

Effect of Annealing Temperature on the Structural and Optical Properties of Nanocrystalline Strontium Titanate Thin Film Prepared by PLD

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Abstract: The study was carried out by the preparing of SrTiO₃ thin films and studying the effect of annealing temperatures at (723, 773, 823) K for 2h on structural and optical properties. The SrTiO₃ thin films have been prepared by pulse laser deposition in a vacuum condition at about (4×10⁻²) mbar. X-ray diffraction pattern of the films confirmed that all the grown films have polycrystalline structure rather increase in average grain size with increase temperature from 7.03nm to 9.25nm. The optical measurements show that the SrTiO₃ thin films have direct energy gap which show that energy gap decrease from 3.7eV to 3.4 eV with increasing the annealing temperature, the transmittance decrease with increasing temperature.

Keywords: PLD, SRT, XRD, Optical Properties.

I. INTRODUCTION

Strontium Titanate (SrTiO₃) has perovskite structure like CaTiO₃, the mineral from which the name was derived. It is a centrosymmetric paraelectric material with a perovskite structure. At room temperature it exists in the cubic form, but transforms into the tetragonal structure at temperature less than 105° K, at very low temperature, STO exhibits piezoelectric and superconducting characteristics. Thin films made of high dielectric constant materials based on alkaline earth Titanates of BaTiO₃ (BTO) and SrTiO₃ (STO) have received much attention due to their applications, that films (with nanometers or micrometers of thickness) of Strontium Titanate possess very different properties in comparison to bulk materials^[1,2]. The SrTiO₃ (STO) thin film is a candidate dielectric material for capacitors in the next-generation dynamic random access memory (DRAM) with 1-Gbit density or higher, as well as in monolithic microwave integrated circuits (MMICs) because of its high dielectric constant approximately 300^[3].

STO is the best characterized complex oxide. It is a prototypical soft-mode incipient ferroelectric with a perovskite structure. At low temperatures, STO shows a non-linear, electric field tunable dielectric permittivity, which is of interest for the tunable microwave devices operating at cryogenic temperatures. In addition to their practical importance, STO film that represent a good model system for paraelectric, tunable dielectric thin films^[4]. Ferroelectrics are technologically important for capacitors, sensors, actuators, electro-optics, and non-volatile memory. These materials have many desirable properties as electronic materials. For example, their high dielectric constant over a broad temperature range makes them very attractive for charge storage devices, i.e. capacitors. As already indicated in the precedent text, the main applications of SrTiO₃-based compositions are related to memory and tunable device application^[5].

**International Journal of Innovative Research in Science,
Engineering and Technology**

(An ISO 3297: 2007 Certified Organization)

Vol. 2, Issue 9, September 2013

II. EXPERIMENTAL WORK

Titanium dioxide TiO₂ with high purity (99.5%) supplied by Redel De Haen Germany company and Strontium Carbonate SrCO₃ supplied by BDH chemical Ltd (England) with purity > 98% were used as start material to prepare Strontium Titanate (SrTiO₃) using conventional ceramic technique. Stoichiometric ratio of these materials were mixed in a gate mortar, and then fired in an electrical furnace at 1200° C with 2 hours as a soaking time. After that the prepared powder examined using X-ray diffraction method. The SrTiO₃ powder pressed into pellets to use as a target to prepare thin films by PLD technique.

Glass slid were cleaned in an ultrasonic bath with acetone, methanol, deionized water and dried by air blowing and wiped with soft paper, then used as a substrate to deposit SrTiO₃ by PLD technique under vacuum condition at about (4×10⁻²) mbar.

(B) Annealing Temperature

In order to this study, the effects of annealing temperature on the properties of the SrTiO₃ films like structural, optical were studied. After deposited STO films it annealing at different temperature (723, 773, 823) k for 2h.

(c) Thickness measurement

Film thickness measurement by optical interferometer method was carried out. This method was based on interference of light beam reflected from thin film surface and substrate bottom. He-Ne laser of wavelength (632.8nm) was used and the thickness is determined using the formula:

$$t = \frac{\Delta x}{x} \times \frac{\lambda}{2} \dots \dots \dots (1)$$

where, t is the thickness of the films in (nm), Where x is fringe width, Δx is the distance between two fringes and λ is wavelength of laser light

(d) Optical Measurements

A double-beam UV-VIS-NIR 210A Spectrophotometer was used to measure the transmittance and absorption of SrTiO₃ films deposited at different thickness in the range of (200-800) nm. The background correction was taken for each scan. The transmittance and reflectance data can be used to calculate absorption coefficients of the films at different wavelength. Which have been used to determine the band gap E_g.

III. RESULT AND DISCUSSION

(A) Structural properties

The type of SrTiO₃ prepared powder in this work by conventional solid-state reaction method as mentioned in section (2-a), where examined by x-ray diffraction pattern as shown in Fig (1). By comparing between the resulting spectra SrTiO₃ for d-spacing, intensity of peaks, and Miller Indices values in American Standard for Testing Material (ASTM), It is clear that the major peak with the highest of crystallinity in the spectra of this fig. is at (d= 2.7615 Å), and the reflection planes are (100), (101), (111), (200), (201), (211), (202), (212), and (201).

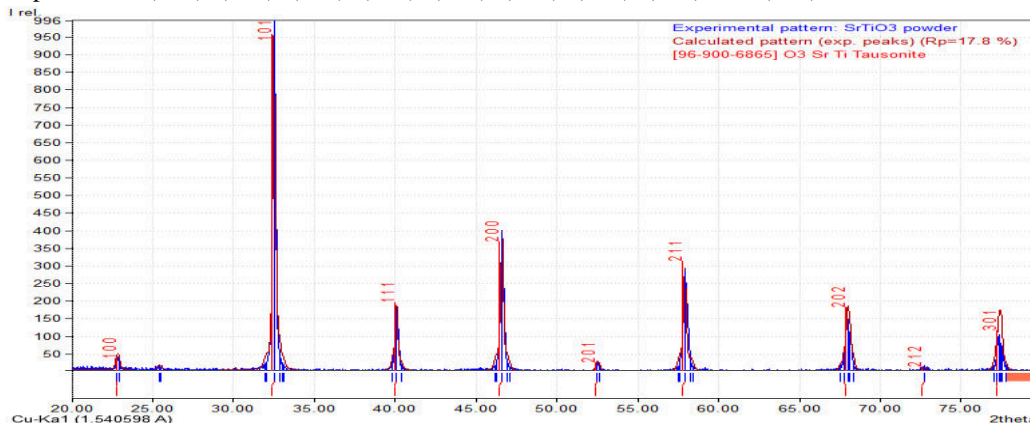


Fig (1): X-ray diffraction pattern for prepared SrTiO₃ powder.

International Journal of Innovative Research in Science, Engineering and Technology

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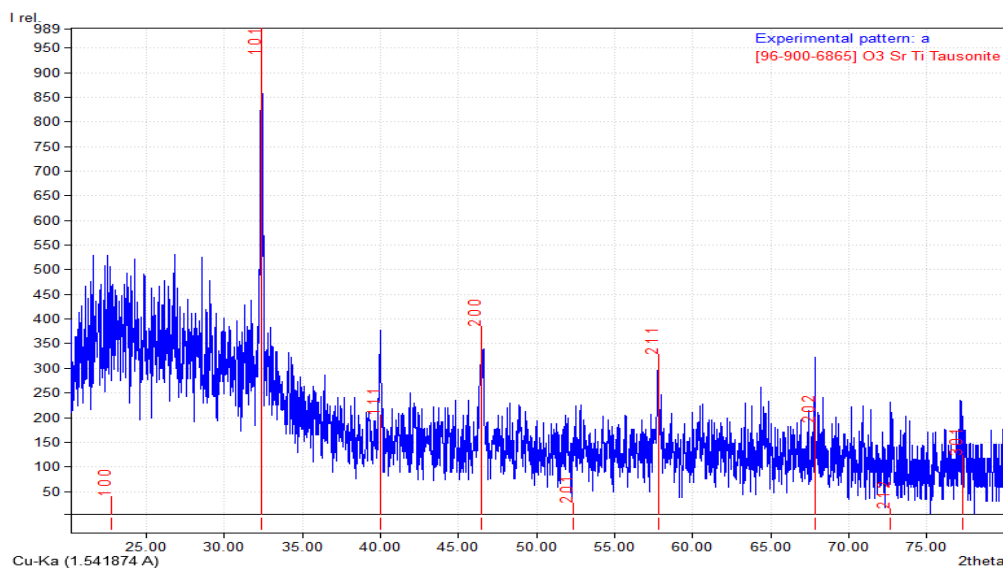
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The annealing temperature plays an important role in determining the structure of SrTiO₃ thin films which are fabricated on glass substrates. Figs ((2) a, b, c, d)) show the XRD measurements results of SrTiO₃ films prepared by Pulsed laser deposition (PLD) technique (at laser source energy 900mJ) in the range of 2θ between (20° -80°) on glass substrate at room temperature RT and different annealing temperatures (723,773 823) K.

XRD pattern of SrTiO₃ Prepared thin film at room temperature is shown in fig 2 (a) only (101), (111), (200), (211) and (202) peak were observed, in other word weak signals suggesting that the film is not well crystallized, while in curves (2 (b), (c) and (d)), it is clearly that intensity of all packs were increase with increasing of annealing temperature. All films grown in this work exhibit the same shape and the patterns assuming that all the films grown on glass substrates are with strongly c-axis orientation. The FWHM of 2θ values linked to the grain size of the film. The smaller FWHM means that the larger grain size, and the better crystal quality of the whole film. Increasing the annealing temperature of the films enhanced the crystal quality of the film, indicated by the decreasing values of FWHM. The XRD measurements indicate that the high annealing temperature films are more crystalline and have larger grains than the low annealing temperature films. The average crystallite size d measured in a direction perpendicular to the surface of the specimen was calculated using Scherrer formula as shown in eq. (1). Where β represents a width measured in radians at intensity equal to half of the maximum intensity, θ_B is the Bragg angle and k is the shape factor of the average crystallite [6]:

$$d = \frac{k\lambda}{\beta \cos \theta} \dots \dots \dots (2)$$

The parameter β is the full width half of the maximum (FWHM) which increases as the crystal size decreases. The calculation was done with k = 0.94 by assuming a Gaussian peak shape and a cubic crystal structure. For this analysis, we have chosen the most intense STO (101) peaks. The crystallite sizes of STO films at room temperature deposition and annealing at different annealing temperature (723,773,823) k are 7.03nm, 7.29nm, 7.53nm, 9.25nm respectively, by using the eq. (2). It is clearly that the crystallite size of the SrTiO₃ films increases with increasing temperature. STO structure exhibited a cubic structure with lattice constant of 3.90 Å. We did not observe any phase transition and all the films showed the same X-ray diffraction patterns.



**International Journal of Innovative Research in Science,
Engineering and Technology**

(An ISO 3297: 2007 Certified Organization)

Vol. 2, Issue 9, September 2013

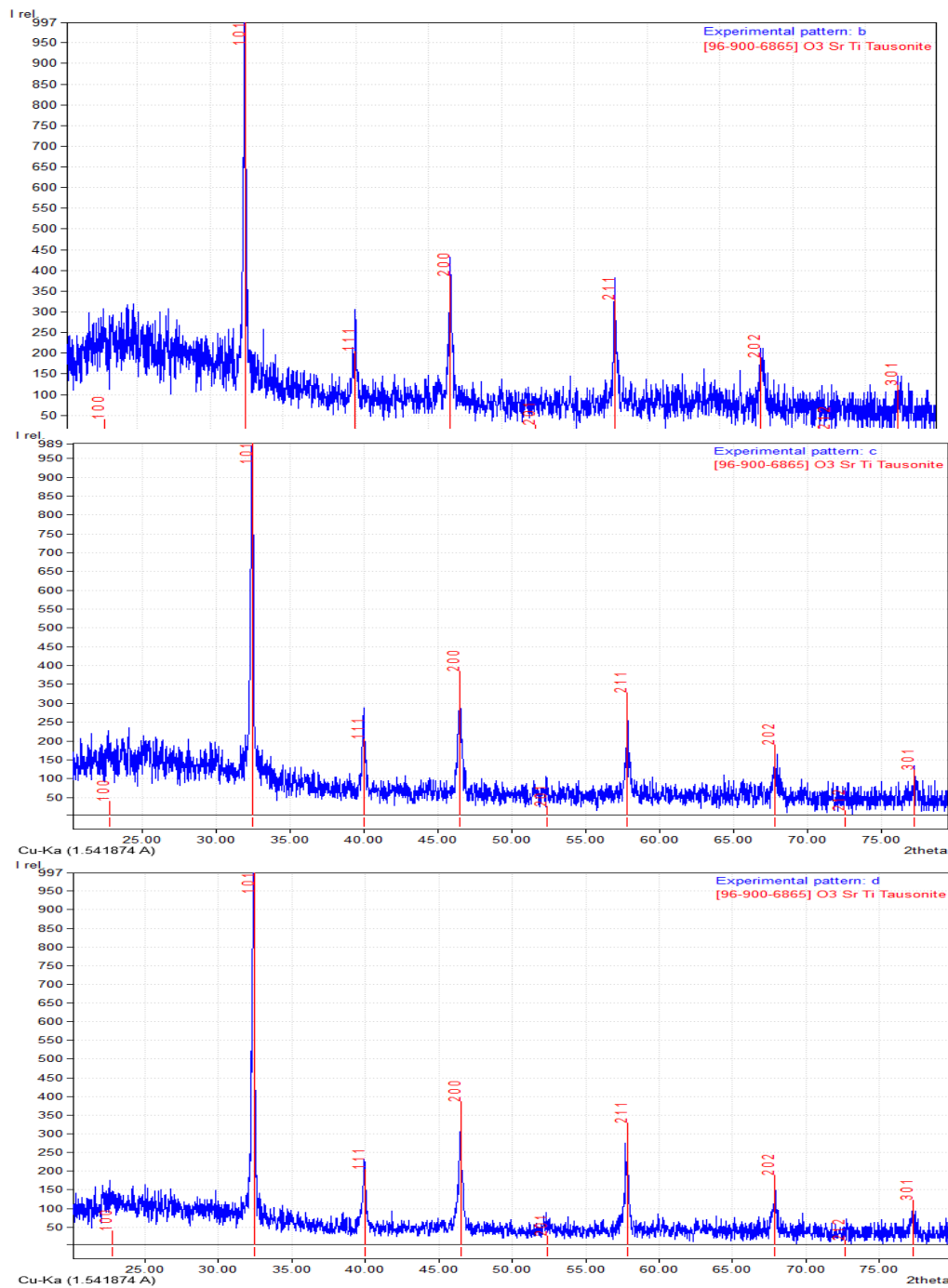


Fig (2): X-ray diffraction pattern for SrTiO₃ thin film at different annealing temperature; (a) 0 K, (b) 723k, (c) 773k, (d) 823k

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(B) Optical Properties

The average transmittance in the visible part of the spectra (300-800nm) is about (80-90)%, for all the films analyzed the transmission spectra demonstrated that the film was highly transparent in the visible region. This means that the thin film absorbs less photons of light imposed on it. Figs (3) and (4) show the transmission and absorption spectra of SrTiO₃ films respectively at different annealing temperature (723, 773, 823) k. It is observed that the film which have higher temperature displayed lower transmittance because of the improving the structure of the films and increase of grain size by annealing which means increase in the absorption.

The Tauc relation between the absorption coefficient and direct and indirect band gap energies (E_g) are given by ^[7]

$$(\alpha h\nu)^2 = (h\nu - E_g)$$

and

$$(\alpha h\nu)^{1/2} = (h\nu - E_g)$$

For allowed direct transitions and indirect transitions, respectively, where $h\nu$ is the energy of the incident photon. We plotted $(\alpha h\nu)^n$, $n = 2$ for direct transition and $n = 1/2$ for indirect transition. Fig (5) shows the plot of $(\alpha h\nu)^2$ as a function of $h\nu$ at various temperatures. The same absorption region has been used to evaluate optical band gap.

For the same annealing temperature, the high temperature films exhibited a reduction in the energy gap because of the crystallinity and the grain size of the films increase with film temperature which lead to decrease the localize states. The shift of optical band gap energy can be also explained in terms of quantum-size effect in which the films with large crystallites.

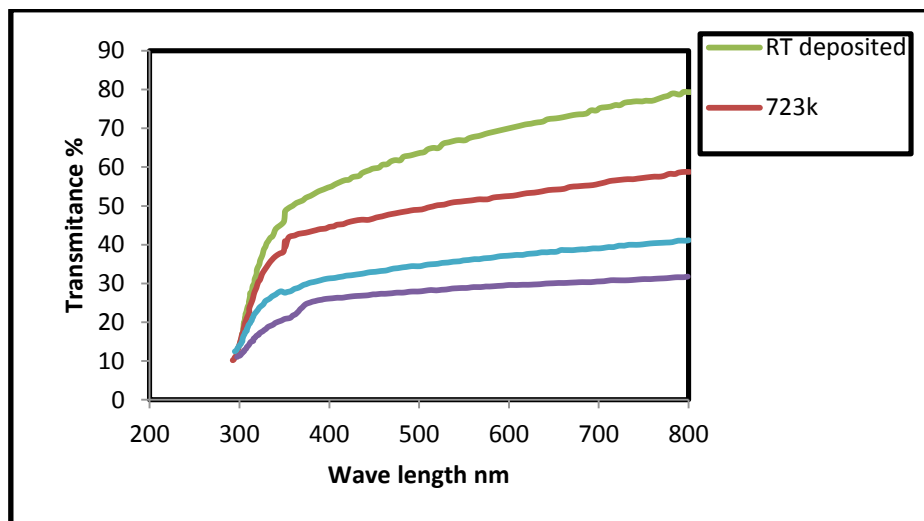


Fig (3): UV-VIS transmission spectra versus wave length of the SrTiO₃/glass films at different annealing temperature.

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Engineering and Technology**

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Vol. 2, Issue 9, September 2013

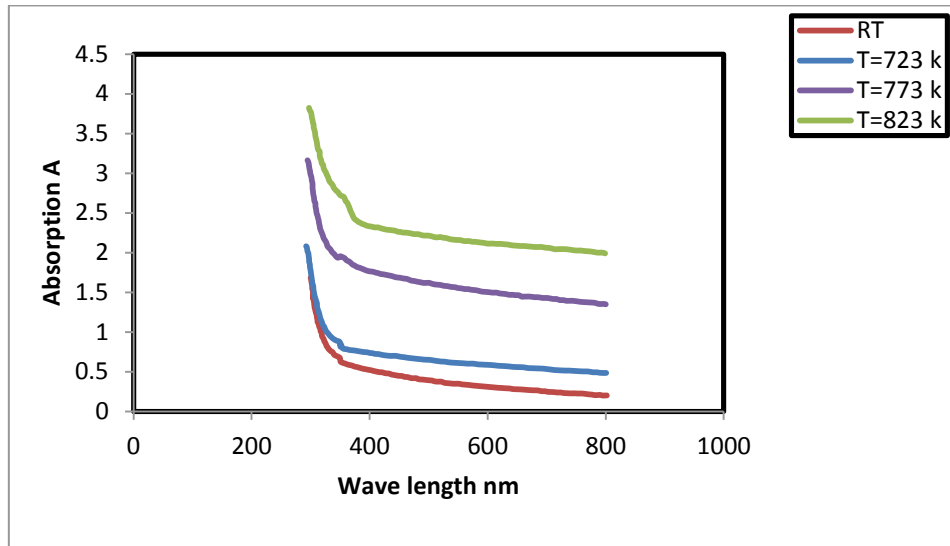


Fig (4): UV- VIS Absorption spectra versus wave length of the SrTiO₃/glass at different annealing temperature.

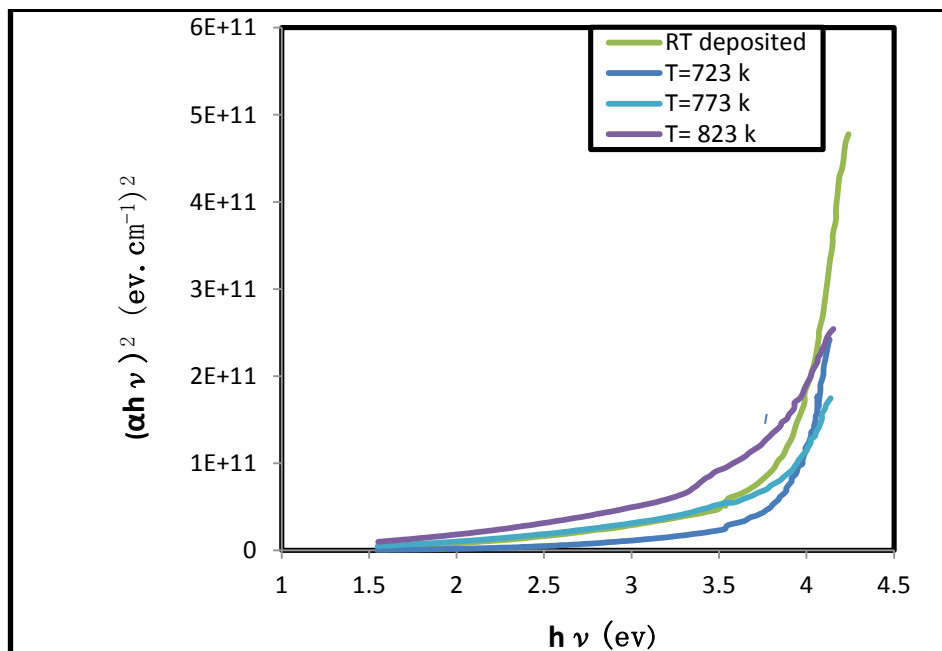


Fig (5): $(\alpha h \nu)^2$ versus photon energy ($h \nu$) of the polycrystalline SrTiO₃/glass films at different annealing temperature.

**International Journal of Innovative Research in Science,
Engineering and Technology**

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Vol. 2, Issue 9, September 2013

IV. CONCLUSION

Crystalline SrTiO₃ thin films have been prepared on glass substrate using Pulse Laser Deposition technique. The structural and optical properties of the films were studied. Our results indicate that the film annealed at 823K show more pronounced crystallinity with large grain size, the optical energy gap of SrTiO₃ thin films is affected by annealing process and decrease with increase in annealing temperatures, it decrease from (3.7)eV at R.T to (3.4)eV at 823° K. The results of optical measurements show that the transmission decrease with increasing annealing temperatures, while the absorbance increase with annealing temperature.

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