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XRD Peak Shift and Enhancement of Repeated Mechanically Exfoliated SnO_2 Thin Films Synthesized from $SnCl_2$ Powder by Direct Heating

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Abstract Mechanical exfoliation (ME) using a duct tape has been conducted upon SnO_2 thin film. The film is synthesized from direct heating of $SnCl_2$ powder. The $SnCl_2$ powder is deposited upon a special arrangement of glass slides and directly heated using an electric stove with a temperature of around 350°C. The material resulted from the heating process occurs on glass slides adjacent to the heated powder glass slides. The materials are then analyzed using scanning electron microscope (SEM) and energy dispersive X-ray (EDX) to confirm the presence of SnO_2 material. The SEM results show stacking of spherical particles with sizes in the ranges of 700 nm to 1 μm. The EDX result confirms the occurrence of 20% and 66% of Sn and O, respectively, as well as 13% of carbon and a very small percentage (0.99%) of chlorine remaining. The thin films are then mechanically exfoliated using a duct tape for as many as 5, 10, and 20 times. For each ME variation, the thin films are analyzed and compared using X-ray diffraction (XRD). The XRD results show semi-crystalline structure of SnO_2 in cubic phase. The XRD results after ME show peaks, which are characteristics to SnO_2 and tend to shift the peaks to higher 2θ. Furthermore, the intensity of the peaks is highest for 10 times ME showing crystalline improvement of the thin film after the ME treatment.

Keywords: *SnO_2, direct heating, mechanical exfoliation, X-ray Diffraction*

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1. Introduction

Tin dioxide (SnO_2) or stannic oxide is an inorganic compound material that has been a subject of various studies especially concerning its applications as catalysts [1,2], ceramic glazes, polishing, coatings [3], antibacterial [4], lithium battery storage [5,6,7], solar cells [8,9,10], gas sensor [11,12,13], supercapacitors [14,15,16], and transparent thin films [17,18,19]. The various applications above use SnO_2 materials in many forms with sizes ranging from micro to nano scales [20], such as nanoparticles [21,22,23], nanowires and nanobelts [24,25,26], nanoribbons [27,28], nanorods [29], quantum dots [30,31], and nanocomposites [32]. Moreover, various methods have been used in order to synthesize SnO_2, such as hydrothermal [33,34,35], electrospinning with side-by-side spinneret [36], spray pyrolysis [37], chemical vapor deposition (CVD) [38,39,40], and dip coating [41]. These methods are put forward to produce good quality of SnO_2 thin films for various uses and applications.

In this study, we use a simple method in synthesizing SnO_2 materials by direct heating of $SnCl_2$ powder in a special arrangement of glass slides using an electric heater, which provides a temperature of around 350°C. This effort is of course acknowledged inferior to the previously mentioned methods, but, for scientific curiosity this study may give additional information in the various methods in preparing and synthesizing thin film materials. Furthermore we have added a treatment, which has not been reported before, that is a repeated mechanical exfoliation (ME) using a duct tape after the materials are printed on the appropriate glass slides.

ME using a duct tape is initially conducted to produce monocrystalline graphitic films from graphite materials [42]. The advantage of this arguably simple method is that it produces graphene layers with extremely good physical and chemical properties. However, this method is usually limited to fundamental scientific interests and has not been used to fabricate large scale graphene for direct applications [43]. In this case, we investigate whether this method may be used for thin films such as SnO_2 produced by simple direct heating of $SnCl_2$ powder. The aim of this study is to understand the effect of repeated ME towards the synthesized SnO_2 thin films based on X-ray diffraction (XRD) patterns by varying the number of ME for as many as 5, 10, and 20 times.

2. Experimental Method

The materials utilized for this study are i) 25 grams of $SnCl_2$ powder, ii) 2 liters of distilled water, iii) one box of

tissue, and iv) a duct tape (Goldtape brand). The equipment used in this study are i) an electrical stove, ii) a stopwatch, iii) glass slides, iv) two clamps, v) an asbestos screen, vi) a measuring cup, vii) a ruler, viii) a digital thermometer, ix) a glass cutter, x) an XRD apparatus (Rigaku Mniflex 600), and xi) an SEM-EDX apparatus (JSM 6510 series).

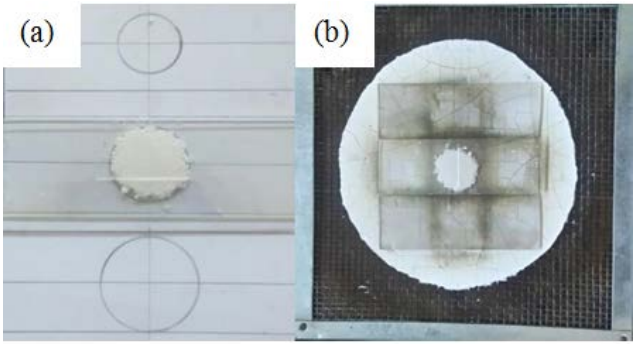

Figure 1. Top view pictures of the $SnCl_2$ powder and glass slides arrangements. (a) The $SnCl_2$ powder (white color) arranged in a circular form with a diameter of 1 cm, and (b) the glass slides arrangements with the sandwiched $SnCl_2$ in the middle and two other glass slides on its the left and right sides

Figure 2. The $SnCl_2$ powder is sandwiched between two glass slides

The procedure in obtaining SnO_2 thin films from $SnCl_2$ powder by direct heating may be explained as follows. Clean the glass slides using distilled water. Wipe the glass slides using tissues to dry them. Weigh a mass of $SnCl_2$ powder as much as 0.2 grams. Put the weighted $SnCl_2$ powder on a clean glass slide in a form of a circular shape with diameter of 1 cm (Figure 1a). Place another clean glass slide on top of the prepared $SnCl_2$ powder such that the powder is sandwiched between two glass slides (Figure 2). Lay the sandwiched $SnCl_2$ powder on the middle of the asbestos screen. Put two clean glass slides on the left and right sides of the sandwiched $SnCl_2$ as shown in Figure 1b. Turn on the electric stove with a power of 300 watts and wait around 10 minutes to get a constant temperature of around 350°C. Set the asbestos screen on top of the electric stove. Heat the $SnCl_2$ powder for about 10 minutes. SnO_2 films will gradually appear on the left and right glass slides of the sandwiched $SnCl_2$ powder. Turn off the electrical stove and let the SnO_2 films materials cool down.

Once the glass samples are cool enough, we may proceed with the repeated ME treatment and carry out XRD and SEM-EDX tests. This procedure is done as follows: i) cut some pieces of duct tape with a size matching the glass slide, ii) take a glass slide layered with SnO_2 film, iii) cut a small piece of the slide that consists of SnO_2 film and perform XRD and SEM-EDX tests, iv) stick a piece of duct tape upon the glass slide that consists of SnO_2 layer, v) slowly and firmly press the duct tape one way throughout the glass slide, vi) slowly detach the duct tape from the glass slide and discard it, vii) take a new duct tape and repeat steps iv) to vi) upon the same glass slide using as many as 5 pieces of duct tape, viii) slice a small sample of the glass slide and perform XRD measurement, ix) repeat steps iv) to viii) for 10 and 20 repeated ME.

3. Results and Discussion

Oxide materials are generally synthesized using tools and methods that are fairly complex, but in this study we use a simple method, namely direct heating using an electric stove. The heating is carried out with a temperature of 350 °C in order to exceed the melting point of $SnCl_2$ which is around 247 °C. Furthermore, the oxygen (O_2) in the air will be used to form the layers of SnO_2. The oxygen will react with the tin element contained in the $SnCl_2$ compound. This reaction will form layers of SnO_2 on the glass slides. The simple reaction takes the following form:

$$SnCl_2 + O_2 \rightarrow SnO_2 + Cl_2.$$

The SnO_2 materials produced by direct heating of $SnCl_2$ powder may be observed in Figure 3. Three pairs of SnO_2 layers are obtained by different time duration of the direct heating. It may be observed that all layers of the SnO_2 materials show different colors starting from white color at the outermost layer, and then changing to yellow, violet, blue, and green. The pattern is then repeated. These colored layers are produced due to the thin-film interference effect caused by different thickness of the SnO_2 layers. As the white colored layer is the thinnest layer, the farther the distance of the left and right substrates from the $SnCl_2$ powder, the thinner the layer produced. This might be due to less exposure of the heated $SnCl_2$ on farther parts of the glass slides. The SnO_2 layers are also not uniformly distributed through the glass slides. The longer the time duration of the direct heating process, the more area of the glass slides are covered by SnO_2 materials. For 5 minutes of direct heating, the layers on the right and left glass slides form a heart-like structure, whereas for 10 and 15 minutes of direct heating, the layers form leaf-like structures where the top regions are wider than the lower regions. Furthermore, for 5 minutes of direct heating, the right and left layers are quite symmetric; however, it is not the case for layers resulted from 10 and 15 minutes of direct heating.

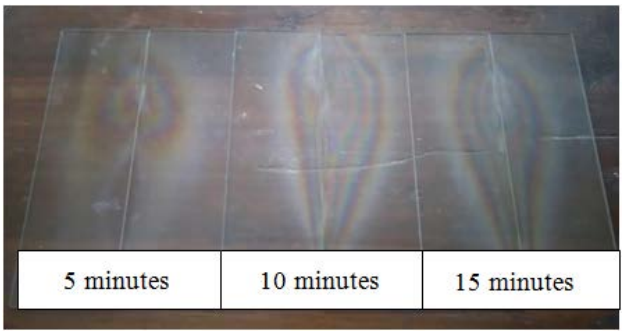

Figure 3. The SnO_2 layers produced by direct heating of the $SnCl_2$ powder. Three pairs of SnO_2 layers on glass slides are produced. The first, second, and third pairs (from left to right) are produced by 5, 10, and 15 minutes of heating, respectively. The first and second layers of each pair are on the glass slides located on the right and left of the $SnCl_2$ powder, respectively

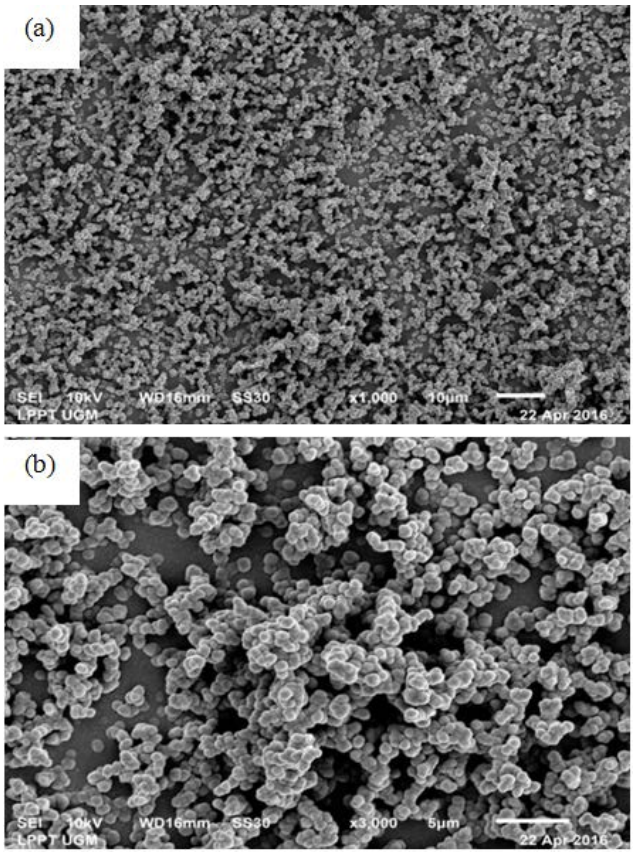

Figure 4. SEM images of the SnO_2 layers with (a) 1000X and (b) 5000X magnifications

Next, the SEM results of the SnO_2 material may be observed in Figure 4. The SEM images show spherical grains distributed throughout the glass slides. The sizes of these grains range from 700 nm to 1 micron. The grains appear to be stacked on top of each other. Figure 4a and Figure 4b show that some regions have more stacked grains than others; hence the stacking is not homogenous throughout the sample. This different stacking may contribute to different thickness of the SnO_2 layers, and hence produces different colors in Figure 3.

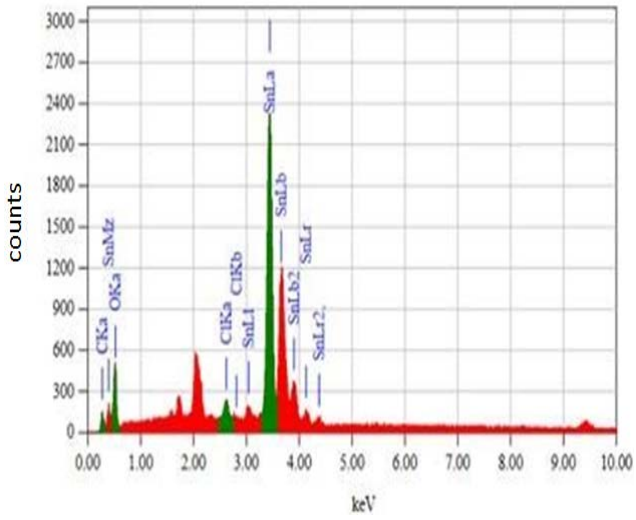

Figure 5. The EDX results of the SnO_2 sample obtained by direct heating of $SnCl_2$

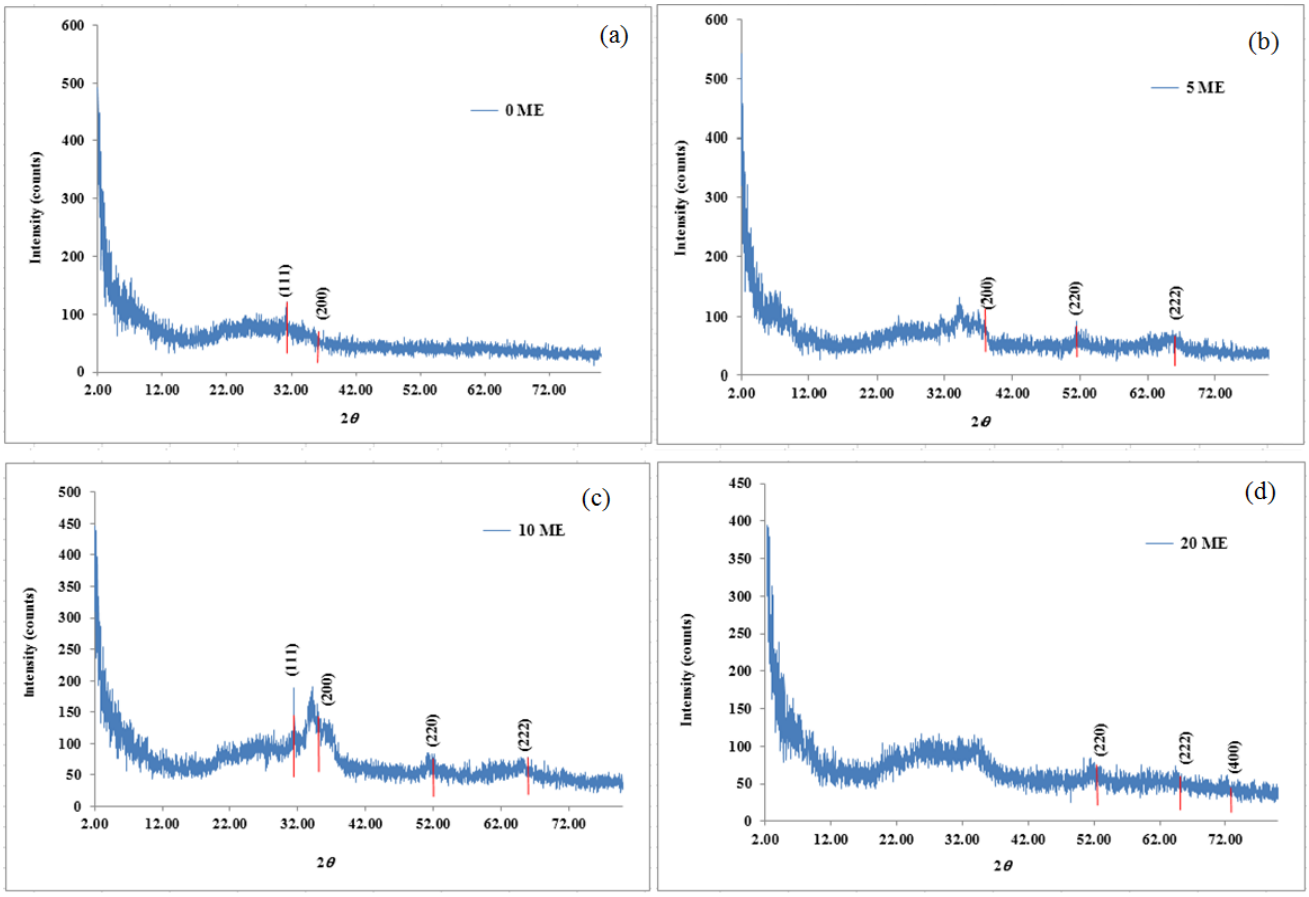

Figure 6. The XRD results of the SnO_2 samples obtained by direct heating of $SnCl_2$ with variations of the number of ME treatments, a) 0X, b) 5X, c) 10X, and d) 20X

The EDX results may be viewed in Figure 5. From the EDX results of Figure 5, the substances that occur on the sample include 20% of tin, 66.2% of oxygen, 12.8% of carbon, and a remaining of 1% chlorine. It can be deduced that the SnO_2 layer formed on the sample has a molarity ratio of Sn : O of around 1.0: 3.3, which theoretically should be 1 : 2. This mismatch may be due to the carbon atom impurity that is high enough to eliminate places for Sn atoms in a thin layer. If the carbon atoms of 12.8% are replaced with Sn, then the Sn atoms will become 32.8%, and hence the ratio is closer to 1: 2. Moreover, the data also shows that the chlorine element contained in the sample is very small. This suggests that the compound of $SnCl_2$ material has been separated; the most likely elements are separated into the air in gaseous form.

Finally, the XRD results of the samples being treated using repeated ME may be perceived in Figure 6. Figure 6(a) to Figure 6(d) is XRD results of SnO_2 layers with 0, 5, 10, and 20 times repeated ME, respectively. It may be observed from the XRD data that the SnO_2 materials are semi-crystals as no sharp distinctive high peaks are found. Furthermore, the XRD patterns of SnO_2 samples show a cubical crystal phase. The result from XRD of SnO_2 thin film without ME treatment shows two peaks on (111) and (200). For 5 ME treatment the XRD result shows peaks at (200), (220), and (222). However, the peak at (111) disappears. For 10 ME treatment the peak at (111) occurs again with other peaks at (200), (220), and (222). Finally, for 20 ME the peaks at (111) and (200) disappear, but a deeper 2θ at a peak of (400) occurs. It can be observed that increasing ME treatment makes the peaks tend to shift to larger diffraction angles. ME treatment may cause the X-ray to penetrate deeper into the SnO_2 layers. Moreover, the XRD results show that the ME treatment makes the crystal phase becomes more visible. This is shown by the peak at (200) where the X-ray intensity increases from 5 to 10 times ME treatments. But, for 20 times ME the intensity drops again.

It can also be observed that the FWHM values of the XRD data at certain peaks change due to the ME treatment. The FWHM values tend to increase when the ME treatment is applied. FWHM values for 5, 10, and 20 times ME at the peak of (220) are shown in Table 1. The table shows that FWHM data increase from 5 to 10 times of ME, but then decrease when ME treatment is applied for 20 times. This might be associated to the surface stress of the SnO_2 layer caused by the ME treatments. From 5 to 10 times of ME the surface stress increases as the FWHM also increases. But after 20 times of ME, the treatments do not have any more effect towards the surface stress of the SnO_2 layer.

Table 1. FWHM values from XRD results for 5, 10, and 20 times ME at the peak of (220)

No.	ME treatment	FWHM
1	5	1.8(3)
2	10	4.73297
3	20	2.3(3)

4. Conclusions

The SnO_2 thin film layers produced by direct heating of $SnCl_2$ powder show a range of different colors in certain areas of the layers indicating different thickness of the layers. This is also supported by the SEM results that show non-homogeneity of spherical particles with sizes in the range of 700 nm to 1 micron. Furthermore, EDX results show the sample consisting of tin, oxygen, carbon, and chlorine atoms with a composition of 20%, 66%, 13%, and 1%, respectively. The XRD results show that ME treatments cause the XRD peaks to shift to higher diffraction angles. The XRD intensities especially at the peak of (200) indicate that after 10 times of ME treatment the crystallinity of the SnO_2 thin layer increases, but then decreases after 20 times of ME. Finally, the FWHM values at the peak of (220) indicate an increase of surface stresses after 10 times of ME but decreases after 20 times of ME.

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