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Growth of TiO_2 Thin Films by High Energy Milling Assisted Pulsed Laser Deposition Method

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TiO_2 thin film can be deposited on the silicon substrate using pulse laser deposition method. To prove homogeneity of grain size on surface, this study uses milling treatment for TiO_2 powder before it is deposited. Milling treatment was conducted on samples of commercial TiO_2 powder with high energy milling method. The variation of milling time was 0, 1, 3 and 6 hours. Furthermore, the samples were shaped as disc with diameter of 1 cm and used as a target source in growth of thin film. Variations in time for the milling treatment of the TiO_2 powder has no effect on the phase change, but rather on the homogeneity of grain size on a thin layer of TiO_2. In this study, the optimum milling time to produce a homogeneous grain size of a thin layer of TiO_2 for 3 hours.

Keywords: TiO_2, HEM-PLD, Milling Treatment, Thin Film.

1. INTRODUCTION

The development of science and technology of thin layers, especially for electronic device applications was increasingly with a variety of methods. On the industrial scale, the method of chemical vapor deposition (CVD) has been established is used for thin film deposition. However, deposition of thin film with CVD methods required expensive support systems by utilizing precursors that are toxic and flammable. Some methods are more secure and cost, among others, pulsed laser deposition (PLD), sputtering and sol–gel. Especially for PLD and sputtering system can produce a thin layer with good quality. As for the sol–gel method usually produces relatively less homogeneous layer if deposited by spin coating system.

Titanium dioxide (TiO_2) is one of the electronic materials that have been widely used for various applications. There are three types of the crystal structure of TiO_2, the rutile, anatase and brookite.[1] Brookite structure is thermodynamically highly unstable when compared with the structure of rutile and anatase.[1,2] Rutile structure has better stability because it contains atoms which are solid.[3] TiO_2 thin film deposition using PLD method is relatively easier than the CVD method. Utilization of the high power laser pulses have been used to deposit a thin layer of TiO_2 on silicon substrate.[4] There are some drawbacks about PLD naturally. One of the major problems is the splashing or the deposition of particulates on the film. Two main causes for particle formation during laser evaporation are the breakaway of surface defects under thermal shock and splashing of liquid material due to superheating of subsurface layers. Some methods have been developed to reduce splashing. One is using a mechanical particle filter that consists of a velocity selector that acts as a high-velocity pass filter to remove slow moving particulates. The second is using targets of high density and smooth surface. The third is using relatively low energy density or low deposition rate.

Using high density and smooth surface of target can be prepared with milling treatment of target powder. Milling treatment prior to deposition of the target sample is usually required to obtain homogeneity in the particle size of the powder targets. This paper reported the results of thin layer deposition using PLD method with previously performed milling treatment of the TiO_2 target material.

2. EXPERIMENTAL DETAILS

Materials used in this study was a commercial TiO_2 powder from Merck ($M = 79.90$ g/mol) and a silicon substrate (111). Equipment used for milling is high energy milling-3D motion ellipse (HEM-E3D) with a rotation speed of 1000 rpm, the motor power of 1 kW and a size of 100 ml vial. This system has a three-dimensional motion and rotation in the vial so that the formation of nano particles homogeneously can more quickly and effectively. PLD equipment used by utilizing high-power laser pulses on the order of nanoseconds narrow pulse type Nd-YAG (Lab series, $\lambda = 532$ nm, 20 mJ, 6 ns).

Preparation of the TiO_2 targets was done by preparing each 5 grams TiO_2 powder milling process was then performed with a

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variety of milling time 0, 1, 3 and 6 hours. Furthermore, the TiO_2 powder was molded into cylindrical pellets or tablet measuring 1 cm and a thickness of 0.5 cm by applying pressure using a pressing apparatus. Results of TiO_2 pellets with a variation of milling time were then used as the source or target material was deposited on silicon substrate using a PLD method. TiO_2 pellets as the target and the silicon substrate were placed in the sample chamber. The silicon substrate was set to form angle of 45° to the direction of the laser beam. The pressure in the vacuum chamber about 5 Torr was measured using digital Piranimeter (Diavac PT-1DA). Samples and quartz lens can be driven in two directions relative to the direction of the laser radiation by using step motors and with a micrometer in the direction perpendicular to the laser radiation. In order to obtain a high power density on the target surface, the laser radiation pulse was focused with quartz lens ($f = 15$ cm) through the quartz window to the target surface of TiO_2. The laser was operated with a repetition frequency of 10 Hz.

Results of thin layer deposition of TiO_2 with a variety of milling time were further characterized using XRD (X-ray diffraction) to determine the crystal structure and using SEM (scanning electron microscope) to determine of the surface morphology.

3. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction pattern of TiO_2 powder used to make target. Based on the resulting diffraction pattern of the powder has a commercial TiO_2 rutile and anatase phases.

Figure 2 shows the pattern of X-ray diffraction of a thin layer of TiO_2 was deposited on silicon substrate (111) with the untreated milling (Fig. 2(a)) and treatment with milling for 1 hour (Fig. 2(b)), 3 hours (Fig. 2(c)) and 6 hours (Fig. 2(d)). It is seen that all the thin layer of TiO_2 produced has the same phase consisting of rutile phase (R) and anatase (A). In the milling process is carried out both for 1, 3 or 6 hours does not lead to a new phase and is the same as that of the untreated milling. However, the highest intensity is generated in all the peaks in the samples with the treatment process of milling for 3 hours (Fig. 2(c)). It is shown from anatase peak FWHM value of the 400 orientation (A400) in the samples #c are relatively small compared to other samples as shown in Table I, so that the quality of the crystallinity relatively better.

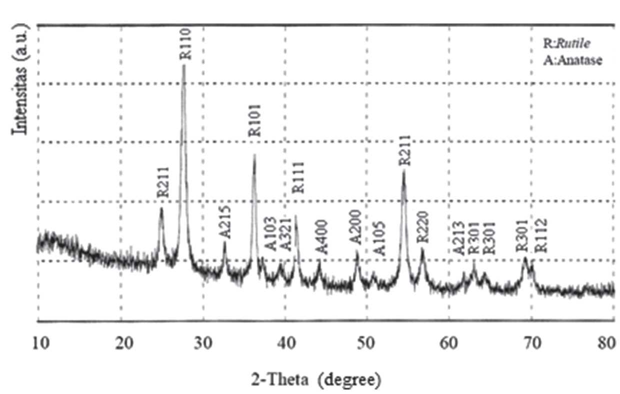

Fig. 1. Pattern of X-ray diffraction of commercial TiO_2 powder.

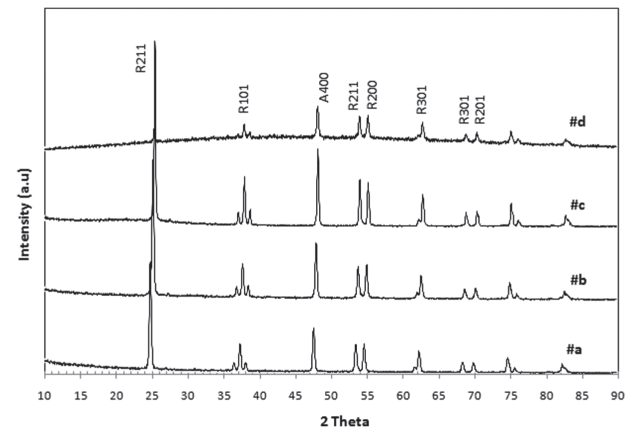

Fig. 2. The pattern of X-ray diffraction of a thin layer of TiO_2 was deposited on silicon substrate (111) with milling treatment of the TiO_2 powder for (a) 0, (b) 1, (c) 3 and (d) 6 hours.

Figure 3 shows the SEM image of a cross section of a thin layer of TiO_2 with a variety of milling treatment for 0, 1, 3 and 6 hours. The thickness of all layers of thin TiO_2 produced relatively the same, however the sample with milling treatment of 3 hours (Fig. 3(c)) relatively more regularly without the appearance of bumpy grains.

This is also shown in Figure 4 which shows SEM images of the surface of a thin layer of TiO_2 with a variety of milling treatment for 0, 1, 3 and 6 hours. The size of the grain produced in the sample by milling treatment for 3 hours relatively uniform or homogeneous.

In the treatment without milling (Fig. 4(a)) and the milling treatment for 1 hour (Fig. 4(b)) still indicates a droplet that causes irregularities in the granules. Meanwhile, milling treatment for 6 hours (Fig. 4(d)) produces porosity in thin layers. Milling treatment on TiO_2 material before it is made of pellets as the target aims to make more homogeneous material with a smaller particle size resulting compactness when made in the form of cylindrical pellets or tablets. The condition of the target density will affect the resulting film thickness. Increasing of the density and homogeneity of pellet sample will increase the rate of deposition by the number of ions, atoms or radicals generated by laser ablation. It will be able to improve the efficiency of the resulting thin layer deposition.[5,7] However, on the other hand if the deposition rate is too high will lead to increased growth rate of grain, resulting in intense competition nucleation process. This is resulting in overlap between grains and irregularities occur on the surface nucleation. Overlap of these granules occurs in the treated sample milling for 6 hours (Fig. 4(d)).

Thin film growth process itself is an amalgamation of a random collection of single particles, such as atoms, molecules or clusters to form a set of granular solids above a substrate surface which eventually form a thin film. This process involves

Table I. Value of FWHM on TiO_2 peak of the (400) orientation.

	FWHM (degree)			
Peak	Sample #a	Sample #b	Sample #c	Sample #d
A400	0,3	0,4	0,2	0,3

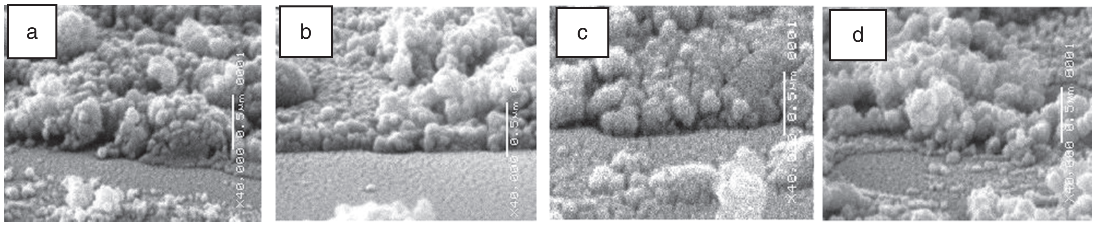

Fig. 3. SEM image of a cross section of the TiO_2 thin film grown on Si substrate (111) using PLD method with milling treatment of the TiO_2 powder for (a) 0, (b) 1, (c) 3 and (d) 6 hours.

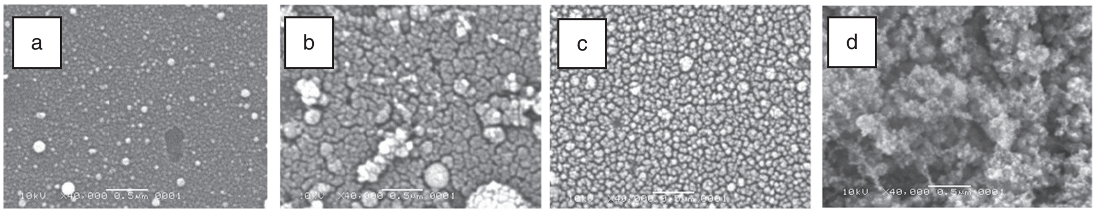

Fig. 4. SEM images of the surface of a thin layer of TiO_2 with a variety of milling treatment for 0, 1, 3 and 6 hours.

the transfer mechanism particles to the surface of the substrate which then undergo a process of lateral transport that will form a monomer which will be nucleated with characterized by adsorption, diffusion surface, re-evaporation and nucleation.[7] After nucleation occurs on the surface of the substrate, the next process is crystal growing, cultivation of grain, the coalition between the grains and the growth of film thickness. In samples with milling treatment for 3 hours allowed the coalition between the grains than other samples.

4. CONCLUSIONS

In conclusion, this study shows that a thin layer of TiO_2 produced relatively homogeneous for a given sample milling treatment during the manufacture of TiO_2 target as target material for 3 hours.

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References and Notes

1. S. D. Mo and W. Y. Ching, *Phys. Rev. B* 51, p13023 **(1995)**.
2. C. K. Jung, B. C. Kang, H. Y. Chae, Y. S. Kim, M. K. Seo, S. K. Kim, S. B. Lee, J. H. Boo, Y. J. Moon, and J. Y. Lee, *Journal of Crystal Growth* 235, p450 **(2002)**.
3. A. Fahmi, C. Minot, B. Silvi, and M. Causa, *Phys. Rev. B* 47, 11 717 **(1993)**.
4. W. Setiabudi and A. Subagio, *Proc. of Seminar of Physics*, Semarang State University **(2010)**.
5. M. Zhu, J. Zhu, J. M. Liu, and Z. G. Liu, *Appl. Phys. A* 80, 135 **(2005)**.
6. N. Sato, M. Matsuda, M. Yoshinaga, T. Nakamura, S. Sato, and A. Muramatsu, *Top Catal.* 52, 1592 **(2009)**.
7. C. E. Sittner and A. Bergauer, *Mat. Res. Soc. Proc. of Spring Meeting* 1 **(2001)**.

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