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Effect of Heating Rate on Morphology of Anti-Reflective TiO_2 Film coated by Sol-Gel with Poly(Ethylene Glycol)

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Abstract

This research aimed to investigate the formation of thin porous TiO2 film prepared by sol-gel process with spin coating. Poly(ethylene glycol) with molecular weight of 6,000 g/mol (6kPEG) was used as a pore generating agent. The TiO2 film was calcinated at 450°C for 1 hour. at different heating rates, 1, 5 and 10°C/min. It was found that the heating rate strongly affected the morphology of TiO2 film due to grain coalescence as grain coarsening and increase in pore size was found at lower heating rate. At higher heating rate, film density increased due to lower number of pores. On the other hand, for dense TiO2 film without poly(ethylene glycol) (noPEG), the heating rate did not affect film morphology.

Keyword:: Sol-gel; Titania; Spin coating; Calcination

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Introduction

TiO_2 film has been widely used as an anti-reflective and self cleaning coating layer due to its unique properties such as transparency, appropriate reflective index and super-hydrophilic property. One application of TiO_2 film is a coating layer on silicon solar cell to minimize reflection of light and to increase efficiency of silicon solar cell. However, reflection of TiO_2 film strongly depends on several parameters: phase of TiO_2 and porosity. Tanemura *et.al.* reported that anatase TiO_2 refractive index values are about 1.9-2.4 which are lower than rutile TiO_2 resulting in lower reflection of visible light (1) . Several studies (1-4) have previously shown that porosity in TiO_2 filmcan reduce reflective index to nearly 2 which is the most suitable value to apply as an anti- reflective coating layer due to the lowest reflection. Theporesize in TiO_2 film also plays an important role on reflection. Large porosity can cause light scattering resulting in high reflection, therefore, the appropriate porosity size ranges between 2-50 nm (4-7).

In order to fabricate TiO2 thin film, several methods can be employed such as physical vapor deposition (PVD) by sputtering or evaporation. However, the PVD technique can be limited because of its low productivity and high equipment investment cost. Moreover, formation of porosity within the film cannot be controlled by PVD process. Alternatively, the sol-gel process together with spin coating offersa method to fabricate TiO2 film with various, controllable pore sizes. This process has low investment cost, simple equipment and high productivity. Porosity in TiO_2 film, which is one of the most important parameters, can be formed and controlled by adding various types of pore generating agents, for example, Pluronic F127, cetyltrimethylammonium Bromine (CTAB) or poly(ethylene glycol) (PEG). During calcination process for polymer decomposed, heating rate and calcination temperature can be varied to control size and morphology of pores in TiO_2 film. Hence, the properties of porous TiO_2 film formed by sol-gel process can be designed. Acronada*et.al.* reported that Pluronic F127 and CTAB cannot used as pore generating agents for TiO_2 coating by sol-gel process since F127 and CTAB decrease sol stability and become a titanium gel resulting in unsuccessful TiO_2 film formation (8) . Guo*et.al.* found that formation of

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porous TiO_2 film can be done by sol-gel process using PEG as a pore generating agent. By using PEG at different molecular weight of 600, 2,000 and 6,000 g/mol, size and amount of porosity can be varied. The higher content of PEG as well as the increase in molecular weight of PEG tend to increase thepore size in porous TiO_2 film (9-10).

PEG is a widely used pore generating agent in sol-gel process for TiO_2 film formation. PEG is an appropriate pore generating agent due to its low decomposition temperature, and is inexpensive. Moreover, PEG alsoprovide an advantage on controlling size and porosity by varying amount and molecular weight of PEG. However, effects of various calcination parameters on morphology of TiO_2 film have not yet been investigated. This research aims to study effect of heating rate during calcination on morphology and porosity ratio of TiO_2 film coated by sol-gel process using PEG as a pore generating agent.

Materials and Experimantal Procedures

In this research, TiO_2 film coating on Silicon wafer with (100) orientation was done by sol-gel process and spin coating. Samples can be divided into 2 catagories according to sol that was used for coating: with PEG and without PEG.

In case of sol without PEG, the coating TiO_2 layer was prepared by sol without adding PEG (noPEG group). The preparation of sol for noPEG group to fabricate TiO_2 film starts from mixing titanium iso-butoxide [Ti(C4H8O)4], acetylacetonate ($C5H_8O_2$) and n-propanol [(CH3)2CHOH] with the volume ratio of 1:1.2:7.5, respectively.

For sol with PEG (PEG group), PEG with molecular weight of 6,000 g/mol(6kPEG) was added into sol. Preparation of sol for PEG group was done by mixing two types of solution: titanium precursor solution and PEG solution. The titanium precursor solution was prepared by mixing titanium iso-butoxide 1 ml with acetylacetonate 1.2 ml and n-propanol 5 ml (1:1.2:5 by volume). The PEG solution was prepared by adding 0.3 g of 6kPEG into n- propanol 2.5 ml. After mixing titanium precursor solution with PEG solution together and left for 30 minutes, sol for porous TiO2 coating (PEG group) can be used for spin coating.

Spin coating is the selected method to coated sol on Si wafer surface. The spin rate is fixed in this experiment at 2,000 rpm for 30 seconds. After that, all samples were dried at 120°C for 1 hour and then calcination for 1 h. Calcination temperature is determined by using thermogravimetric analysis (TGA, NETZSCH model STA449F3) with heating rate of 10°C/min under oxygen atmosphere and furnace cooled. After calcination temperature was set, the heating rate for calcination process was varied from 1, 5 and 10°C/min. Fourier transform infrared spectroscopy (FTIR, Bruker model Optics Vertex 70) is employed to examine organic substance in coating film after calcination. Phase analysis of the coating layer was done by X-ray diffractometer (XRD, model D/Max 2200 P/C). Surface morphology of the coating layer was observed by field emission scanning electron microscope (FESEM, model JSM- 7100F). Grain size and pore size were measured by image analysis (characteristic length method).The films porosity can be considered by area fraction of pores which were calculated by Image J software. The optical properties of samples were measured by UV-visible light technique in reflectivity mode.

Results and Discussion

Thermal decomposition of PEG sample analyzed by TGA is shown in Figure 1. There are three steps of weight loss during heating up to 800°C. The first small weight loss was found at 53-101°C which should be due to dehydration in the sample (11) as had been reported that dehydration typically took place between 25-200°C. The second step weight loss, which is much larger than the first step, was detected around 275-325°C. This second step weight loss is due to PEG molecule decompositionas reported by Yu *et.al.* at temperature ranging from 268-351°C. The third weight loss occurs at temperature around 310-420°C. This should be due to decomposition of titanium complex molecules. This is in good agreement with Kuznetsva work that found decomposition of Titanium complex molecule and acetylacetonate at 350°C (12). From TGA result, it can be concluded that the calcination process should be done at 450°C to achieve complete decomposition of all organic substances.

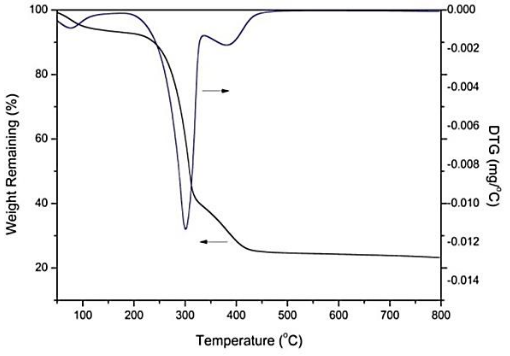

Figure 1. Thermal decomposition of the uncalcined 6kPEG film

In order to confirm the decomposition of organic substances in the samples, FTIR technique is employed. FTIR spectra of noPEG and PEG samples, which are calcinated at 450°C for 1 h with heating rate of 10°C/min, are shown in Figure 2. Absorption bands detected at 450 and 657 cm^{-1} indicates stretching of Ti-O and Ti-O-Ti, respectively. The absorption bands at 1640 and 3200 cm^{-1} represent stretching and bending of OH bonding in H_2O molecule. Small amount of CO_2 contaminant in air also found in FTIR as can be seen from the absorption band at 2350 cm^{-1}

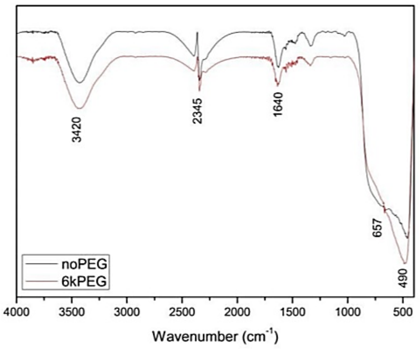

Figure 2. FTIR spectra of samples were heated with 10°C/min (a) noPEG and (b) 6kPEG

Phase analysis and crystallinity of thin film can be examined by XRD technique. Figure 3 shows XRD profiles of all samples which consisted of only anatase (JCPDS 78-2486). According to XRD profiles, average crystallite size of all samples can be calculated by Scherrer's equation. It was found that with increasing heating rate, the average crystallite size tends to be smaller. However, for slow cooling rate (1, 5°C/min), the increasing of heating rate does not show significant effect on reducing of average crystallite size as can be seen that the crystallize size of 1 and 5°C/min heating rate are in the range of 17-18 nm for both noPEG and PEG samples. In contrast, using high heating rate (10°C/min) can reduce the average crystallite size of both PEG sample (14.4nm) and especially noPEG sample (11.9 nm). The slow heating rate of calcination causes long calcination processing time (heating to 450°C and holding for 1 hour) allowing agglomeration and coarsening of crystallite. Therefore the average crystallite size tends to be larger. Comparing noPEG and PEG samples, it was found that PEG sample tends to have larger average crystallite size than noPEG even using high heating rate (10°C/min). This is because noPEG samples receive heat from furnace only, but PEG samples receive heat from furnace and exothermic reaction causing by PEG combustion at high heating rate.[(13)] Therefore, the average crystallite size of PEG samples is higher than noPEG samples when the heating rate of calcination process exceeds 10°C/min

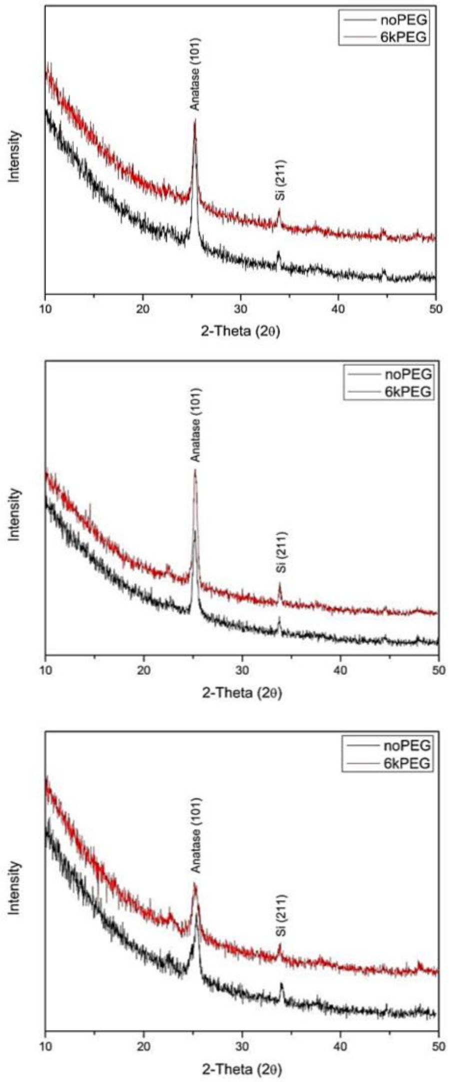

Figure 3. XRD patterns ofnoPEG and 6kPEG films were heated with difference heating rate (a) – (c) 1, 5, and 10 °C/min, respectively

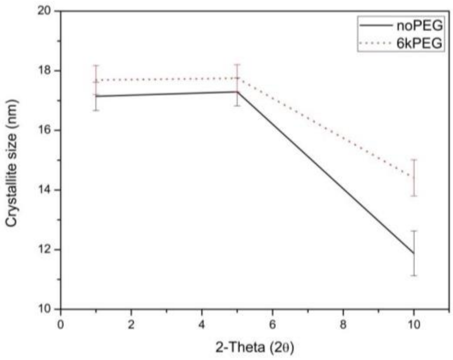

Figure 4. Average TiO_2 crystallite size of noPEG and 6kPEG were heated with 1, 5 and 10°C/min

According to XRD and crystallite size, the sample with heating rate 1°C and 5°C are not significantly different; hence, morphology study will be done for the samples with heating rate of 1 and 10°C/min. For sample with heating rate 1°C/min and calcination at 450°C for 1 hour, the surface morphology observed by FESEM of both noPEG and PEG is similar as shown in figure 5. Since the heating rate is slow, there is enough time for coarsening resulting in grain growth. For high heating rate (10°C/min), noPEG sample shows small grain size (Figure 6(a)) because short heating time to calcination temperature suppresses grain growth. On the other hand, PEG sample shows localize coalescence and coarsening of grain as shown in Figure 6(b) due to heat generated from combustion of PEG in some areas. The result correlates well with XRD result discussed previously

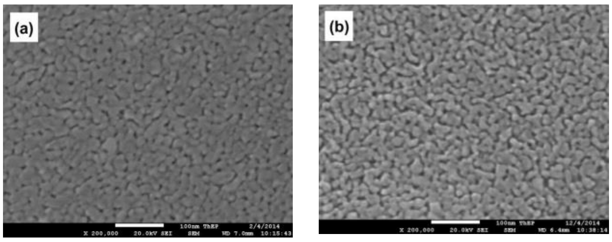

Figure 5. Morphology of films were prepared with heating rate 1°C/min (a) noPEG and (b) 6kPEG

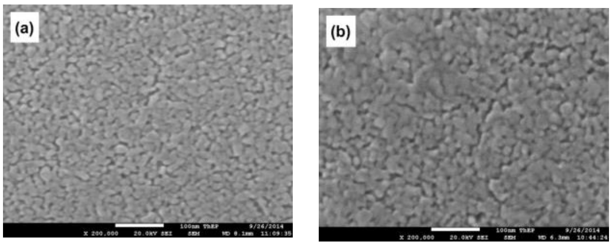

Figure 6. Morphology of films were prepared with heating rate 10°C/min (a) noPEG and (b) 6kPEG

Distributions of grain size in both noPEG and PEG sample with slow heating rate during calcination (1°C/min) are shown in Figure 7. It can be seen that, with slow heating rate, grain size distributions of both noPEG and PEG samples are similar which are in form of unimodal distribution with average grain size of 15 nm for noPEG sample and 17 nm for PEG sample. In case of high heating (10°C/min), combustion of PEG, which is an exothermic reaction causes large amount of heat transferred to the adjacent area, must be taken into account. For high heating rate samples, the noPEG sample still received heat only from the furnace; grain size distribution is still in form of unimodal as can be seen in Figure 8(a). In contrast, the PEG sample, combustion of PEG in film took place and supplied large amount of auxiliary heat to localize area around combusted PEG leading to coalescence and coarsening of grains in those areas. Because of this reason, the grain size distribution of PEG sample with high heating rate (10°C/min) is in form of bimodal distribution as shown in Figure 8(b).

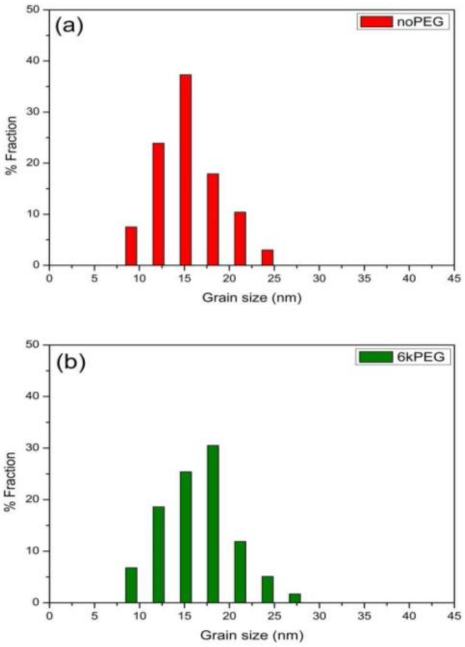

Figure 7. Grain size distribution of films were prepared with heating rate 1°C/min (a) noPEG and (b) 6kPEG

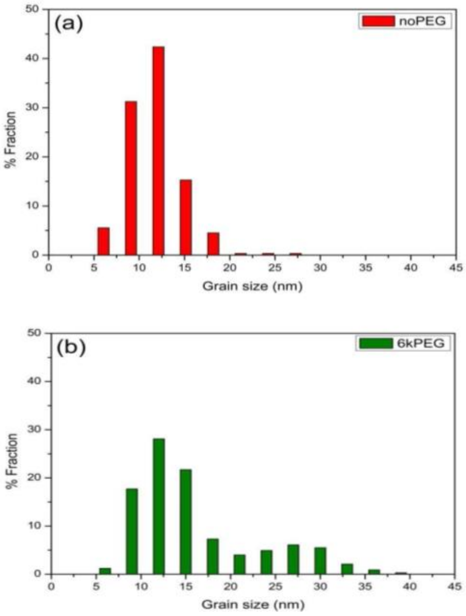

Figure 8. Grain size distribution of films were prepared with heating rate 10°C/min (a) noPEG and (b) 6kPEG

Heating rate also affects pore size as can be seen from morphology observed from FESEM. Both noPEG and PEG samples with slow heating rate contain pores with the size about the same which are 9.2 and 9.7 nm, respectively. When the heating rate was increased to 10°C/min, it was found that the pore size slightly smaller than pores in samples with slow heating rate (7.4 nm for noPEG sample and 9.0 nm for PEG samples). Poresenlargement occurred together with agglomeration and coarsening of grain. It can be concluded that by using slow heating rate with long period of heating time, pores becomes larger than the sample with high heating rate. In the case of PEG samples, even though high heating rate of 10°C/min is applied, average pore size is not as small as noPEG sample because this sample receives extraheat from combustion of PEG leading to enlargement of pore size.

Amount of porosity in all samples was measured in term of area fraction by image analysis program (Image J software). The area fractions of pores in noPEG and PEG samples those werecalcinated with 1°C/min heating rate are about the same, which are 6.8 and 7.6%, respectively. After increasing heating rate to 10°C/min, the area fraction of pores in noPEGabout 6.0% remained which is almost the same as slow heating rate (1°C/min). On the other hand, the area fraction of pores in 6kPEG sample is remarkably decreasedfrom 7.6% to only 6.0% with increasing heating rate. This means that heating rate strongly affect amount of porosity in PEG sample while there is no effect on amount of porosity in noPEG sample. This might be because heat from PEG combustion at high heating rate activates coalescence which is a process to eliminate porosity. While, only grain coarsening, which has no effect on porosity volume, occurs in noPEG sample

The optical properties of TiO_2 films were measured by UV-visible light technique in reflective mode. The reflectivity profiles of samples were calcinated at 1°C/min which shown in Figure 9 and 10, respectively. Whereas, we found the reflectivity of noPEG samples did not significantly change with the heating rate because their grain size and porosity were similar and their pore sizes were suitable for anti-reflective application. However, the reflectivity of 6kPEG samples were slightly deceased with the heating rate due to bigger grains had lower grain boundary areas causing light scattering. In addition, reflectivity of 6kPEG samples were lower than noPEG samples. However, their reflectivity of all samples significantly decreased from original Si wafer (reflectivity of all samples were lower than 10% from 38% of original Si wafer)

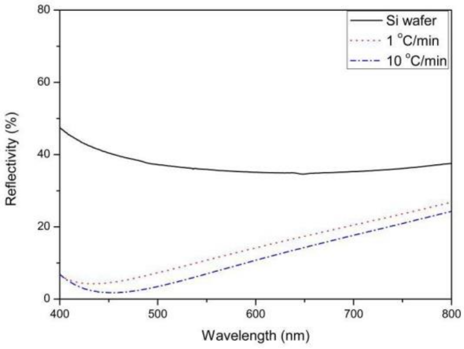

Figure 9. The reflectivity profiles of noPEG samples were calcinated at 1 and 10°C/min.

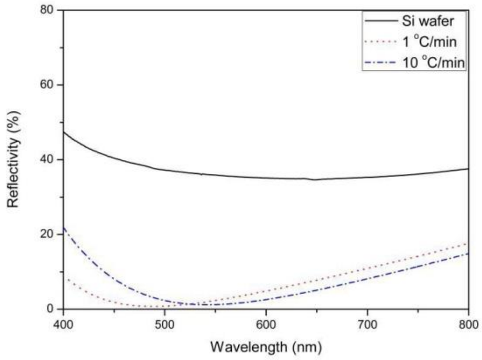

Figure 10. The reflectivity profiles of 6kPEG samples were calcinated at 1 and 10°C/min.

Conclusions

Coating of nano-porous thin TiO2 film as an anti-reflective coating on Si wafer can be successfully done by sol-gel and spin coating process. Calcination process to eliminate organic substance can be performed at 450°C for 1 hour. FTIR confirmed that all PEG and other organic substances are completely decomposed by calcination condition. All TiO2 films coated and calcinated by this process are in form of anatase with different morphology according to film preparation conditions: with/without PEG and heating rate to calcination temperature. The porous TiO2 film fabricated by this process contains pore with average pore size between 7.4-9.7 nm which are appropriate sizesfor anti-reflective coating layer for solar cell. Crystallite size, grain size, pore sizeand amount of porosity of TiO2 films depend on heating rate during heating to calcination temperature. Crystallite size, grain size and pore size of all samples (noPEG and PEG) tend to decrease when heating rate reaches 10°C/min. This is because of high heating rate,there is only short duration time for grain coarsening and enlargement of porewhich mainly take place during heating to calcination temperature. However, amount of porosity in noPEG and PEG are not in the same trend. Heating rate has no effect on amount of noPEG sample since only coarsening process takes place. In contrast, heating rate strongly affects on amount of porosity in PEG sample. The high heating rate (over 10°C/min) causes PEG combustion providing extra heat transferred to localize area resulting in not only coarsening but also coalescence of grain in those areas. This coalescence process helps elimination of porosity, hence, porosity of PEG sample using 10°C/min heating rate is reduced to only about 6.0% by area. The reflectivity of noPEG samples did not change with the heating rate.On the other hand,their reflectivity of PEG samples slightly decreased with the heating rate because the lower grain boundary areas.However, their reflectivity of all samples significantly decreased from original Si wafer.

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