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Development of nano-structured titanium oxide thin films using a gas carving technique

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ABSTRACT

A method is developed for producing nano-structured titanium oxide thin films using H_2 gas interaction with titanium thin film at a high temperature. These nano-structured thin films have been formed on a quartz crystal substrate. Titanium (Ti) thin films were deposited on the quartz crystal using a RF magnetron sputterer. The samples were placed in the oven at 500-800°C for 5 hours. The gas mixture of 1% H_2 in N_2 was introduced in the oven. The process of Ti annealing in the presence of H_2 carves Ti films into nano-structure shapes. The process is a gas-solid interaction. Thin films were characterised using Scanning Electron Microscopes (SEM) and X-Ray Diffraction (XRD) technique. The nano structures formed have dimensions in a range of 25nm – 150nm obtained after gas carving.

Keywords: Nanostructures, titanium, H_2, thin film

1. INTRODUCTION

Micro and nano structured thin films have received considerable attention in recent years due to their high potential for commercial and technological applications. These materials have utilization in optical, electrical, and micromechanical devices. These nano-structures are promising, especially for the preparation of large surface to volume area with high aspect ratios, which are difficult to form by lithographic processes when dimensions approach features of less than 100nm.

One of the materials, with plenty of applications in nanostructure form, is titanium oxide. It is the most widely used white pigment because of its brightness and very high refractive index [1]. When it is deposited as a thin film, its refractive index and colour make it an excellent reflective optical coating for the development of dielectric mirrors. In cosmetic and skin care products, titanium dioxide is used both as a pigment and a thickener. It is also an effective opacifier in powder form. Titanium dioxide is a photocatalyst under ultraviolet light. Additionally, it offers possibilities in the development of gas sensors and solar cells [2]. TiO_2 is one of the most important engineering materials which has been used in chemical sensors [3, 4]. Titanium oxide in the shape of nanowires [5] [6] and nanoporous structures [7] is desirable for these applications because of its large surface area. Larger surface area provides more active sites for enhanced molecular interaction, high surface activity and high sensitivity.

Several approaches have been explored for modifying the surface morophology of titania by several researchers. Imhof and Pine reported macroporous material of titania, silica and zirconia by using the emulsion droplets as templates around which material is deposited through sol-gel process [8]. Pan et al. reported ultra-long nano-belt of zinc, tin and indium oxide by evaporating commercial metal oxide powder at high temperature [9] and Sehaoon et al. reported producing of titania surfaces compromised of nanofibres by reaction with gases at high temperature [10].

The increased demand for nanostructured materials is often complicated by the conflicting demands for precise control of fine features and for large scale mass production [10]. In this paper, we developed a simple method by using titanium thin films to produce nanostructures titanium oxides by gas carving technique. Titanium thin films were deposited using a

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RF magnetron sputterer. The effect of gas carving process on titanium is investigated by studying the electron microscopy (SEM) images and X-Ray diffraction (XRD) graphs.

2. EXPERIMENTAL

2.1. Titanium Thin Film Deposition

Ti films of 2μm thickness were sputtered on the smooth surface of the polished quartz crystal substrates using a RF magnetron sputterer. For cleaning, the samples were rinsed in acetone, isopropanol and with deionised water before placing in the chamber. The chamber of the sputterer was evacuated to a pressure of 10^{-3} Pa. The distance between the target and sample was 80mm. Power of 120W was used and argon gas was introduced in the sputerring chamber at a pressure of 1.33Pa. During the process the samples were heated at elevated temperatures of 120°C.

2.2. Characterization of Ti thin film

Morphology of Ti thin films was investigated using SEM and XRD. Figure 1 shows the SEM image of the surface of the titanium thin film. It shows that the crystallites of titanium film are densely packed and consists of nano polygonal shapes. Most of these polygonal have dimensions of less than 100nm.

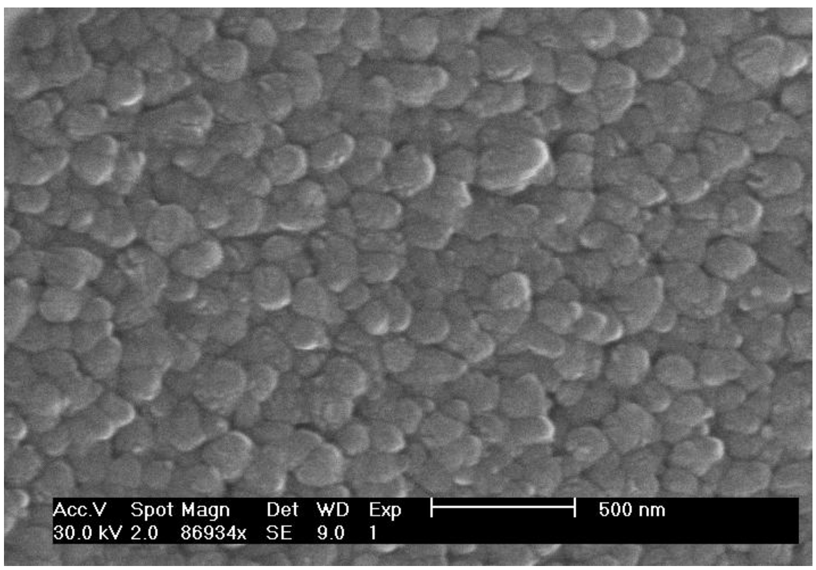

Figure 1 SEM image of the titanium film surface sputtered on quartz

Figure 2 shows the XRD pattern for Ti film before carving. It shows that the dominant faces are [0,0,2], [1,0,2] and [1,0,3].

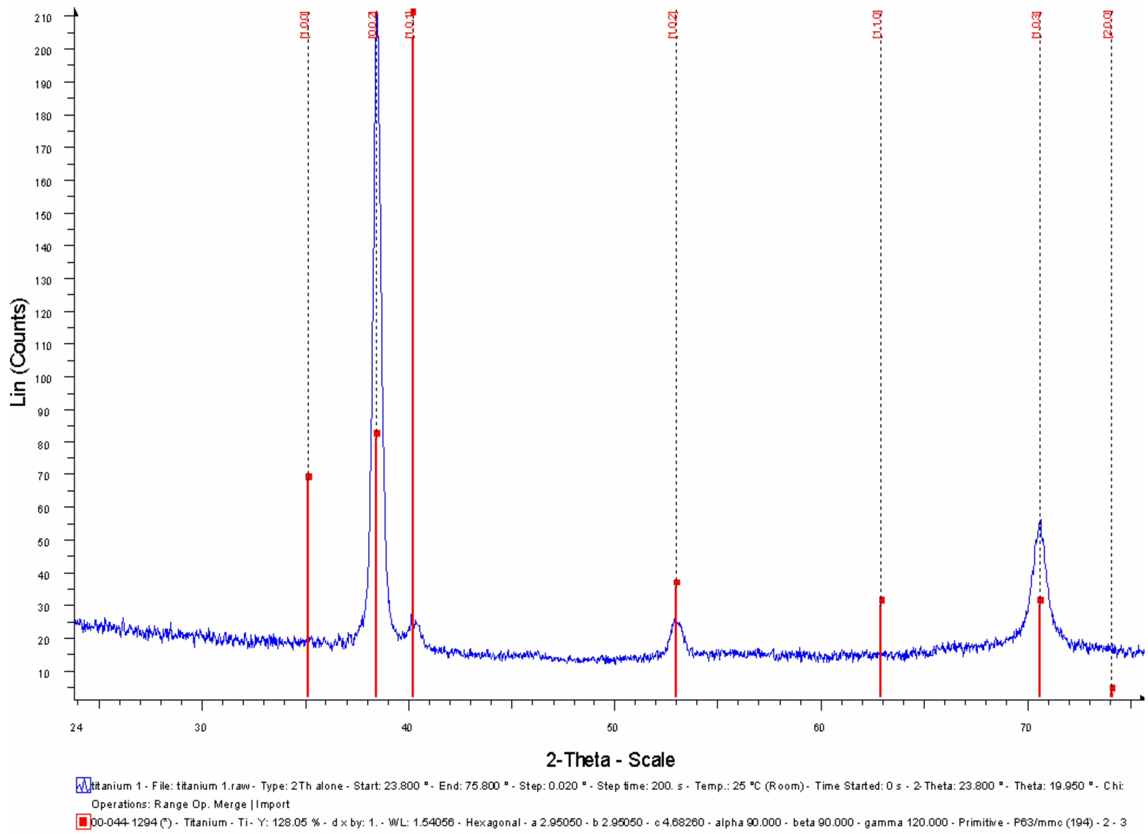

Figure 2 XRD pattern of titanium film on quartz

2.3. Gas carving of Ti films

The gas carving process was conducted in a temperature range of between 500°C to 800°C. A combination of 1% H_2 in N_2 was used as the etchant. Flow rate was approximately 250 ml/minute. The process lasted for 5 hours.

3. RESULTS AND DISCUSSION

3.1. SEM images of thin films

Figure 3, Figure 4 and Figure 5 shows the SEM images of the surface of the titanium etched at 640°C. The resulted thin film consist of nanorods and nanostructures having one of the dimensions in the order of 20-150nm.

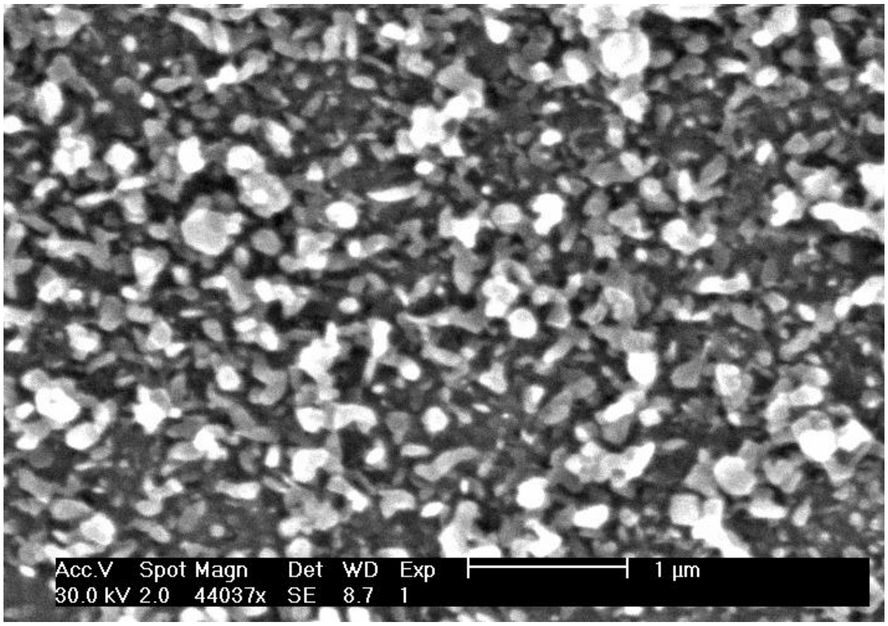

Figure 3 Titanium film surface carved at 640°C

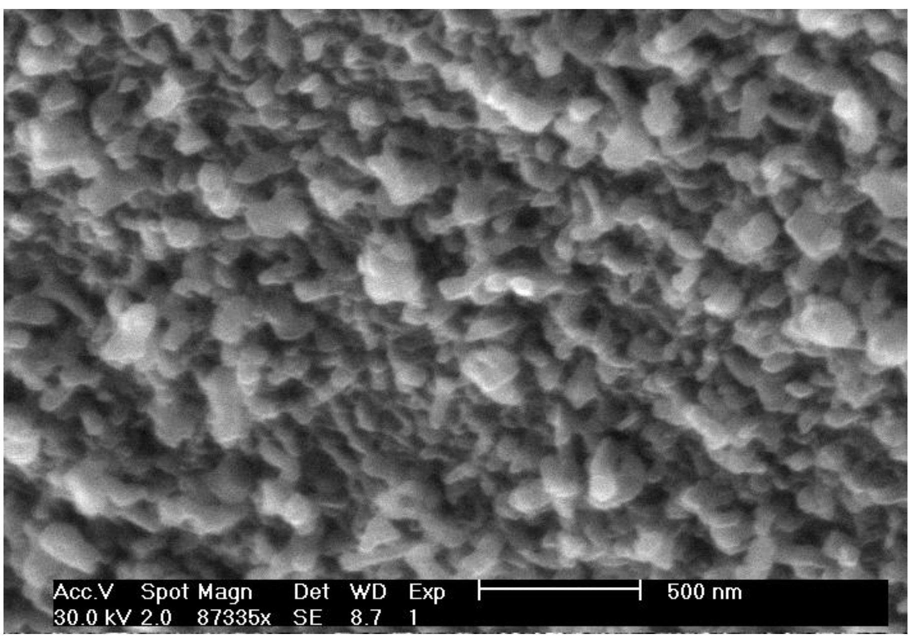

Figure 4 Titanium film surface carved at 640°C (shown at 45° angle)

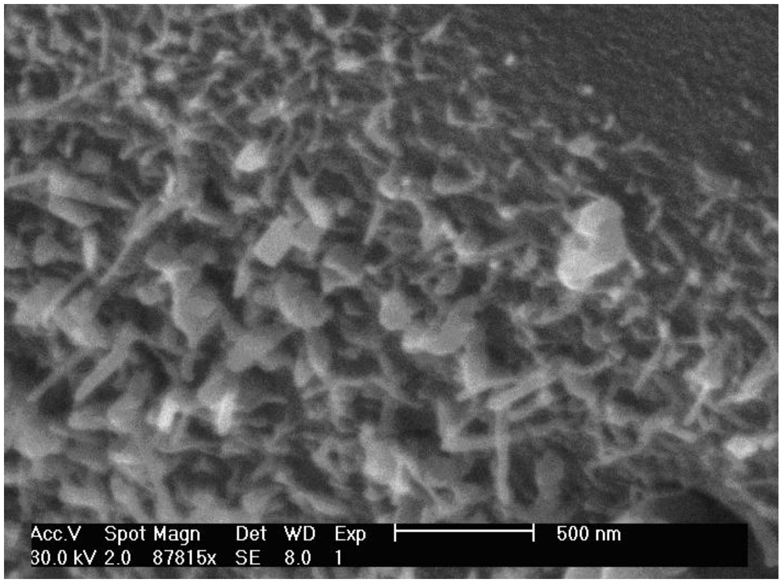

Figure 5 Titanium film surface carved at 640°C (shown at 45° angle)

Figure 6 and Figure 7 shows the SEM images of the surface of the titanium etched under 1% hydrogen in nitrogen. The samples were etched at 700°C. The figure shows that the titanium film forming crystals with spacing and dimensions in the range of 70-150nm.

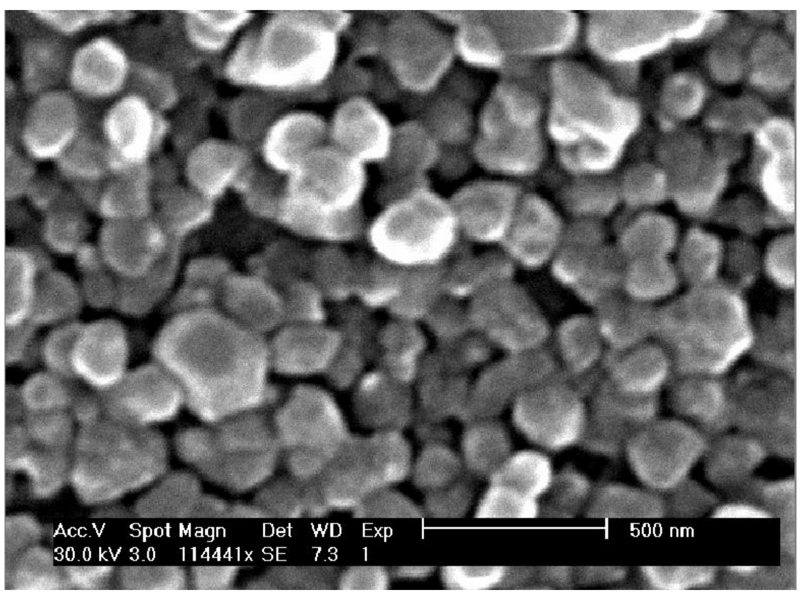

Figure 6 Titanium film surface carved at 700°C

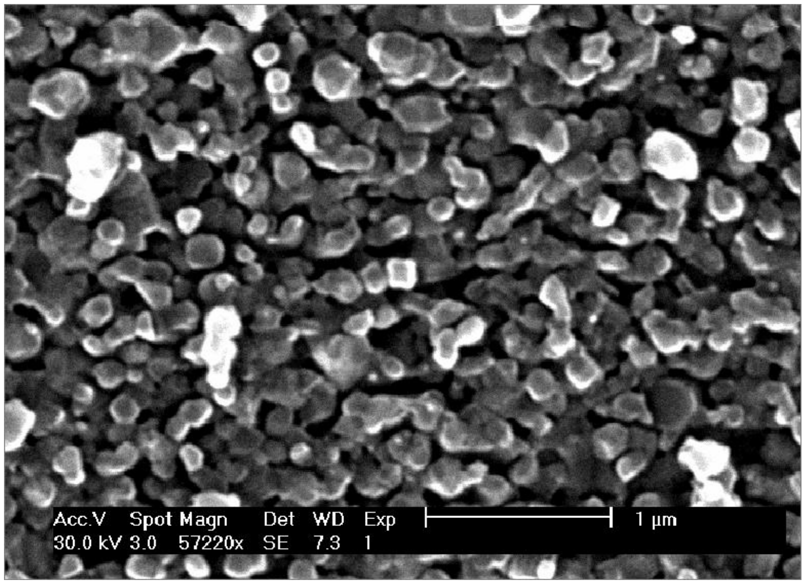

Figure 7 Titanium film surface carved at 700°C

Figure 8 and Figure 9 shows the different scale SEM images of the surface of the titanium etched under 1% hydrogen in nitrogen this time at 800°C. The etched titanium consists of structures consists of nano plates with thickness in an order of a few 10^{th} of nm and having other dimensions less than 100nm.

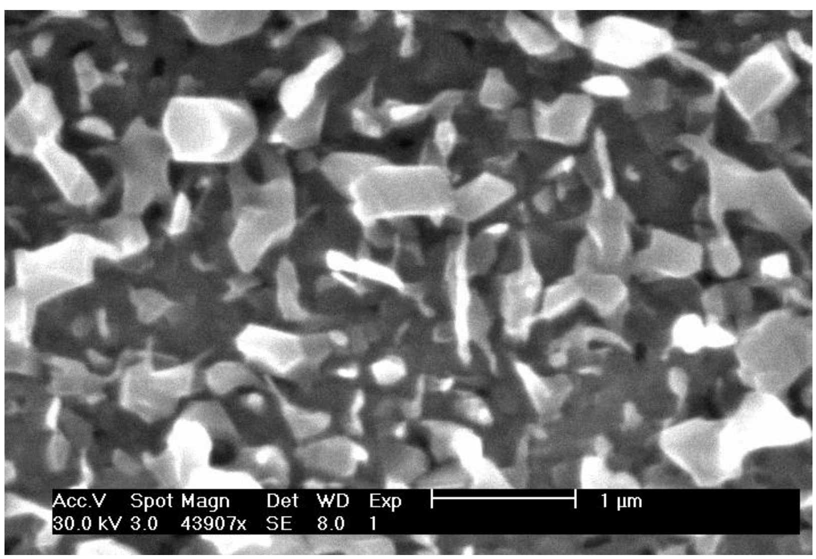

Figure 8 Titanium film surface carved at 800°C

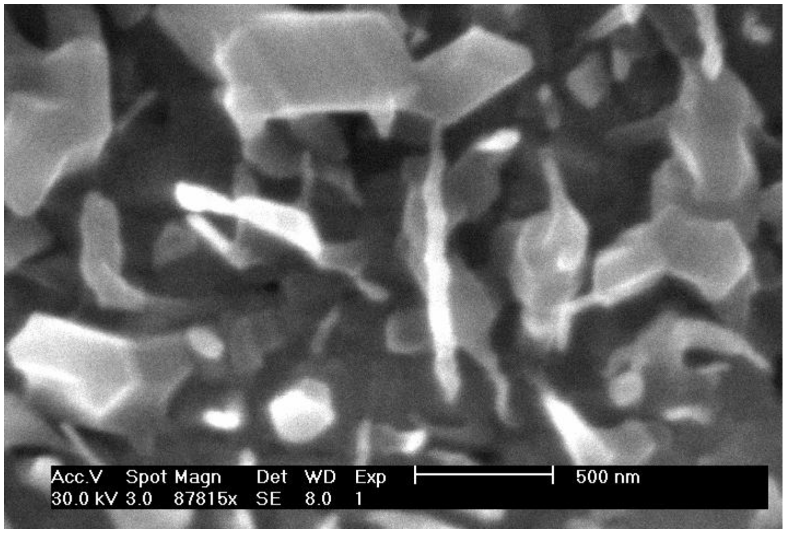

Figure 9 Titanium film surface carved under hydrogen at 800°C

3.2. XRD patterns of the etched films

Figure 10 shows the XRD pattern for the sample carved at 700°C. The XRD patterns for other temperatures are fairly similar. It reveals that thin films have changed into rutile form of titanium dioxide. The dominant faces of the rutile form are [1,1,0], [1,0,1], [1,1,0], [1,1,1], [2,1,1] and [2,2,0].

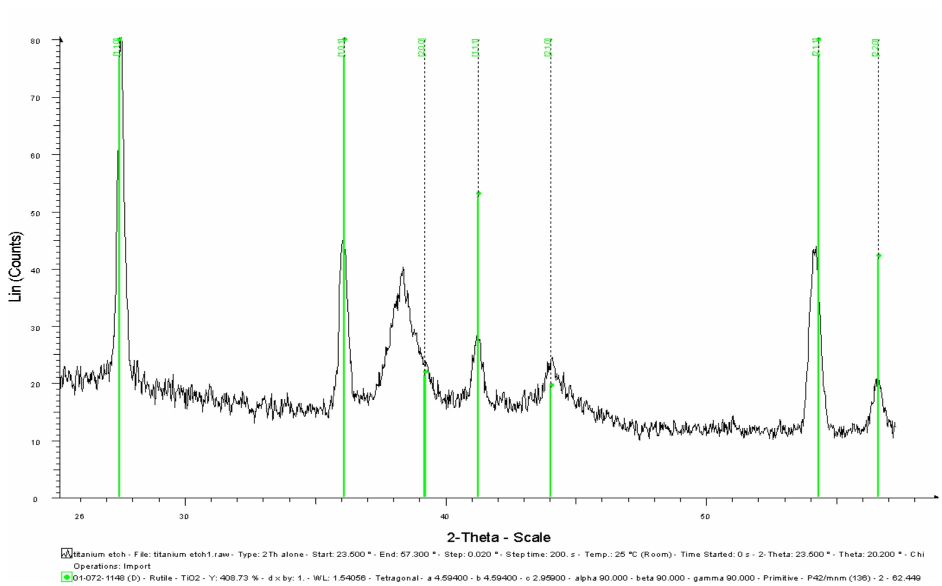

Figure 10 XRD pattern of titanium on quartz after gas carving

4. CONCLUSIONS

A simple method has been developed for producing nano-structured titanium oxide thin films using H_2 gas interaction with titanium at high temperatures. Our experiments revealed that H_2 gas can carve Ti film into nanorods at temperatures below 700°C. On the contrary, at higher temperatures plate type structures appeared. H_2 did not have any effect on Ti films at temperatures less than 600°C. This work describes a simple way of shaping Ti films into nanostructured form of titanium oxide. Such films have numerous applications in electronics, optical, sensing and device fabrication industries.

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