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Experimental Study of a Synthesis Ti Nanoparticles with Nanosecond Laser Pulses

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ABSTRACT

We report the growth and characterization of Ti nanoparticles thin film of on glass substrate by pulse laser deposition method. The Ti thin film prepared with different parameters (different energy 600,1000 mJ)and (different substrate temperature 150,200,250 ċ). Surface topography studied by atomic force microscopy revealed narrowed size distributions, with particle sizes ranging from 19.18 to 65.89 nm. X-ray diffraction showed nanostructured phase with (2θ = 35.093 , 38.421 , 40.170 , 53.004, 62.49 degree). The results showed the Average Gran Size increased with increasing substrate temperature and RMS roughness increased with increasing substrate temperature. The results showed the increasing of energy pulse leads to increasing the grain size .Optical properties measurements showed transformation from metallic properties of bulk Ti to semiconductor properties when formed by sort of nanostructure evidenced by the formation of optical energy gap about (2.2 to 3.5 eV) with different conditions.

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INTRODUCTION

Pulsed laser deposition (PLD) has been shown to be a flexible, simple and controllable method for producing thin films of non-volatile materials. Its advantages over other deposition techniques such as molecular beam epitaxy and metallorganic vapor phase epitaxial include the unique process of source material transfer which limits the amount of heated material virtually only to that which is liberated; its pulsed nature ,which affords high controllability of the deposition thickness, plus the potential of synchronizing the high flux/short duration pulses with pulsed reactive gas sources , the high kinetic energy of the ablation plume, which promotes surface mobility on the growing film and the ease of source material replacement (P. Guptasarma *et al*, 1992).

Since many decades, Titanium (Ti) films have been extensively studied for their applications in various fields especially in aerospace, microelectronics and diffusion barrier properties due to its high mechanical strength, excellent chemical and thermal stability and good corrosion resistance .Various groups has reported the effect of thickness on the properties of the Ti film deposited using a single deposition technique (A. *Gupta et al 1992*).

Titanium is a cheap, non-toxic and one of the most efficient material photo catalysts for extensive environmental applications because of its strong oxidizing power, high photochemical corrosive resistance and cost effectiveness . Titanium material could be classified for contemporary processing methods according to their magnetic properties, density, mechanical, thermal and other characteristics. Titanium is a material difficult to process, due to its high melting and boiling points (Milosavljević *et al* 1996).

In PLD technique the energy source, which creates the plasma plume of the target material, the laser, is independent of the deposition setup.(M. Caidi *et al* 2004). The fundamental laser emission of Nd:YAG laser is at 1064 nm which is well outside the desired range for pulsed laser deposition of most of the materials. The fundamental emission of Nd:YAG can be frequency doubled to 532 nm wavelength using a suitable nonlinear optical crystal at the cost of nearly half the laser energy at fundamental(S. A. Chambers *et al* 2002).

In this work, we report on the results of initial experiments exploring the possibility of preparation of Titanium thin films by Pulsed Laser Deposition (PLD). The optical properties have been investigated.

MATERIAL AND METHODS

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To preparation Ti Nanoparticls, we used the PLD system it consist of two main parts shows in figure (1). First, vacuum chamber includes multiple accessory, target holder, substrate holder, laser window, thermocouple, vacuum gage, substrate heater use I.R. lamp that easily field replaceable, substrate can heated to 300 ċ The substrates are placed on substrate holder at distance (4cm) from the rotated target. The pressure in the stainless steel vacuum chamber having many viewing ports chamber be can decreased under 10-6 mbar by use two stages rotary and diffusion pump.

Second, Q-switched Nd:YAG laser system that works in the TEM00 mode and generates fundamental pulse at wavelength of 1064 nm and doubled frequency 532 nm by a second harmonic generation. The laser pulse characterized by duration 10 ns with repetition rate of 6 HZ and energies (400-1000) mJ/pulse . The laser beam is focused on the target surface by using lens with focal length (30)cm at the incident angle of approximately 45°. The PLD thin films were analyzed by AFM, XRD and UV-Visible spectrophotometer.

Fig. 1: PLD system Set-Up.

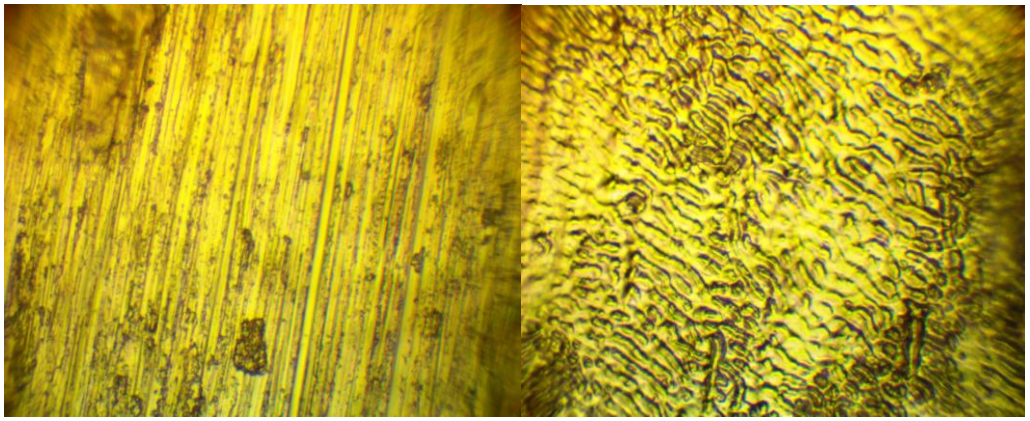


Fig.2: (a) Ti target Before ablation (b) Ti target After ablation

RESULTS AND DISCUSSION

First:

Figure(3) shows AFM images of titanium films deposited on SiO2 glass substrate and diameter percentage of nanoparticles at pulse energy 60mJ at vacuum chamber pressure (10^{-4}) mbar as a function of substrate temperature. The patterned surface obtained this way consists of smooth metallic structures; also in our case we obtain grating lines, on top of the substrate In (Figure 3-b). These are apparently the result of the second laser ablation that leaves behind clusters that attach to the Ti stripe on the surface. It is shown that the size of these clusters can be controlled to some extent by the second laser pulse power density. At low enough patterning laser energy (first pulse), narrow lines are formed where the clusters, otherwise alongside the smooth Ti stripes, coalesce to form a single narrow line. [7]

The Substrate temperature plays an important role in determining the structure of Ti thin films which are fabricated on SiO_2 substrate.

From the topographic images it can see that the films deposition at 150C° appears to be more uniform then the topography of the sample deposition at 200C°and 250C°. The RMS roughness also increased with increasing substrate temperatures, the roughness value are (0.52nm, 0.702nm and 1.49nm) for thin films deposited at (150C°, 200C°and 250C°) respectively in figure(4). It can be clearly seen from the images that up to the substrate temperature of 200 ◦C, the grains are of Three-dimensional hexagonal structure and with further increase in the

substrate temperature, the grains size increases.

Second:

Fig.6. Shows AFM images of titanium films deposited under atmosphere 10^{-4} mbar at flow of Ar gas pulse energe100mJ at deferent substrate temperature .

Third:

When we increase the substrate temperature this improve the adhesion of deposited material

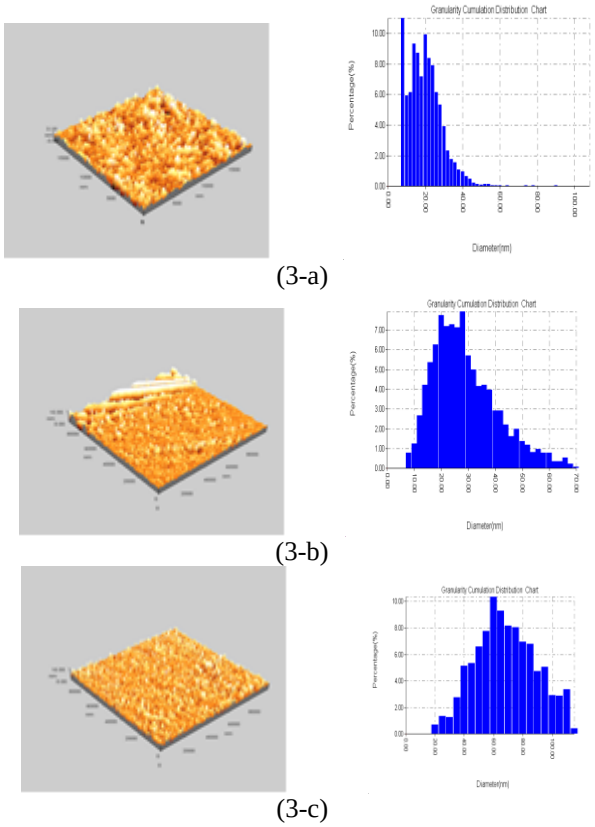


Fig. 3: AFM images of titanium films deposited on SiO_2 substrate at vacuum chamber pressure (1×10^{-4}) mbar, and pulse energy(60mJ) at different substrate temperature: (a) 150ċ (b) 200ċ (c) 250ċ.

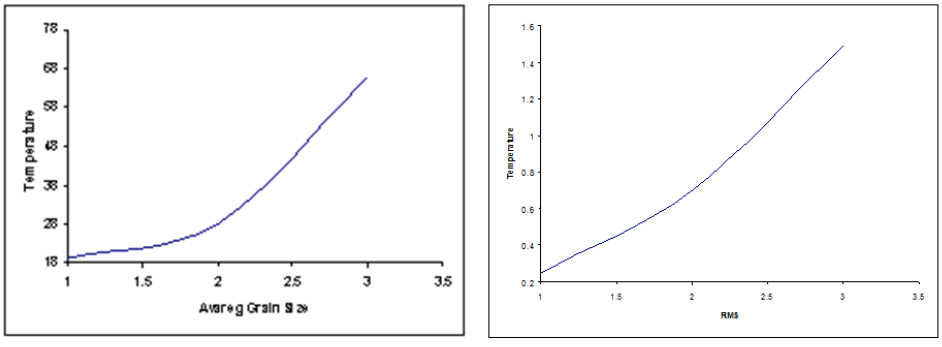
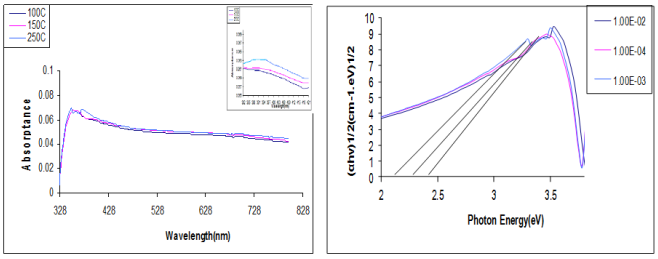


Fig. 4: Ti films for different substrate temperatures 150, 200, and250°C(a) The Average Gran Size increased with increasing substrate temperatures.(b) The RMS roughness increased with increasing substrate temperatures



(a) *(b)*

Fig. 5: UV-Viseble spectrum of Ti films for different substrate temperatures 150, 200 and 250°C Absorption spectrum, (b)band gab spectrum.

UV-Visible spectrum for sample that indicate the peak at ultraviolet wavelength region. The observation absorption peak in the ultraviolet wavelength region which can be attributed to the absorption due to the interband transition in Ti nanoparticles. An interband absorption can be possible at shorter wavelengths due to the transition of an electron from the occupied d-level state to an empty state in the conduction band above the Fermi level in noble metals.

The physical idea underlying the blue-shift trend observed in noble metal clusters is based on the assumption that due to the localized character of the core-electron wave functions, the screening effects are less effective over a surface layer inside the metallic particle. Close to the surface the valence electrons are then incompletely embedded inside the ionic-core background. Surface effects are identical for large spherical particles, it was shown that the blue-shift of the Mie-resonance is a consequence of the reduced screening interaction in the surface region (S. Fedrigo *et al* 1993).

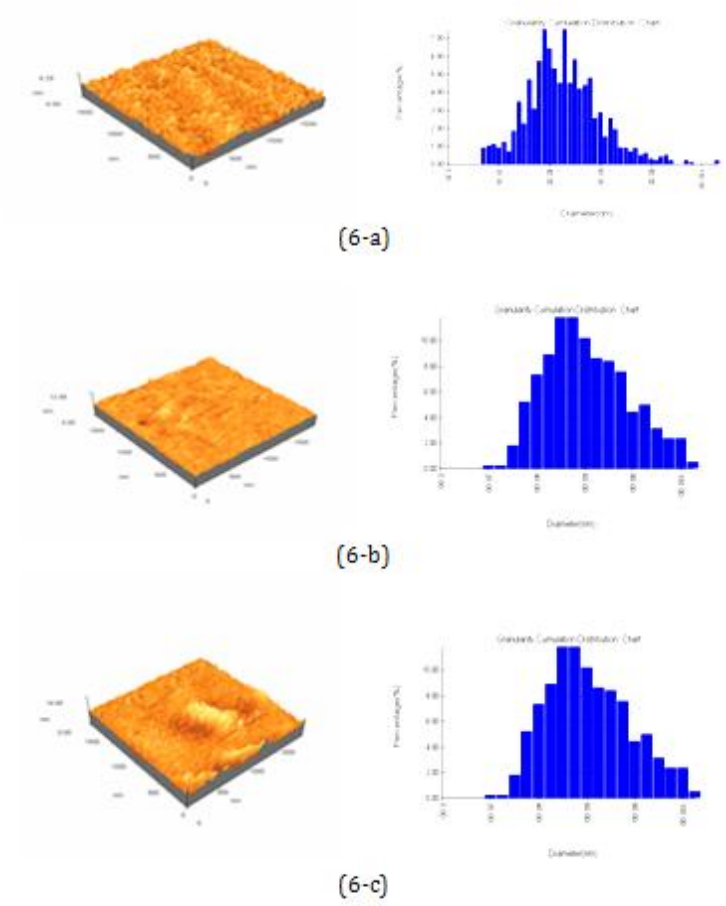
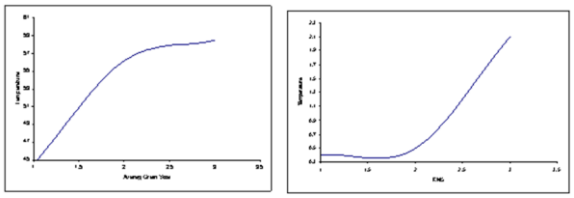


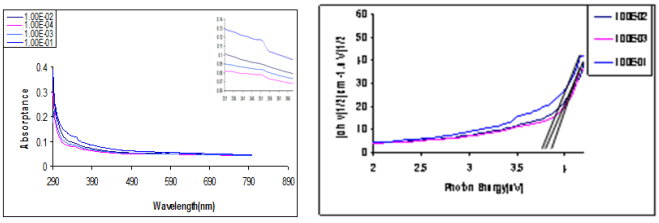
Fig. 6: AFM images of titanium films deposited on SiO_2 substrate at vacuum pressure (1×10^{-4}) mbar, and pulse energy (100 mJ),substrate temperature: (a) 150ċ (b) 200ċ (c) 250ċ.

At flow of Ar.gas.



(a) (b)

Fig. 7: Ti films for different substrate temperatures 150,200,a nd250°C (a) The Average Gran Size increased with increasing substrate temperatures. (b) The RMS roughness increased with increasing substrate temperatures



(a) *(b)*

Fig. 8: UV-Visible spectrum of Ti films for different Ar pressure. (a) Absorption spectrum, (b) band gab spectrum

In the pressure range in which the films were grown the interactions between the ejected species and the gas atom or molecules have been understood in terms of the scattering of the ejected species by the gas atoms or molecules (J.Gonzalo *et al* 1995),(D.B.Geohegan1994),(J.C.S. Kools 1993)and (J.Gonzalo *et al* 1996). In this case, the effect of the gas environment on the angular distribution of the deposited material film composition should be related to the mass and size of the species present in plasma. Assuming that the plasma is mainly formed by atomic species (Ti) and considering a simple scattering model based on hard spheres. From table (1) the RMS roughness was found to increase with increasing film thickness (number of pulses), which is associated with the increase in the crystal size due to surface energy minimization when the film gets thicker.The SEM pictures and EDX of Ti thin films deposited on to SiO2 in vacuum chamber pressure (10^{-4} mbar) and 60 and 100 mJ showed Ti particle less than 70 nm (19,28,65 nm) in vacuum and (44,56,58nm).

Table 1: Results of average Grain Size and Roughness with different laser parameters in vacuum and Argon gas.

sample	Energy	Temperature	Average Grain Size	Roughness	Pulse number	Used Gas	Target to Substrate distance
(2-a) (Ti)	60mJ	150 ċ	19.18	0.52	20	Vacuum	4 cm
(2-b) (Ti)	60mJ	200 ċ	28.09	0.702	30	Vacuum	4 cm
(2-c) (Ti)	60mJ	250 ċ	65.89	1.49	40	Vacuum	4 cm
(3-a) (Ti)	100mJ	150 ċ	44.46	0.402	150	Ar	4 cm
(3-b) (Ti)	100mJ	200 ċ	56.15	0.499	150	Ar	4cm
(3-c) (Ti)	100mJ	250 ċ	58.47	2.11	150	Ar	4 cm

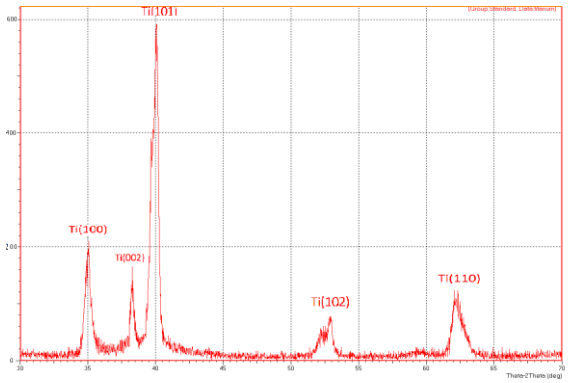


Fig. 9: XRD Patterns of Ti Nanoparticles Samples.

Table 2: Results of grain size from x-ray diffraction.

2θ Degree	(h k l)	FWHM Degree β	Grain size nm	int-f
35.093	(100)	0.026179938	5.554	25
38.421	(002)	0.008726646	16.825	30
40.170	(101)	0.030543261	4.833	100
53.004	(102)	0.021816615	7.101	13
62.49	(110)	0.030543261	5.309	11

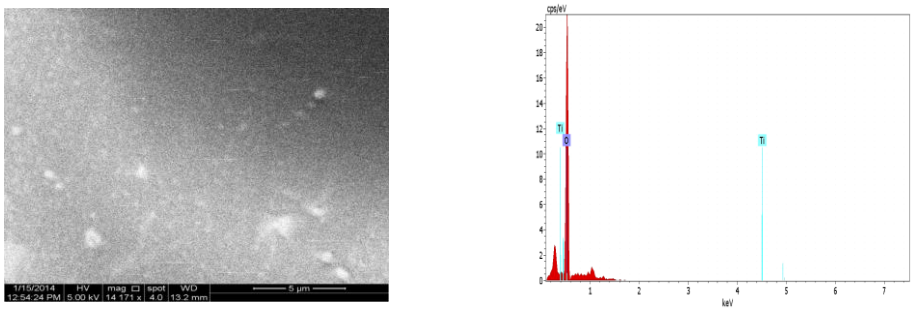


Fig. 11: SEM and EDX of Ti thin films deposited on to SiO2 in vacuum chamber pressure ($1 * 10^{-4}$) mbar, at 600mJ, 250 ċ, 50 pulse/s.

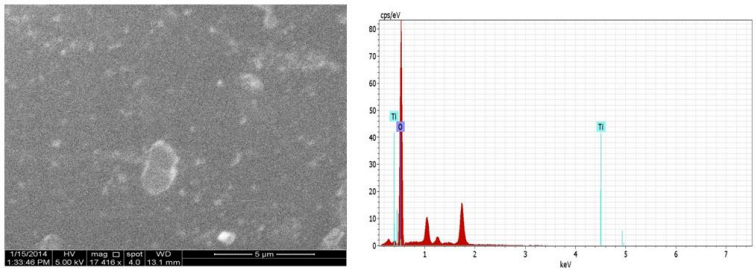


Fig. 12: SEM and EDX of Ti thin films deposited on to SiO2 in vacuum chamber pressure ($1 * 10^{-4}$) mbar, at 1000 mJ, 250 ċ, 50 pulse/s.

Conclusion:

The morphological characteristics of Titanium films deposited on SiO_2 substrates at different substrate temperatures were investigated in the present work. The increase in grain size of Ti thin films with increasing deposition temperature was confirmed by AFM. the RMS roughness also increased with increasing substrate temperatures. The grain size distribution is uniform for the films deposited at 150 ◦C,200 ◦C and 250 ◦C. The titanium films grown by PLD depend only on the pressure and not on the nature of gas environment. The SEM pictures showed Nano size of particles formed by laser ablation.

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