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Crystallization of As-anodized Titania Nanotubes Grown in Low Acid Electrolytes

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This research work reports a slow growth rate inducing *in-situ* crystallization of anodic TiO_2 nanotube array formation in fluoride-based diethylene glycol electrolyte. The focus is to clarify a consequent effect of the growth formation in DEG medium leading to the development of partial crystalline grains on the tube wall. In the very low hydrofluoric acid content as low as 0.5%, the intriguing nanostructure of grain-like crystallites forming tubes has been observed, with those crystalline nanograins characterized as anatase. The high resolution TSEM has confirmed the as-anodized films grown with low water content additive that the consisting 20-nm nanograins has been initiated on the tube wall during anodization, attaining the early phase transformation temperatures for the as-anodized sample to anatase and subsequently rutile appearance at 260 ºC and 380 ºC, respectively. It is believed that the initially formed nanograins could probably play a catalytic role enhancing the development of crystalline phases at early transformation temperatures. Further, we report for the first time for the possibly *in-situ* crystallization in DEG electrolyte system, schematically illustrating as a function of reaction rate-cation size of fluoride bearing species relation.

Keywords: TiO_2 nanotube arrays, electrochemical anodization, crystallization, low acid concentration

1. INTRODUCTION

Improved nanotube array crystallinity plays a key role in promoting charge transport.[1-5] The crystalline or amorphous phase of the titania nanotubes varies with processing methods and parameters in oxide formation. The as-grown titania nanotube arrays are typically amorphous, while high temperature annealing in oxygen induces crystallization.[6] Crystallization and phase transformation generally take place in the material through nucleation and growth processes. In solid-state sintering, it is well known that high temperature crystallization leads to the consequent results of grain growth, densification, and finally structure collapse.[6] The high temperature annealing induces crystallinity in the oxide film usually leading to the formation of a thick oxide barrier, separating the nanotube array film and the underlying metal substrate. Acting as a disadvantage, this barrier layer is known to block electron transfer to the underlying metal electrode. Further, the elevated-temperature heat treatment is considered to cause the reduction of porosity and surface area of the annealed oxide film, due to the pronounced effect of nucleation and growth of the oxide during the phase transformation.[6]

Many attempts have been reported for crystallization evidence attainable in the anodic bath. In aqueous-based electrolyte, Kunze et al. reported the conversion of amorphous to nanoporous rutile in a fluoride-containing medium at room temperature.[7] They reported the effect of pre-anodization on crystallization of the titania film; this favors the formation of a thick crystalline nanoporous layer of rutile structure. It was suggested that the presence of fluoride ion could induce crystallization of rutile TiO_2 film in strong acid; phosphoric acid and hydrofluoric acid. Titanium substrate treatment prior to anodization was found to promote crystallization of the anodic titania film. Allam et al. studied a two-step fabrication process on crystallization of titania nanotube film. This work focused on the use of strong oxidizing agents to produce a thicker crystalline oxide layer; subsequently the thick film is converted into the nanotube architectures. The Ti foil sample was first treated in an oxidizing peroxide (H_2O_2) containing electrolyte at 80 ºC before anodizing such anodized film in aqueous containing ammonium fluoride electrolyte, resulting in the purely anatase nanotube array film.[8] This layer is converted into a crystalline nanotube film by subsequent anodization. Xiao and co-workers reported the fabrication of anatase titania nanotube arrays in dimethyl sulfoxide electrolyte containing low HF concentration of 1.0 % at the temperatures between 40 ºC and 60 ºC. Described in addition to the increased potential, the high temperature giving rise to driving force for ionic conduction plays a key role in inducing the crystallization of nanotube array film.[9] Nonetheless, the exact formation mechanism of anatase crystallization has not been clearly understood.

Is it possible to obtain the crystallized nanotube film without high temperature annealing? An aim of this work is to seek possibilities to *in-situ* crystallize, to obtain crystalline TiO_2 nanotube array films without high temperature annealing. We report a study of growth formation in DEG-fluoride medium and its consequent effect on the development of partial crystalline grains on the nanotube wall. Herein we present a facile pathway to achieve crystalline TiO_2 nanotube arrays through one-step anodization. The film crystallinity influenced by the synthesis parameters has been carried out through a particular modification of electrolyte composition and anodization conditions. The phase transformation temperatures for the nanotube array films consisting of initially formed nanograins have been investigated. Observation of film morphology and crystallinity has been brought into a relationship, and proposed in terms of the rate of reaction and the ionic size of fluoride bearing species. A study of anodization current behavior is also included.

2. EXPERIMENTAL

Titanium foils (0.25 mm, 99.7%, Sigma-Aldrich) were cleaned with acetone, soap and isopropanol prior to anodization. The potentiostatic anodization for the Ti foils as anode electrode was performed at room temperature in a two-electrode electrochemical cell with platinum foil as the counter electrode. Anodization electrolytes were prepared using diethylene glycol (DEG, 99.7%, Sigma-Aldrich), hydrofluoric acid (HF, 48% solution, Merck), and DI-water. Anodization current was tracked by a Keithley (2000) digital multimeter interfaced with a computer; the current density was determined and plotted against anodization time. Morphological study was carried out by SEM and transmission mode (Zeiss Supra 40 and transmission setup), and HRTEM (Philips 420). Crystallization of the as-anodized films was investigated by glancing-angle X-ray diffractometer (GAXRD, Scintag, Inc.). The *in-situ* study of phase transformation and crystallinity was performed using Panalytical Xpert Pro MPD Theta-Theta Diffractometer. The 1×1 cm^2 as-anodized TiO_2 nanotube array film fabricated in DEG−2% HF−3% H_2O electrolyte at 60 V was selected for this study. The inter-electrode spacing was fixed at 2.0 cm. [10] Using platinum foil as the heating substrate, the nanotube film was heated in air with a constant ramping rate of 1 ºC min^{-1}. The first XRD pattern was collected at 25 ºC and the next at every 20 ºC interval from 200 ºC to 600 ºC. During the pattern collection, the temperature was dwelled for 20 min before rising to the higher temperature.

3. RESULT AND DISCUSSION

As previously reported, it was evident that anatase can crystallize at room temperature in a low acidic medium such as DEG electrolyte containing ammonium fluoride (NH_4F).[11] Replacing NH_4F with HF, the condition that yielded the as-anodized titania nanotube film with detectable crystalline form was found particularly when the very low concentration of 0.5% HF was employed, anodizing at 60 V for 48 h at room temperature. Such low HF content electrolyte is of considerable interest since the obtained nanotubes morphology appears to construct their tubes with an intriguing feature of nanograins shown in

Figure **1**. The HRTEM image in

Figure **2** (a) revealed more clearly the structure of nanograins with their sharp ends agglomerating and forming tubes. Dimensions of the grain-like particles are approximately 10-nm diameter and 40-nm length. In

Figure **2** (b), the selected-area diffraction pattern indicates that those grains are polycrystalline anatase phase. Some bright spots in the ring pattern in the selected area diffraction pattern indicate that those particles contain a random distribution of crystallites along the length of nanotubes. This observation is similar to the precipitate of needle-like shapes reported from Gopal et al., suggesting that the small grains are anatase rather than rutile phase, where the lower acid concentrations promoted anatase formation.[12] The anatase crystallite is more favored to occur than rutile when the crystallite size is less than 14 nm.[13, 14] Narita et al. noted that although the size of crystallites is small, they tend to grow with aging time in fluoride solutions.[15]

When acid is present in solution, the aggregation processes are inhibited due to the repulsion from the adsorbed H^+ ions, with higher acid concentration resulting in larger repulsion and slower aggregation.[16] At low acid concentration, the small crystallites may be formed in the similar way as those obtained by the catalytic effect of solid precipitation on the substrate surface that strongly depends on the pH, nature and concentration of solution.[17]

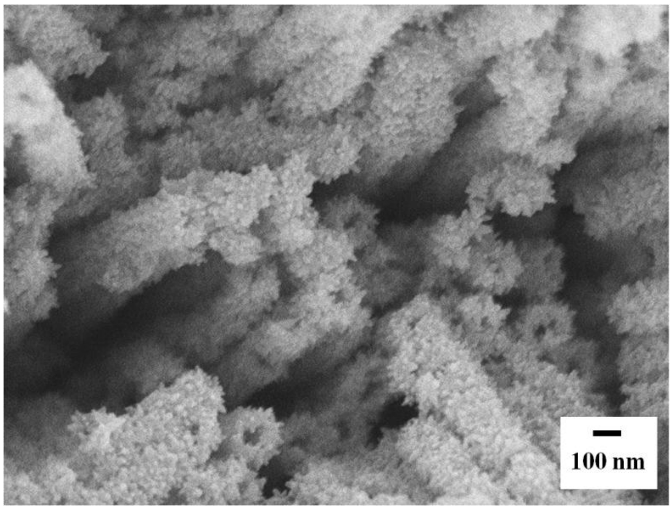

Figure 1. FESEM image of TiO_2 nanotube array films anodized in DEG–0.5% HF electrolyte at 60 V for 120 h.

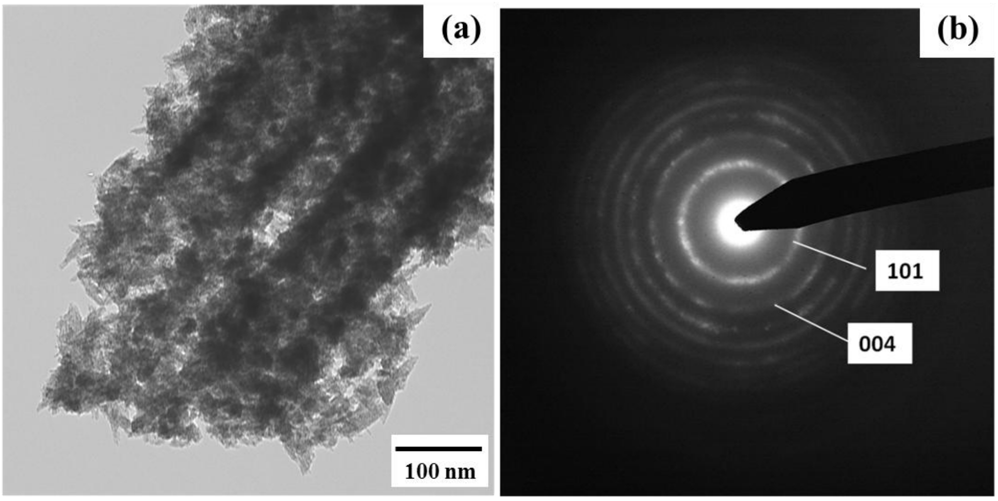

Figure 2. (a) A HRTEM image of nanograins forming tubular structure obtained from the condition shown in Figure 1. (b) A selected-area diffraction pattern resulted in the crystalline anatase phase.

The phenomenon of particulate forming nanotubes is attributed to a potential-induced nucleation and growth of crystallites initially occurring on the substrate; the formation of crystalline phase is governed by the aggregation rate of the octahedral complexes. Precipitation in solution without an applied electric field does not result in needles.[12] The electrolyte nature of DEG is believed to play a key combination role with the optimum anodizing conditions, in slowing down the rate of simultaneous anodization reactions, hence leading to nanograin crystallization along the tubes.

With prolonged duration, the crystallite size could become larger, while the barrier oxide layer thickens. Grain growth and densification may also take place,[18] and the particles tend to be more stable with time.[17] Finally, the pore generation proceeds and the tube formation takes place, as the constant potential primarily determines pore dimension on the basis of high field potentiostatic anodization.

In the anodization bath, the *in-situ* crystallization to achieve high crystallinity is restricted by the nucleation-growth kinetics. The crystal growth rate is limited by diffusion of cations or anions towards the substrate surface, where the low conductivity of the bulk electrolyte plays a key role in controlling the ionic mobility.[19] The formation of the hydrogen bond network of DEG may solvate the dissolving ions; as a result, the reactivity of small ions essential for anodic oxidation/dissolution such as F^- and OH^- may be inhibited due to the strong solvent solvation.[20-23] In this work, anodization current for the very low HF concentration and its growth behavior was also monitored. The current density as a function of anodization time for the DEG–0.5% HF electrolyte, 60 V condition is shown in Figure 3. The increment behavior of titanium anodization is linear as same as those typically seen in other conditions for DEG-based electrolytes, but of lower current density regime.[24] With its low electrolyte conductivity of 20 μS cm^{-1}, the approximate slope of the current-time curve is 0.003 mA/cm^2/h. Compared to those previously reported for the higher amount of HF and with water additive, the increment slope for the DEG–2.0% HF and DEG–2.0% HF–3% H_2O electrolyte conditions has been found to be higher by a factor of 6; about 0.017 mA/cm^2/h.[11]

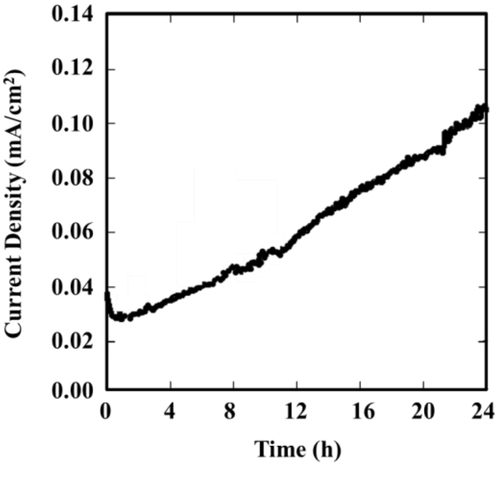

Figure 3. Current density plotted against anodization time for a titanium anodization in DEG–0.5% HF electrolyte using 60 V for 24 h.

A schematic diagram for the *in-situ* crystallization possibly occurring in the low conductivity region for the DEG-fluoride bearing species electrolyte system is proposed in Figure 4. At this point of view, as the cation size of fluoride bearing species varies and gives their consequent effects on the rate of anodic reactions; morphology and pore cell alignment of the resulting nanotube arrays could be different. Those characteristics obtained for the ammonium fluoride (NH_4F) and tetrabutylammonium fluoride (Bu_4NF) containing DEG electrolytes summarized from our previous reports[11] have been included in this drawing for a better visualization. It was evident that the *in-situ crystallization* could be observed particularly for the DEG-NH_4F based electrolyte giving discrete, self-ordering pores. Containing larger cation size for fluoride bearing species, the DEG-Bu_4NF electrolyte was found to give the faster growth rate, resulting in the highly ordered, self-organized nanotube arrays like the most popular structure of EG fabricated films. For the DEG-HF medium containing solvent additives, the crystalline phases with small intensity could possibly appear for the DEG electrolytes containing tetrahydrofuran (THF), hexamethylphosphoramide (HMPA), and propylene carbonate (PC). Due to the limitation effect of relative permittivity and miscibility of those solvents with DEG, this enabled them to result in low conductivity of the anodized electrolytes to be lower than 50 µS cm^{-1}, as such particular conditions producing the titania films with connecting pore morphology.[11]

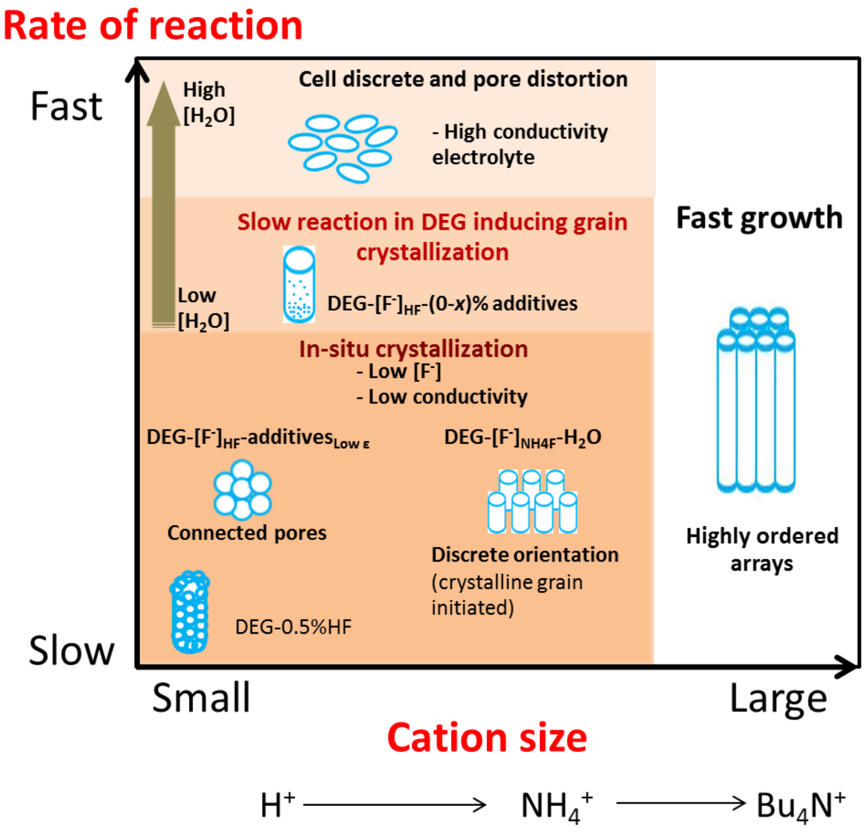

Figure 4. A schematic drawing for DEG-fluoride based electrolyte system shows different types of pore cell formation obtained by varying cation size of fluoride bearing species, consequently affecting anodic reactions, nanotube formation, and possibly *in-situ* crystallization.

Using water additive in DEG, discrete tube orientation is commonly obtained, with higher water content tending to give more tube-to-tube separation and disordering pores. An example of the well aligned titania nanotube film grown in the low conductivity, 66 µS cm^{-1}, of DEG-2%HF-3%H_2O possessing a promising hemocompatibility is shown in Figure 5.[25] For the low water condition, the film was formed in a slow growth rate reflecting the small nanograins initiating on the tube wall as in Figure 5 (a). This effect has left behind a certain degree of surface roughness on the titanium surface after the film array was detached; see Figure 5 (b). Considering the high-resolution top surface of a tube in

Figure **6** (a), the in-depth investigation shown in

Figure **6** (b) was sensitively detected through TSEM. The result visualized an evidence of precipitates on the tube wall, with the 20-nm nanograins distributing randomly over the tube. For this condition, there was no significant phase detected by XRD for the as-anodized tubes. Nonetheless, by the nature of DEG solvent governing the process reaction rate, it is believed that the slow growth formation in this DEG medium could possibly give rise to partial crystallization, to some extent, as similar to that observed for the DEG-HF-solvent additives conditions.[26]

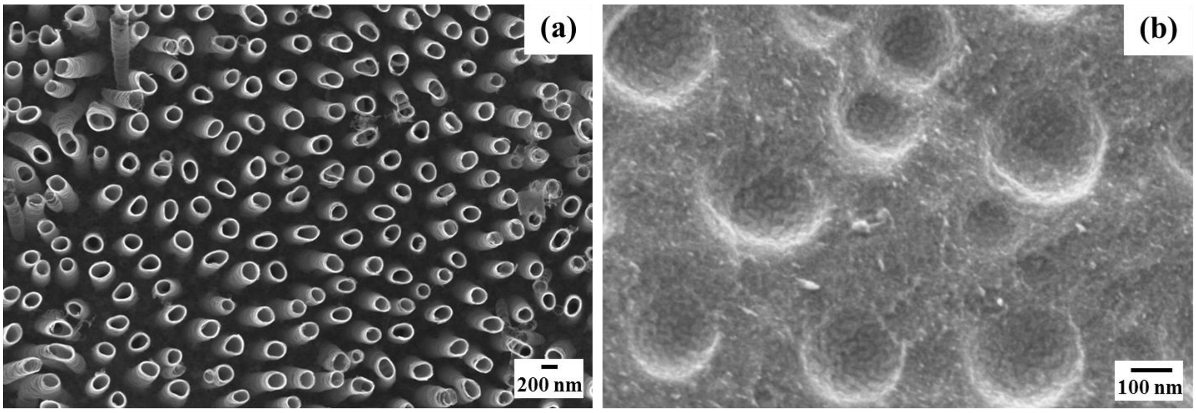

Figure 5. SEM images of TiO_2 nanotube array films obtained in DEG-2%HF-3%H_2O electrolyte, as-anodized at 60 V for 24 h. (a) Top view of the nanotube arrays and (b) surface of Ti foil substrate after the titania nanotube arrays were detached.

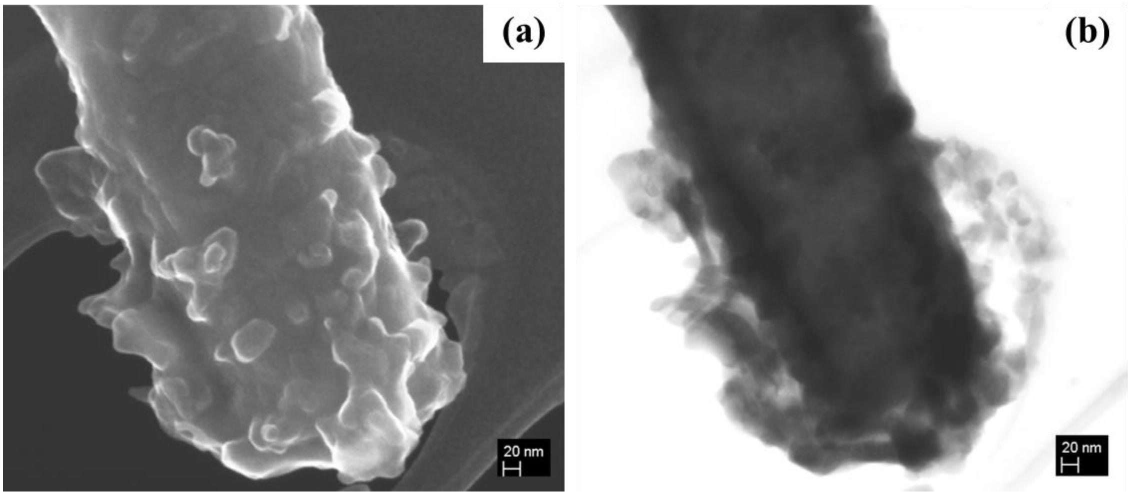

Figure 6. SEM images of a TiO_2 nanotube grown in DEG-2%HF-3%H_2O electrolyte at 60 V; (a) high resolution wall surface and (b) a tube taken in the transmission mode (TSEM).

To further investigate phase transformation temperatures and film crystallinity, the *in-situ* XRD study was designed to observe the crystallization temperature once the crystalline peaks appeared. Using the nanotube array film grown in the DEG-2%HF-3%H_2O electrolyte, the sample was annealed under air ambient at elevated temperatures. In Figure 7 (a), the first pattern was collected at 25 ºC, undoubtedly reflecting the amorphous phase for the as-anodized film. As the temperature was elevated, the amorphous oxide film started to crystallize; the formation of anatase appeared to be seen at 260 ºC; see Figure 7 (b). After the grain nucleation, the anatase grain progressively increases in size with temperature. At 280 ºC, the stronger peak of anatase (101) is seen more clearly indicating the larger crystallite size and higher crystallinity. Among these conditions, the maximum intensity of anatase peak was obtained at 560 ºC. For rutile phase, the first peak appeared at 380 ºC; see Figure 7 (c). The peak broadening characteristic with wide base expansion indicates a distribution of grain size in the nanotubes.

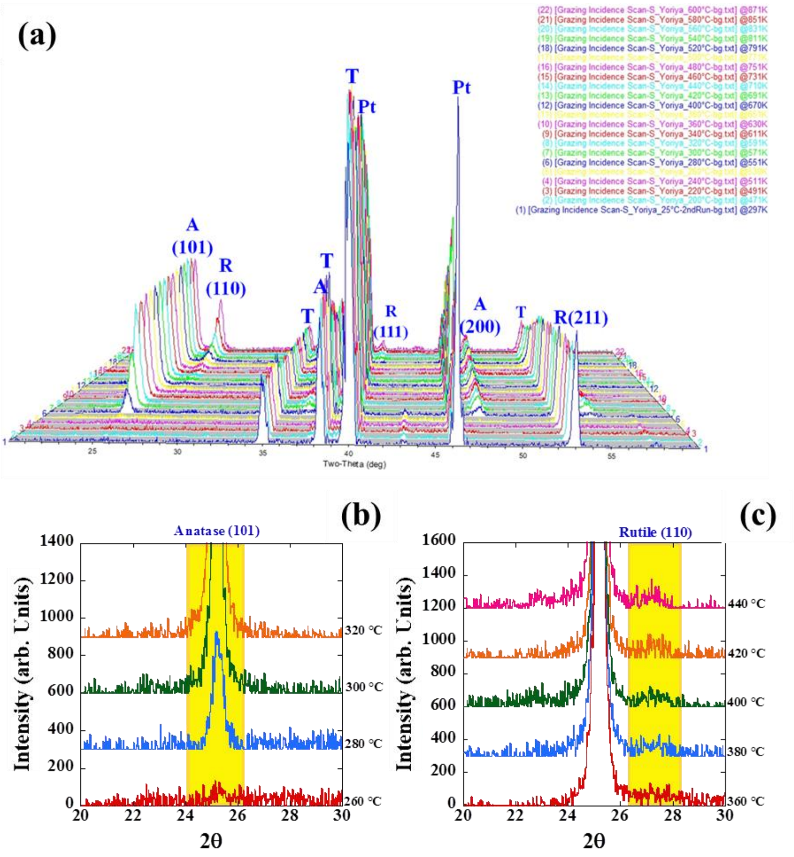

Figure 7. GAXRD patterns of a 1-μm thick TiO_2 nanotube sample grown in DEG–2.0% HF–3.0% H_2O electrolyte (60 V). (a) A 3D overlay plot of diffraction patterns collected at different temperatures. The magnified patterns showing appearance of (b) the onset crystalline anatase (1 0 1) peaks, and (c) the onset crystalline rutile (1 1 0) peaks.

Summarized for this work, it is important to note that the phase transformation temperatures for the as-anodized sample converting into anatase and rutile are 260 ºC and 380 ºC, respectively.

Comparing the phase transformation temperatures observed for the DEG-based electrolyte to those of the nanotube films grown in aqueous electrolyte. These temperatures are slightly lower than those reported for the amorphous aqueous-grown samples of 280 ºC and 430°C in that order.[6] Such early temperatures at which those phases crystallized directly reflect an indication of thermal stability of the phases that require relatively lower activation energy than the higher transformed temperatures. The onset of crystallization–a thermally-activated phenomena, at early temperatures is attributed to the initially formed crystalline on the growth surface, which is a result of slow anodization growth rate in DEG medium. When the as-anodized sample is sintered, these nanograins could facilitate the crystalline growth forming anatase crystals at relatively lower temperatures, the lower energy intake for phase stability. Considering partial-nanocrystalline titanium dioxide, principally a large fraction of atoms are situated on the surface and the surface energy is high, thus it is energetically favorable to increase the phase transformation rate and to reduce the total surface area as reflecting grain growth.[27] Accordingly, it is believed that those nanograins could probably play a catalytic role enhancing the development of crystalline phases at early transformation temperatures. Generally, the activation energy of surface nucleation varies from ~150-850 kJ mol^{-1} depending upon crystallite size, synthesis techniques and conditions.[13] Nucleation can be controlled by modification of solid-liquid surface tension, pH variations and ionic strength of precipitation solution.[17]

4. CONCLUSION

This work presented our findings describing a concern on *in-situ* crystallization of TiO_2 nanotube arrays obtained as a function of electrolyte composition and its consequent effect of slow growth rate in DEG-HF electrolyte medium. The hydrofluoric acid content as low as 0.5% was found to give grain-like crystallites forming the tubular structure. With water additive, the nanograins with a fraction of partial crystalline phase are believed to appear on the tube wall due to the slow growth rate by the nature of DEG. The phase transformation temperatures for the DEG organic-based medium were found to be in the lower regime compared to those of the aqueous electrolyte. It is believed that those initially formed nanograins could probably play a catalytic role enhancing the development of crystalline phases at early transformation temperatures. A schematic diagram for possible *in-situ* crystallization in the DEG electrolyte system was proposed as a function of reaction rate-cation size of fluoride bearing species relation. The concept of slow growth fashion has been proved by investigating the anodization current density behavior, confirming the oxide formation growth process acting its rate in the very low regime of anodization current of less than 0.1 mA/cm^2 in the 24 h anodization period.

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