Influence of annealing temperatures on Nb$_2$O$_5$ nanostructures prepared using Pulsed Laser Deposition method

Makram A. Fakhri$^{1, a)}$, Farah G. Khalid$^1$, Evan T. Salim$^{3, b)}$

$^1$University of Baghdad, College of Agricultural Engineering Sciences
$^2$Laser and Optoelectronic Engineering Department, University of Technology, 10066 Baghdad, Iraq
$^3$Applied Science Department, University of Technology, 10066 Baghdad, Iraq

$^{a)}$Corresponding author: mokaram.76@yahoo.com & 140017@uotechnology.edu.iq.
$^{b)}$Corresponding author: evan_tarq@yahoo.com, & 100354@uotechnology.edu.iq.

Abstract: Nb$_2$O$_5$ nanostructures were successfully deposited by a Pulsed Laser Deposition technique (PLD) onto quartz substrates. The effects of annealing temperature on the optical morphological and structural properties deposited nano-thin films were investigated. The X-ray diffraction (XRD) results indicated the formation of the monoclinic crystalline structure, with a preferential orientation at the (301) direction. The optical energy band gap found to increase from 2.9 to 3.3 eV.

Keywords: Nb$_2$O$_5$; nanostructures; Optical properties; Structural properties; morphological properties

1. Introduction

The Nb$_2$O$_5$ (Niobium pentoxide) is a metal oxide with great potential but so far it has not been fully achieved [1-3]. The interest in this oxide goes back to the early forties of the last century when the multiple forms of niobium pentoxide were first studied [4-6]. Niobium pentoxide contains many polymorphs that lead to an exciting series of interesting structural phases [7, 8]. Where the presented phases are based generally on the octahedral NbO$_6$ groups, forming different configurations are formed of columns or rectangular blocks. Where the Niobium pentoxide is abundant relatively in nature and it has high resistance corrosion as well as being stable thermodynamically [9-11].

On the other hand, due to the wide energy band gap of nanoparticles of niobium pentoxide, it can be used in the synthesis and fabrication of electro-optical devices, photonics devices, and optical detectors, as well as in multiple layers coatings for anti-reflection coatings [12-13]. Where this matter requires careful knowledge and study of the values of light constants such as (the values of refraction coefficients, n, and extinction coefficients k) of the thin films of nanoparticles of niobium pentoxide [15-18]. Whereas, the optical properties and optical constants (n and k) of Niobium pentoxide nanoparticles have been an important subject for several studies [19, 20].

Mostly the niobium pentoxide has been studied in the forms of bulk or in the forms of the thin layer, as well as in suspensions in the early stages of its research [21, 22]. The distinctive and unique performance of a niobium pentoxide in studying its properties is due to understanding and studying the optical energy gap band diagram for it and studying and determining the crystalline phases as well, as this topic created a high interest among researchers to discover the distinctive and important capabilities of this oxide [23, 24].

However, most of the investigations that were conducted on niobium pentoxide are still insufficient and have not covered all of its properties, applications, and capabilities, so more studies, and research should be conducted to discover the rest of its capabilities and reveal its true capabilities, its various uses and applications [25, 26].

Bhembe et al. [27] are reported the coordination of Nb$_2$O$_5$ nanoparticles with FL-BP in order to form a heterogeneous bond. This modulation showed that the improvement of the structure...
of niopium pentoxide has a good effect on the values of the photocatalytic properties. On the other hand, Zhou et al. [28] are reporting the formation of highly stable P-O-P bonds within the peeled BP working area through the formation of a fully oxidized layer that enables it to resist the corrosion process inside the water. In contrast, the BP shielded layers continued to display high values for portability of charge. While Seo et al. [29] have incorporated orthorhombic niobium oxide formulations into an antimony-based formula in order to improve the electrochemical performance of the prepared compound for use in storage and rapid reversal of lithium cells.

The nano Nb$_2$O$_5$ (niobium pentoxide) thin films have been used in a variety of applications, such as the solar cells [30], windows of the electrochromic [31], gas sensors [32], and catalysts.[33]. The niobium pentoxide nanostructures have been deposited using different methods and techniques such as RF Sputtering [34], Pulsed Laser Deposition [35], hydrothermal method [36], and sol-gel [37].

In this manuscript, we deposition niobium pentoxide using the pulsed laser deposition method and study its structural and optical properties at different annealing temperatures. These investigations will be utilized later and the optimal preparation conditions are used in the Photonics, optoelectronic applications, and in the solar cells.

2. **Experimental process**

The process of preparation and deposition of the niobium pentoxide was beginning by cleaning and preparing substrates of quartz. Distilled water and high purity of ethanol inside the ultrasonic cleaner were used to remove the fingerprints, dust layers, and the ionic contamination on the substrates of the quartz. Finally, the used substrates were dried under a shower of nitrogen. The Nb$_2$O$_5$ nanofilms have been deposited using the pulsed laser deposition method without further purifications. Ultra-pure (99.99%) Nb$_2$O$_5$ powder from Merck (Kenilworth, NJ) was used and was applied pressure of 7 tons onto the powder to produce a disk with a diameter of 2.5 cm, and height 0.5 cm as present in figure 1.

![Figure 1. Lithium niobate Target](image)

Pulsed laser deposition (PLD) technique was used to deposit the Nb2O5 nanocrystalline films on the quartz substrate which heated by the hydrogen lamp at a temperature which is 250ºC with the pressure of about 10–3 bar. The deposition process was done by using Q-Switched Nd: YAG laser at the wavelength of 1064nm, 250 laser pulses, pulse duration 10ns, 1800J laser energy, 6Hz frequency, and the distance between the target and the substrate is about 4cm. After the deposition process, the obtained thin films were annealed at different annealing temperatures of 400, 500, and 600 ºC, respectively for 3hrs using (Lenton VTF/12/60/700) tube furnace.

A high-resolution X-ray diffraction system equipped with Cu-Ka radiation at 40KV and 30 mA of the wavelength of 0.15418 has been used for structural investigated. The thickness of
the prepared samples has been measured using a scanning optical reflectometer. Surface morphology and roughness of the thin films is performed using scanning electron and atomic force microscopes, respectively. Finally, other optical properties such as transmission and reflections as a function of the wavelength were investigated in the wavelength range 200nm - 1100nm using a double beam UV-VIS spectrophotometer. Optical constants were carefully calculated based on the results found. Such constants are the absorption coefficient and the optical bandgap energy.

The energy of the incident photon was estimated using equation (1) [38-40]:

\[ E_g (eV) = \frac{1.24}{\lambda \, (\mu m)} \]  \hspace{1cm} (1)

where \( E_g \) is the bandgap energy and \( \lambda \) is the wavelength of the incident photon. The dependency of the absorption coefficient as a function of excitation ratio was calculated by using The Tauc equation (2) [41-43]:

\[ (\alpha h\nu) = B (h\nu - E_g)^r \]  \hspace{1cm} (2)

where \( (\alpha) \) is the absorption coefficient, \( (h) \) is Planck's constant, \( (\nu) \) the speed of light in the medium, \( (B) \) is constant that is inversely proportional to the amorphously and \( (r) \) is a constant that takes different values based on the material type.

To obtain the value of the optical bandgap energy, we used to recall this value from the linear relationship (straight portion) between \( (\alpha h\nu)^{1/r} \) versus \( (h\nu) \), considering that the term \( (\alpha h\nu)^{1/r} \) is equal to zero. Equation (3) is used to calculate the absorption coefficient of the wavelength [44-46]:

\[ \alpha = 2.303 \left( \frac{A}{t} \right) \]  \hspace{1cm} (3)

where \( A \) is the absorptance and \( t \) is the thickness of the thin film.

3. Results and discussion

3.1 Structural properties

The presented results showed the emergence of a different set of diffraction peaks and this indicates a polycrystalline structure where the results showed the presence of pure niobium metal and different stages of oxidation of the niobium element such as Nb, NbO, NbO\textsubscript{2} and Nb\textsubscript{2}O\textsubscript{5}. The main peaks of the diffraction are located at values of 13.90, 16.70, 21.70, 28.50, 30.70, 36.20, 37.90, 39.20, 43.60 and 57.50, which indicated (-203), (301) (-705), (12 11), (811), (111), (110), (-531), and (113) respectively. Where there were previously published results similar elsewhere [47-49].

From the presented results it can be seen that a clear reconstruction and improvement process has been achieved in the nanoparticles of Niobium Pentoxide in terms of intensity and crystallinity with an increase in the degree of thermal annealing, as shown in Figure 2. Where the XRD patterns represent the preparation of samples of the prepared Niobium Pentoxide films and the treatment with thermal annealing degrees different 400, 500, and 600 respectively. The diffraction peaks are at 13.90, 16.70, 36.20 and 57.50 corresponding to (-203), (301), (811) and (113) respectively. Where there were previously published results similar elsewhere [47-49].
It can also be seen that the peak diffraction intensity appears at 2θ is 16.70 for all temperatures of annealing. As the intensity of diffraction increased with the increase in the degree of thermal annealing to 600 °C, due to the increase in the crystallization of the niobium pentoxide atoms with the increase in the annealing temperature, also it can be clearly relatively low values of diffraction intensities for other types of niobium oxides such as NbO₂, NbO, Nb. The same observation has been observed in the ref. [43, 50, 51].

![X-ray diffractions for Nb₂O₅ nano films at different annealing temperatures](image)

**Figure 2.** X-ray diffractions for Nb₂O₅ nano films at different annealing temperatures

### 3.2 Optical properties

Figure (3) presents the spectrum of the absorption for the niobium pentoxide nanofilms deposited on the substrate of quartz at different annealing temperatures, it's a clear that the reduction in the absorption values can be recognized at the range of wavelengths abut (200-400) nm for all nanofilms annealed at different temperatures of annealing, but its more clearly at the annealing of 400 °C, as a result of the reduction of the density of nanofilms of the niobium pentoxide deposited on the quartz and annealed at 400 °C, and also because of the low thickness at lower annealing temperatures.

![Absorption for Nb₂O₅ nano films at different annealing temperatures](image)

**Figure 3.** Absorption for Nb₂O₅ nano films at different annealing temperatures
The transmission spectrum of the deposited and annealed nanofilms of the niobium pentoxide is presented Figure (4), it's a clear that the increase in the transmissions with the annealing temperatures of annealing, as a result of the increased of the density of the annealed samples with the temperatures of annealing, and also because of reducing the thickness with the annealing temperatures as a result of increasing the particles size.

![Image of transmission spectrum](image1)

**Figure 4.** Transmission spectrum for Nb$_2$O$_5$ nano films at different annealing temperatures

The optical energy band gap spectra are presented in the fig. 5. The niobium pentoxide important in the multi applications of the optoelectronics and photonics and have been reflected from its optical properties, bandgap properties, and its optical constants. The values of the optical energy gap for the deposited niobium pentoxide and treated at different annealing temperatures have been present increasing with the annealing temperature as a result of changing the sizes of the grains (increasing in the grain size), and its values 3.55 eV, 3.75 eV, and 4.1 eV for 400 °C, 500 °C, and 600 °C, respectively. Where there were previously published results similar elsewhere [52-55].

![Image of energy gap spectrum](image2)

**Figure 4.** Energy gap spectrum for Nb$_2$O$_5$ nano films at different annealing temperatures
The sizes of the particle and the grain size are present in the topographical results (AFM). According to the presented results and mentioned above, an indication has been found that the stability of the thermal for the niobium pentoxide nanofilms deposited using the PLD method are more stable in the range of annealing of 500 °C to 600 °C, where the surface morphology is a very interesting parameter for the optoelectronic and photonics applications. Figure 5 presents the AFM images of niobium pentoxide nanostructures, which deposited on the substrates quartz and treated at different temperatures of annealing. Both of the roots mean-square values and the size of the grain can be clearly affected by the temperatures of the annealing. The increase in the grain size with the increasing of annealing up to [500]°C then and the increase continues significantly as it reaches [600]°C, where the values of the grain size are 57.43, 73.54, and 88.78 nm for temperatures of annealing 400, 500, 600 °C respectively. Also, the AFM results prove that the treated nanostructures by annealing have a uniform density surface, and also it is a uniform distribution within the scanning area of (4μm x 4μm) with a reduction in surface roughness with the annealing temperatures where the values of the roughness are 2.41, 1.95, 1.38 nm for temperatures of annealing 400, 500, 600 °C respectively. Finally, the values of the roots mean square was a reduction with the increase in the annealing temperatures and its values of 2.12, 1.75, 1.33 nm for temperatures of annealing 400, 500, 600 °C respectively. All these changes in the topographic structure are a result of the arrangement and the restructuring of crystals to improve the structural characteristics, and it is a natural product of increased thermal annealing.

![Figure 3. AFM 2-D images of Nb₂O₅ nanostructure films at different annealing temperatures](image-url)
Table 2. roots mean square values, roughness's and size of grain fot Nb$_2$O$_3$ nanostructure films at different annealing temperatures

| Annealing Temperatures (°C) | Grain Size (nm) | Roughness (nm) | RMS (nm) |
|-----------------------------|-----------------|----------------|----------|
| 400                         | 57.43           | 2.41           | 2.12     |
| 500                         | 73.54           | 1.95           | 1.75     |
| 600                         | 88.78           | 1.38           | 1.33     |

Conclusion

The optical results of the nanoparticle pentoxide nanoparticles showed a marked decrease in the absorbance values and a significant increase in the values of the transmission as a realistic result of increasing the size of the nanoparticles of the precipitated films and thus increasing the thickness of these films, thus clearly affecting the optical energy gap values as these values increased by increasing the annealing temperature from 3.55 ev at 400 °C Annealing temperature to 4.1 ev when annealing at 600 °C

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