Synthesis of Titanium Nanoparticles with Controlled Size Variation by Physical Vapor Deposition

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ABSTRACT

We report the synthesis of Ti nanoparticles by e-beam physical vapor deposition technique. We were able to control the diameter of the formed Ti nanoparticles by varying the deposited film thicknesses in the fabrication process to different values of 2, 4, 6, 8, and 18 nm. Topography images taken by atomic force microscopy have revealed clear formation of Ti NPs with various ranges for diameter and height of Ti nanoparticles for the different deposited thicknesses. The produced results showed that an increase in the deposited film thickness leads to an increase in the diameter of Ti nanoparticles. Average diameter of Ti nanoparticles varied from 55 nm, for film thickness 2 nm, to 145 nm for film thickness 18 nm. Coverage and separation of nanoparticles were also affected by the deposited thickness. Nanoparticles were separated by 17.5 nm to 153 nm for thicknesses 2 nm and 18 nm, respectively. Moreover, almost all NPs have height between 8 and 15 nm in case of thickness 18 nm. This variation in height is different for the different deposited thicknesses. Our study provides deep insight on the process of controlling size of nanoparticles and its effect on their structural properties.

Keywords: Ti nanoparticles, size variation, e-beam PVD, thermal annealing, thickness variation.

1 INTRODUCTION

Synthesis of nanomaterials with metal nanoparticles (NPs) (Ag, Au, Cu, Pd, Ti, etc.) deposited on glass or silicon surfaces, have gained much attention in material science over the last decade [1]. The utilization of such nanocomposites and their novel properties can lead to expanding their applications in optics, medical diagnostics, analytical chemistry, catalysis, photo catalysis etc. [2, 3]. The properties of the NPs are mainly governed by the type of material and structure parameters of the NPs which are mainly affected by the synthesis technique [4, 5]. Hence, controlling the variation in size of NPs leads to a control over their enhancement role in application devices.

Titanium, which is among series of materials that we are synthesizing and investigating, is as strong as steel but with much less density. This makes Ti an important alloying element with many metals including aluminum, molybdenum and iron. Moreover, Ti is considered to have a relatively high anti-corrosion property and high optical reflectivity. A study of such unique properties at the nanoscale can expand the benefits of utilizing the Ti nanomaterials [6 - 8].

In this paper we report the synthesis of Titanium (Ti) nanoparticles of different sizes (diameters and heights) by controlling the thickness of deposited films of Ti during the electron-beam physical vapor deposition (e-beam PVD) process. Thermally annealing all deposited Ti films at 800 ^{o}C in tube furnace under ambient pressure is a necessary step to form the individual Ti nanoparticles. Sizes, distribution, topography of the formed Ti NPs were investigated.

2 EXPERIMENTAL

Thin films of Ti material (Ti pellets of 99.99% from Kurt J. Lesker) were deposited on Silicon substrates (B doped <100>, and 625 µm with 200 nm thermal oxide) by e-beam PVD inside high vacuum chamber with pressure ~ 10^{-6} Torr. Deposition rate was about 0.1 Å/s. Deposited Ti film thickness were varied to 2, 4, 6, 8, and 18 nm by varying the deposition time. To form the nanoparticles, deposition process was followed by thermal annealing at 800 ^{o}C under Argon inert atmospheric pressure for 30 minutes in tube furnace. Atomic force microscopy (AFM) provided by Agilent Technologies was utilized to investigate the formation of the Ti nanoparticles on Si-substrates for Ti annealed thin-films samples compared to as-deposited ones. Ti thin films with different thicknesses were deposited and processed under same conditions.

3 RESULTS AND DISCUSSIONS

Figure 1(a) shows 5x5 µm topography surfaces of As-deposited Ti 4-nm thin film on Si substrate. Surface is very smooth with very low value of roughness 0.05 nm. On the other hand, Figure 1(b) shows annealed surface of Ti 4-nm thin film with higher roughness value 0.32 nm. Higher roughness is an indicator of formation of nanostructures on the surface. Individual Ti NPs are clear in topography image compared to as deposited thin film in Figure 1(a). A uniform formation of Ti NPs is a result of the thermal

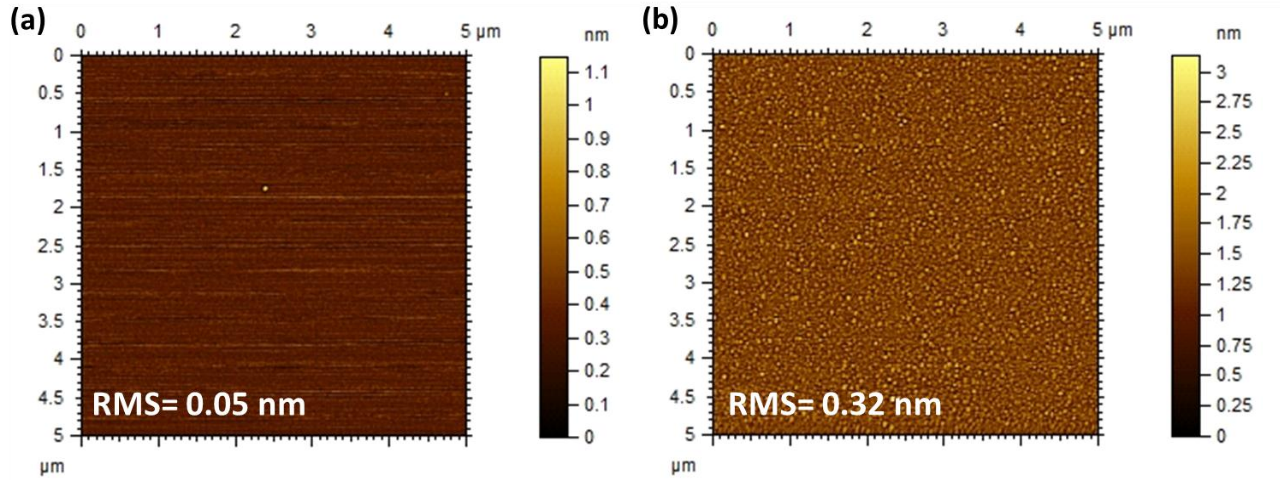

Figure 1 Ttopography AFM images of Ti 4nm samples (a) As-deposited film and (b) annealed film at 800 ^{o}C for 30 minutes.

annealing process followed the PVD process. Topographical scanning was conducted for all the other as-deposited and annealed Ti thin-films with thicknesses (2, 6, 8, and 18 nm). Figure 2 shows the topography images of Ti annealed surfaces with the different thicknesses illustrating clear formation of individual Ti NPs on the surfaces.

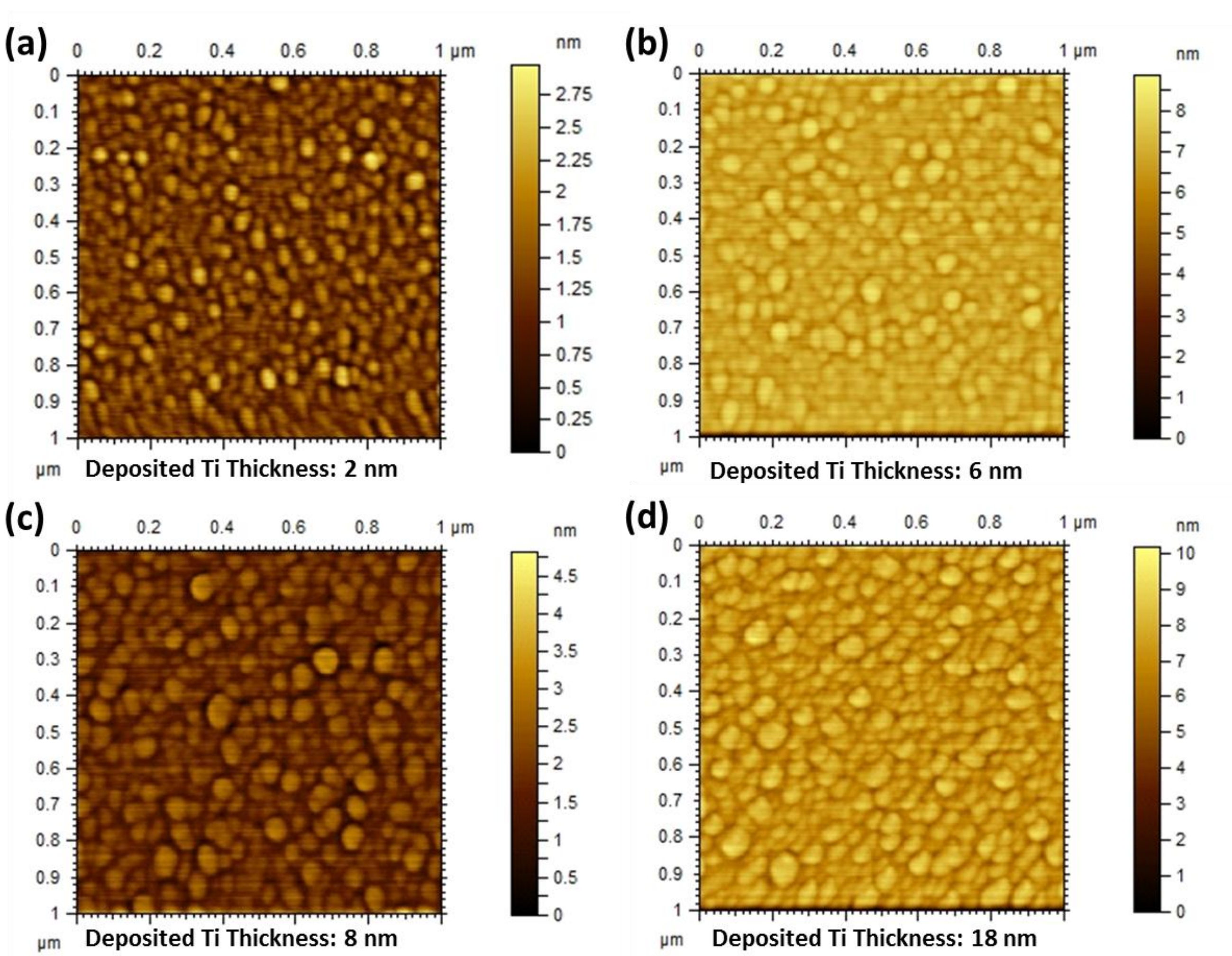

Figure 2 Topography images of the different deposited thicknesses of Ti after annealing at 800 ^{o}C for 30 min.

To measure the structural parameters of the formed Ti NPs, we applied profile lines on the studied surface as illustrated in Figure 3 that shows an example of measuring diameters and separations of Ti nanoparticles. Average separation between NPs varied from 17.5 nm to 153 nm for thicknesses 2 nm and 18 nm, respectively.

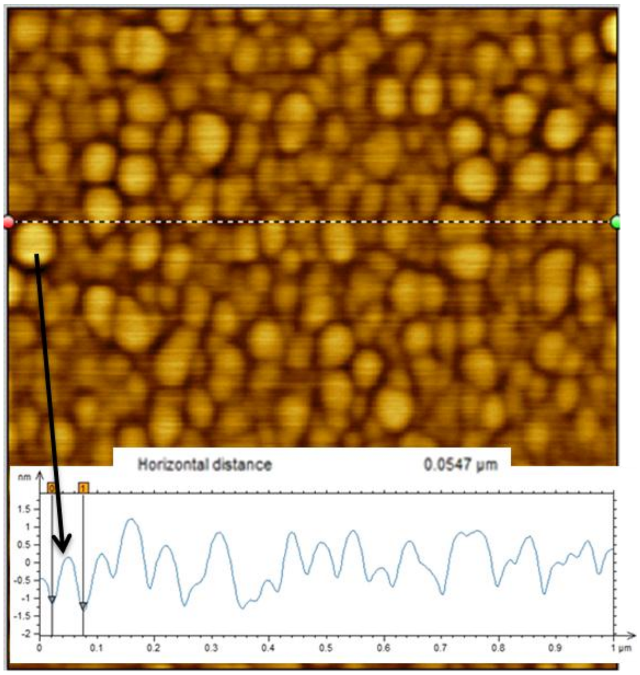

Figure 3 1x1 µm surface of annealed Ti film with dashed profile line showing the diameter of one Ti nanoparticle.

After we performed statistical study on the depicted surfaces of Ti thin-films with the different thicknesses using the provided AFM software, we were able to study the relation between the deposited Ti film thickness and diameter of Ti NPs as shown in Figure 4. Larger size of NPs for higher deposited thickness was observed. In case of thickness 2 nm, we found the minimum diameter of nanoparticles to be 33 nm and maximum about 73 nm with an average diameter about 55 nm. The largest average diameter was 145 nm for film thickness 18 nm.

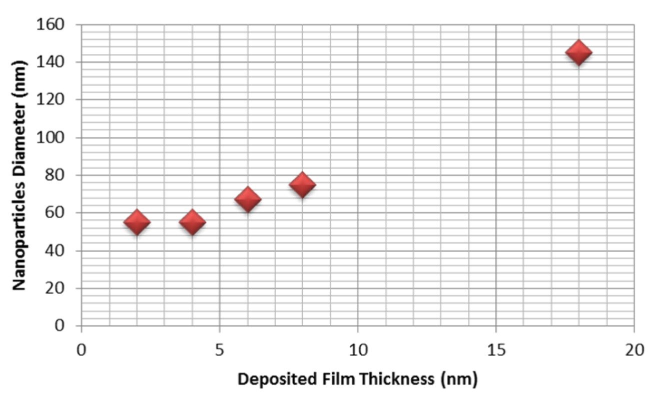

Figure 4 The variation of the formed Ti nanoparticles with the thickness of the annealed deposited Ti films.

This behavior of size variation when varying the deposited Ti film thickness is a result of the thermal conductivity for Ti (31 w/m K). This allows Ti material to be more thermally active when annealed. The variation in thickness can affect the disipation of the thermal wave on the surface and into the bulk material of the deposited thickness. Other reason can be a difference in the surface energy between Ti material (1650 mJ/m2) and Si substrate (1240 mJ/m^2) which affects the adhesion of the metal particles and their physical interaction with the substrate. High surface energy for Ti leads to increase the interaction among the Ti-material and hence lower interaction with the Si substrate. For higher thicknesses, more Ti-material exists which causes higher attraction and adhesion among Ti-NPs leading to larger size of NPs. In addition, the hight of the Ti-NPs formed from the different thicknesses is also affected by this high surface energy of Ti. As a result of the variation of both the diameter and height of the NPs, the roughness of the annealed Ti surface is affected.

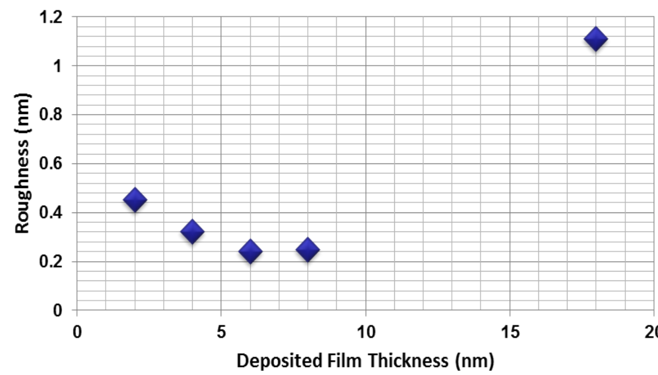

Figure 5 The variation of roughness values of the different annealed Ti film thicknesses.

Figure 5 shows a nonlinear behavior of Ti surface roughness with the variation of deposited thickness. Surface with lowest roughness value 0.25 nm, i.e. smoother surface, was for the film thickness 6 nm while highest roughness value 1.1 nm was for the highest film thickness 18 nm. We notice that the lowest film thickness 2 nm didn't lead to smoothest surface. This is mainly because surface roughness is related to the combination of separation, diameter, and height of NPs. Even though NPs' diameters at the thickness 2 nm were the lowest, they were separated by about 20 nm with their height exceeding the heights of NPs formed at the film thicknesses 4 and 6 nm.

To further understand the surface roughness behavior, we analyzed the height distribution of Ti NPs on each surface of the annealed film thicknesses by the provided AFM software. We noticed a variation in the height of NPs among the surface itself for all thicknesses in different manners which contributes to the nonlinear roughness behavior with various thicknesses. Figure 6 shows the height distribution of Ti NPs for the Ti film thickness 2 nm and 18 nm for comparison. In Figure 6 (a), 90% of NPs are between 3 and 4.8 nm in height which is higher than NPs

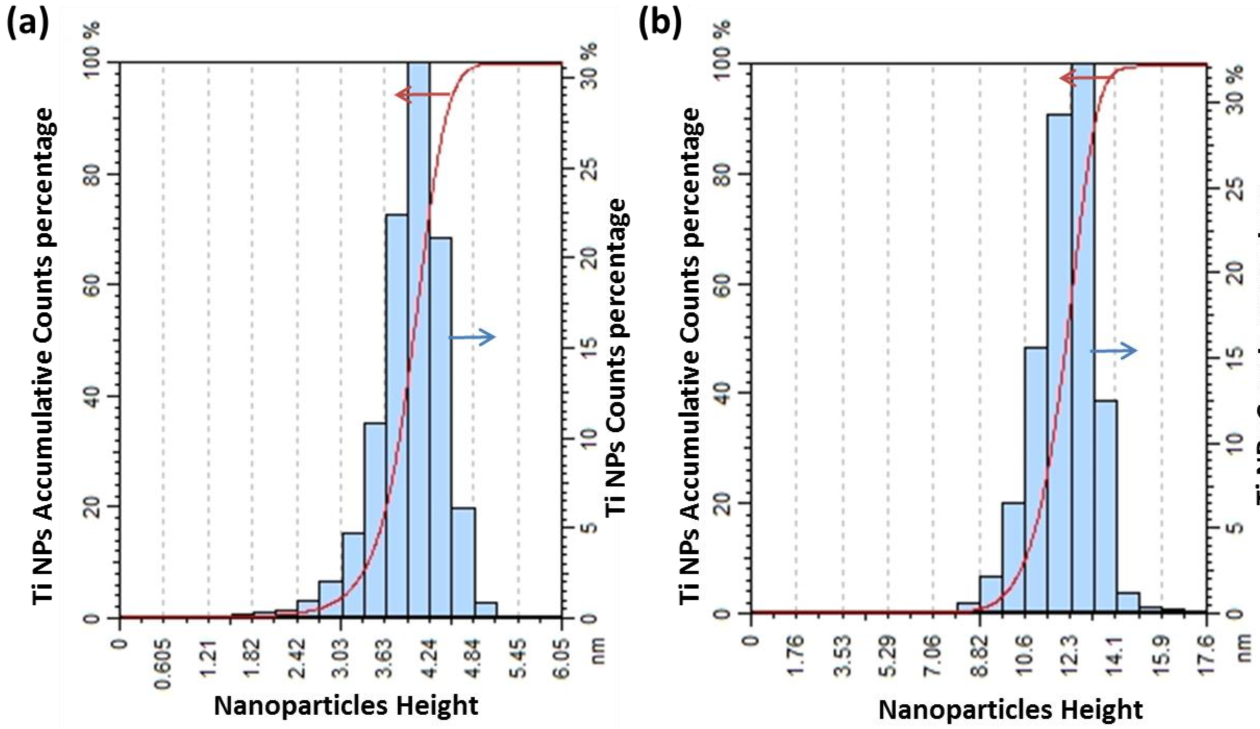

Figure 6 Height distribution of Ti NPs for the annealed deposited film thickness (a) 2 nm and (b) 18 nm.

formed from 4 and 6 nm thicknesses (results not presented). We also notice that the height of the NPs exceeded the original deposited thickness 2 nm which increased the separation between the NPs. This has led to an increase in the roughness value. In Figure 6 (b), 90 % of NPs were between 10 nm and 14 nm i.e. about three times higher than NPs formed from the 2-nm thickness. This caused the higher surface roughness of the 18 nm film, beside the larger diameter of the NPs.

4 CONCLUSIONS

We have successfully formed Ti NPs of size between 50 and 145 nm by e-beam PVD followed by thermal annealing process. Increase in NPs size was observed with increasing the deposited thickness. On the opposite, surface roughness is not linear with deposited thickness. Difference in diameter, height and coverage of Ti NPs can be a result of thermal conductivity and surface energy of Ti material. We have developed a controlled procedure of forming metallic NPs with desired size and distribution.

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