International Journal of Recent Research and Review, Vol. X, Issue 2, June 2017
ISSN 2277 – 8322

Laser Interaction with Tio_2 Nano Material Surface and Plasma Measurements

Haider A. Salih[1], Raad A. Khamis[2], Hussam N. Mohammed Ali[3]
[1&2]*University of Technology, Applied Sciences Dept. Laser Branch, Iraq*
[3]*Al-Furat Al-Awsat Technical University, Engineering Technical collage of Najaf, Iraq*

***Abstract-* In this paper the plasma generated from the surface etching of (TiO_2) surface in nano size, is studied and the surface morphology produced by this process. Since most of the deposited thin films are use the radicals, then these radicals are generated from the absorption of the electromagnetic radiation (laser) in our work are captured using very developed equipments. The generated plasma dramatically should be very dense and differ from those generated in the same way from the raw materials.**

***Keywords-* TiO_2 nano disk, titanium dioxide surface etching, nano plasma properties, plasma generation in nano scale.**

I. INTRODUCTION

Titanium dioxide usually (TiO_2) is used in paints, sunscreen, skin ointment, toothpaste, and pigments, in addition to its uses in the semiconductor devices such as photovoltaic devices [1]. The TiO2 absorbs the UV radiation from sunlight, this leads to generation of electron – hole pairs. The holes are as a OH radicals, with positive sign then the organic pollutant captured by these radicals and split up to harmless products.

The main advantage of TiO_2 nanomaterial is it has the ability to help solving many serious environmental and pollution problems. It also bears tremendous hope in helping ease the energy crisis through effective utilization of solar energy based on photovoltaic and photo catalytic water-splitting devices [2].

There are five different synthesis methods of TiO_2nano-powder synthesis, these are: sol-gel method [3], Micelle and inverse Micelle method [4], sol method [6], hydrothermal method [7], and finally the solvothermal method [4,5, and 8].

II. THEORY

Several theories which were presented years ago, such as the single particle motion where the plasma behavior explaining this theory considers the plasma as a single charged particle and the collective behavior is negligible [9]. The other theory that is used to explain the plasma theory is to consider the plasma as fluid or normal gases [10].In this research, the kinetic theory is the studied theory. This is because the plasma is generated from the interaction between the material surface and the photons or the electromagnetic waves. Besides, the well-known necessary plasma parameters are computed.

III. PREPARATION OF TIO_2 NANO DISC

Titanium dioxide (TiO_2) is an important semiconductor material for use in a wide range of applications, including photocatalysis, environmental pollution control and solar energy conversion. It is famous that titanium dioxide exists in three crystalline polymorphs, namely rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic). Rutile is the most stable phase, whereas anatase and brookite are metastable phase and transform to rutile upon heating. The rutile is the more stable phase as shown in several researches.

The preparation of the TiO_2 nanomaterial procedure including, as another nano materials, several procedures, such as the hydrothermal procedure, the sol-gel procedure etc.

In our work we select titanium oxysulfate sulfuric acid hydrate ($TiOSO_4$. H_2SO_4. H_2O) as a titania radicals, and cetyl trimethyl ammonium bromide (CTAB) as a structure-directing agent for the preparation of titania. Both $TiOSO_4$ and CTAB are cheap and common materials for industries and are available in the local markets and labs. After simply mixed together at a lower range of temperatures (30–60^oC), hexagonal-structured assemblies of nano crystalline titania were formed through hydrolysis of $TiOSO_4$ promoted by CTAB spherical micelles and condensation process (named as Hex-ncTiO_2/CTAB as nano skeleton).

Cetyl trimethyl ammonium bromide (CTAB) was used as template material. Titanium oxysulfate sulfuric acid complex hydrate ($TiOSO_4$. H_2SO_4. H_2O) was used as titania precursor. Hydrochloric acid (HCl) aqueous solutions were used as solvents in the hydrothermal procedure. CTAB/TiO_2 hexagonal structures were prepared in the following procedures:

A concentration of 2.4 g $TiOSO_4$ was mixed with 25 mL H_2O under constant magnetic stirring until the mixed solution turned into colorless solution at 50^oC, and then 20 mL CTAB (40 mM) was added into the colorless solution and hold statically for 24 h at 50^oC. The product obtained was filtered, washed with distilled water for several times, and dried at 120^oC a day.

Hydrochloric acid aqueous solutions with different concentrations were initially prepared from concentrated HCl with distilled H_2O, including 0.1– 7 M. Subsequently, 0.5 g Hex-ncTiO_2/CTAB nano-skeleton was dispersed in 30 mL of the HCl aqueous solutions with stirring for 30 minutes, and then transferred into 50-mL container of a Teflon-lined stainless steel autoclave. The autoclave was heated and maintained at 150^oC for 24 h and then cooled to room temperature. The precipitate was collected, centrifuged, washed with distilled water for several times, and then dried in a vacuum oven overnight at 60^oC. The produced nano (TiO_2) material is in the range of 75-80 nm according to the SEM image.

The resulted nano TiO_2 was tested in surface morphology only scanned using the SEM and ensured that the resulted material is in the nano size.

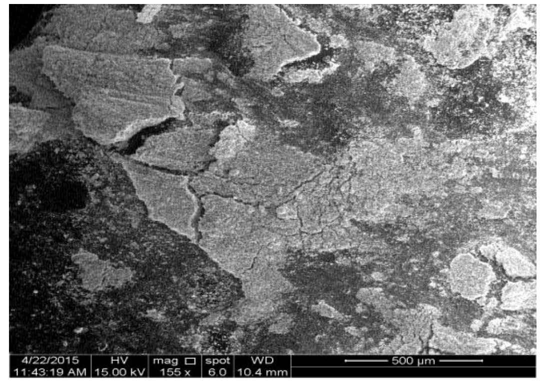

Fig. 1. TiO_2 nanopowder after preparation in the lab.

TiO_2nanopowder is converted to a disc with pressing 2 grams under 1.5-2 Ton. The diameter of the produced disc does not exceeds 2 cm according to the diameter of the templet in sue. This disc is then irradiated by Nd:YAG laser (1064 nm, 700 mJ 220 Vac, 1 Hz) under vacuum (10^{-3}mHg).

According to the previous then the work includes three different steps, these are: preparation of the nanomaterial, preparation of the vacuum chamber, and irradiation by the laser and generation of the plasma.

The most important point in this search is the plasma generated under vacuum; this is because this plasma is generated from a nanomaterial not from the raw material. The generated plasma required to be measured and this process needs to a Langmuir probe. This probe also is prepared in the lab using the tungsten material, and an electronically circuit connected to storage oscilloscope. Then the resulted signal gives the I-V characteristics of the probe which is the plasma diagnostic procedure.

Since the laser radiation hits the TiO2 nano surface then the laser energy is transferred to the material, and the electrons and other particles (such as atoms and molecules) as soon as laser delivered the required energy. These particles or sparkles as shown in fig. (2) are the radicals of the thin film deposited on the vacuum chamber walls. These radicals are shown as sparkles on the vacuum chamber.

These sparkles includes in addition to the electrons which are accumulated on the probe surface the positive ions (molecules and atoms). The plasma then is generated after these sparkles are flying on the surrounding environment of the sample. Fig. (2 a) shows a small amount of the sparkles where a small amount of the laserenergy is delivered to the material surface, then these sparkles are increased as time is increased also these sparkles are continue even the plasma is generated.

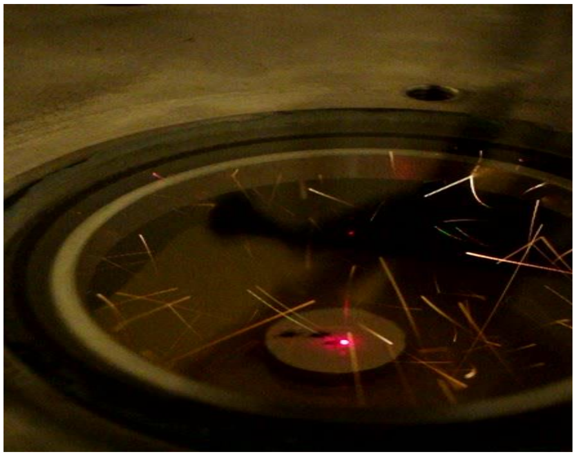

Fig. (2- a) Sparkles generation due to the Nd:YAG laser etching of TiO_2nano disc. These sparkles are the radicals for the nano thin film.

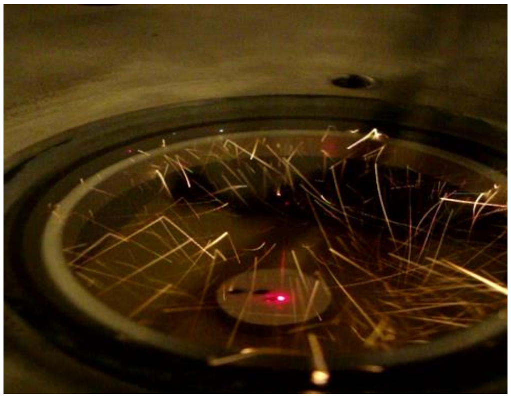

Fig. (2-b) The radicals starts increases while the laser pulse start forwarding

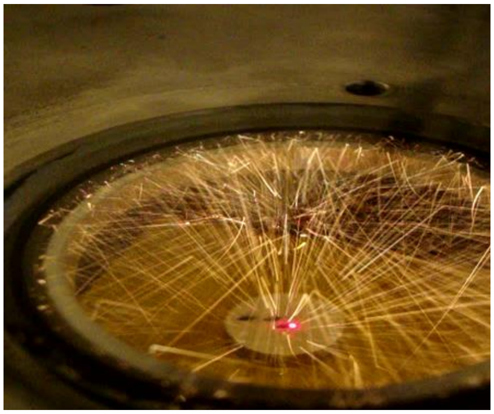

Fig. (2-c) Little before the plasma generation

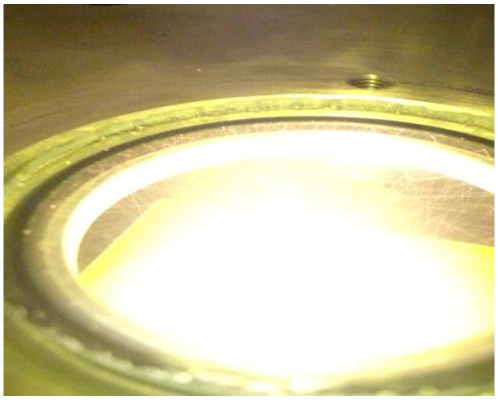

Fig. (2-d) The plasma generation due to the laser etching of TiO_2

The generated plasma then is measured using the classical method (Longmuir probe) where the probe is immersed at the center of the generated plasma (about 5 mm from the sample). This probe gives the I-V characteristics shown below.

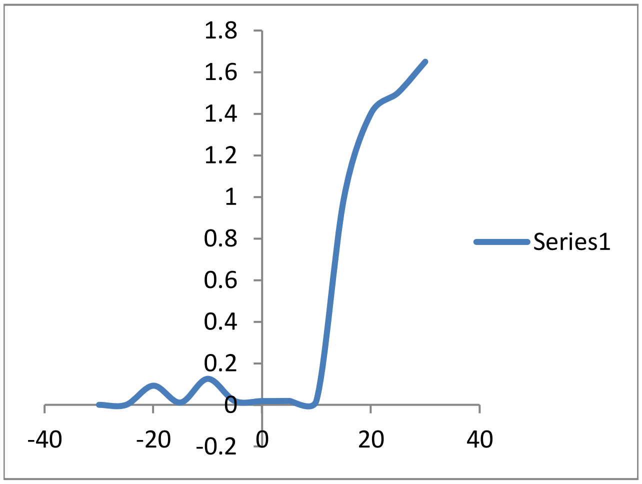

Fig. (3) The I-V characteristics of the Langmuir probe which is used in the experiment.

V. RESULTS AND DISCUSSIONS

According to Fig. (3) it is possible to compute all the plasma parameters which are famous at the physics medium. The floating potential (f_s) and depending on fig. (3) above is estimated to be (9 volt) and then the electron temperature can be calculated according to F.F. Chen as:

$$V_f = -\frac{kT_e}{e} ln\left(\frac{m_i}{4\pi m_e}\right)^{1/2} \dots (1)$$

where the term of $(ln\left(\frac{m_i}{4\pi m_e}\right)^{1/2})$ and according to the boundary conditions is possible to considered as (1). Then the remaining term is ($V_f = -\frac{kT_e}{e}$) which gives the electron temperature where:

T_e = 8.995 eV.

The probe cross section area is given by:

$$A = \pi r^2 \dots (2)$$

($A = \pi r^2 = 1.767 \times 10^{-6} m^2$) then the plasma density can be easily calculated where the saturation current can be conclude from the I-V characteristics (I_{es} = 0.9 mA) and then:

$n_e = 1.597 \times 10^{30}$ m^{-3} or 1.597×10^{32} cm^{-3}.

Figures (4) shows the system which is used in this experiment.

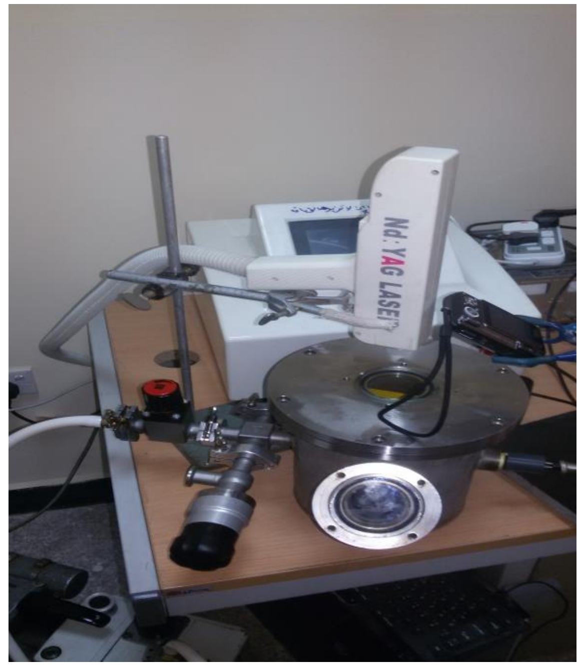

Fig. (4) The system which is used to generate the required plasma from the etching of TiO_2nano disk by Nd:YAG laser pulses (1064 nm, 700 mj)

VI. CONCLUSIONS

The TiO_2 nanoparticles are successfully prepared using the CTAB where the produced phases appeared takes place in two types the anatase, rutile. The most stable phase is the rutile and the cetyltrimethylammonium bromide is used as a template for the TiO_2 nanomaterial preparation. The laser which is used is (Nd:YAG 1064 nm 700 mj) as an agent for the preparation of the nano thin film and generation of the radicals.

The plasma generated in this experiment is differing also form this generated from the raw material while, this is clear from the electron temperature where in the raw materials (T_e)doesn't exceed more than 2-3 eV, while in this experiment it close to be 9 eV. The other parameter is the electron density which is increased more to be in the range of (10^{30} m^{-3}) which gives an idea about the huge number of free electrons in the vacuum.

I-V characteristics of the plasma probe (Langmuir probe) stay same at all time. The generated plasma is denser than those produced by the conventicle procedures. Beside the electron temperature is higher than those generated in the plasma produced by the raw TiO_2 material. The main purpose of using Langmuir probe that it was the simplest technique used to diagnostic plasma.

VII. REFERENCES

[1] Thirugnanasambandan Theivasanthi and *et.al*, *Titanium dioxide* (*TiO_2*) *Nanoparticles* **-** *XRD Analyses – An Insight*, Centre for Research and Post Graduate Department of Physics, Ayya Nadar Janaki Ammal College, Sivakasi, Tamilnadu, India.2012.

[2] M. B. Hopkins, *Langmuir Probe Measurements in the Gaseous*, Physics Department, Dublin City University, Dublin 9, Ireland, Journal of Research of the National Institute of Standards and Technology, Volume 100, Number 4, July–August 1995.

[3] Shuxi Dai and et.al, *Preparation of Highly Crystalline TiO2Nanostructures by Acid-assisted Hydrothermal Treatment of Hexagonal structured Nanocrystalline Titania/ Cetyltrimethyammonium Bromide Nanoskeleton*, Key Laboratory for Special Functional Materials of Ministry of Education, Henan University, Kaifeng 475004, People's Republic of China, 2010.

[4] F.F. Chen, *The Langmuir probe*, lecture notes, Electrical Engineering Department, University of California. Los Angeles. 2003. IEEE-ICOPS meeting, Jeju, Korea.

[5] F.F. Chen, *The Langmuir probe*, lecture notes, Last edited 2007.

[6] Prof. F.F. Chen, *Principles of Plasma Processing*, Electrical Engineering Department, University of California, Los Angeles. Plenum/Kluwer publishers, 2012.

[7] E.H. Silver and et.al., *Plasma Diagnostic Techniques in Thermal-Barrier Tandem-Mirror Fusion Experiments*, Lawrence Livermore National Laboratory University of California, Livermore, California United States of America, 1986.

[8] James C. Richley, *Fundamental studies of diamond chemical vapour deposition: Plasma diagnostics and computer modelling*, A dissertation submitted to the University of Bristol in accordance with the requirements for the award of the degree of Doctor of Philosophy in the Faculty of Science. School of Chemistry, 2014.