigated by Zhou et al.[2]. Other attempt to improve the efficiency of DSSC is by light trapping method. One such method is making pattern at the transparent electrode as surface of solar cell or known as a surface texturing. Some of lights which come on the surface of solar cell will reflect, others will absorb or transmit. With patterning of surface we will minimize reflectance and increasing the transmittance of transparent electrode with obeying the negligible of absorbance. In general, the kind of surface texturing method are acid texturization using chemical [3], reactive ion etching [4], mechanical texturization [5] and laser processing. Each of them has some advantages and drawbacks depend on the application. The application of etches based on acid induces difficult reproducible results due to random etching area and necessity of precise control of composition of etches. Reactive ion etchings such as using plasma need a control of temperature. Mechanical texturing may be effective, but has some limitations since cannot be applied specially for thin and fragile materials [6].
In this research, wet etching method using HCl solution was performed on the surface of FTO. various type of screen were used as pattern mask. UltraViolet-Visible (UV-Vis) spectrophotometer and
Atomic Force Microscope (AFM) were conducted to investigate transmittance and morphology as well as roughness of FTO.

2. Method
The FTO transparent glass substrates with size of 2x2 cm were prepared. Substrates are cleaned with alcohol and aquades by using ultrasonic cleaner for 10 minutes to remove residual contaminant, and then dry. HCl with 1 M of concentration was used as acid solution. The FTO etching process is more complicated since FTO cannot be reduced to the metal by using hydrogen ions in strong acid solution [7]. It need a catalyst such as zinc particles (Zn). In this research, the paste of Zn powder was applied on the surface of FTO which covered by screen as mask patterning and followed by HCl solution. After etching the samples are washed using a solution of Hellmanex to clean up the rest of the etching chemical and followed by alcohol using a ultrasonic cleaner for 10 minutes. In this research, the screens with various of hole size denotes by T32, T49 and T55 were used in order to create a pattern of surface textured. The T32 means the amount of screen’s hole is 32 per inch and so on. The etching times are 1, 2 and 3 minutes for every sample. Characterization of samples is carried out by Atomic Force Microscopy (AFM) to know the morphology and roughness of surface etching. Furthermore, Ultraviolet-Visible (UV-Vis) Spectrophotometer was used to understand the transmittance of samples. Characterization was also performed on the sample without wet etching as reference.

3. Results and Discussion
The 3D AFM image of FTO with 1 minute of etching using T32, T49 and T55 type of screen in comparison to FTO without etching is depicted in Figure 1. Moreover, picture inset shows the distribution of FTO surface topography.

FTO surface is relatively uniform as shown fig. 1(a) while it is shown several domains after wet etching for 1 min as shown in fig. 1(b)-(d). Also, the distribution of surface show the peak is shifted to the lower topography. This results indicates that wet etching process can modify the FTO surfaces through reaction with the HCl solution. In addition, root mean square roughness (Rq) of FTO surfaces in area of 5 \( \mu \text{m} \times 5 \mu \text{m} \) shown in fig. 1 are approximately 18 nm for the without etching sample, 14 nm for the etching sample (T32), 13 nm for the etching sample (T49) and 12 nm for the etching sample (T55). Here, the Rq represents the standard deviation of surface heights. The Rq was decrease after wet etching process since some of surfaces were reacted with chemical and leave many spaces.

The optical transmittance of FTO samples of the without etching and with etching using T32, T49 and T55 type of screen for (a) 1 min, (b) 2 min and (c) 3 min are shown in fig. 2. In general, an etching treatment will increase transmittance due to domain formation of FTO will leave many spaces and will be more passed the visible lights of UV-Vis spectrophotometer. However, it is considering that etching time and type of screen were affect the transmittance. For the shortest etching time, the type of screen does not significantly affect the transmittance as it can be seen in fig. 2 (a). It is because the depth of etch almost same, indicated by Rq. While the transmittance will be seen different for every type of screen when the etching time increase, as shown in fig. 2(c) – 2(d). It is considering to deeper penetration of etching surface will create surface texturing. When light come to the flat surface, it will be directly transmitted or reflected from the surface. However, when light come to surface texturing, some of them will be transmitted and the others will be reflected from one to another side of surface. This process will repeat many time known as light trapping method. And it will reduce or increase the total transmittance depends on the shape of surface texturing and angle of .
**Figure 1.** The 3D AFM image of FTO (a) without etching and with 1 minute of etching using (b) T32, (c) T49 and (d) T55 type of screen. Inset: the distribution of surface topography.

**Figure 2.** The transmittance of FTO for samples without and with etching using T32, T49 and T55 type of screen. Etching time (a) 1 min, (b) 2 min and (c) 3 min.
Finally, the highest optical transmittance of the FTO films is beneficial for efficient transport of light in DSSC applications. Also, transmittance of FTO can affect the efficiency of DSSC because a light trapping structure contributes to increasing the light path length by scattering the incident light at the different angles.

4. Conclusions

The paper presents results of wet etching process on the surface of FTO. Reaction between surface of FTO with Zn and HCl resulting some domains indicate surface texturing. The time of etching and pattern of screen were affect to the morphology and the transmittance of FTO. In summary, wet etching processing of FTO surface can be used as texturization method to enhance the light harvesting of DSSC.

5. References

[1] B. Kılıç, N. Gedik, S. P. Mucur, A. S. Hergul, and E. Gürgül, Band gap engineering and modifying surface of TiO$_2$ nanostructures by Fe$_2$O$_3$ for enhanced-performance of dye sensitized solar cell, Materials Science in Semiconductor Processing 31 (2015) 363–371

[2] H. Zhou, L. Wu, Y. Gao, and T. Ma, Dye-sensitized solar cells using 20 natural dyes as sensitizers, Journal of Photochemistry and Photobiology A: Chemistry 219 (2011) 188 - 194

[3] P. Panek, M. Lipiski, and J. Dutkiewicz, Texturization of multicrystalline silicon by wet chemical etching for silicon solar cells, Journal of Materials Science 40/6 (2005) 1459-1463.

[4] L. Jayanti, Kusumandari, T. Sujitno and R. Suryana, The study of FTO surface texturing fabrication using Argon plasma etching technique for DSSC applications, IOP Conf. Series: Materials Science and Engineering 107 (2016) 012028.

[5] P. Fath, C. Marckmann, E. Bucher, and G. Willeke, Multicrystalline silicon solar cells using a new high throughput mechanical texturization technology and a roller printing metallization technique, Proceedings of the 13th European PV Solar Energy Conference, Nice, 1995, 29-32.

[6] L.A. Dobrzanski, A. Drygala, Surface texturing of multicrystalline silicon solar cells, Journal of Achievements in Materials and Manufacturing Engineering, 31 (2008) 77 - 82.

[7] http://informationdisplay.org/IDArchive/2008/April/TransparentConductiveOxidesforDisplayApplication.aspx