ISSN NO. 2320-5407

Journal Homepage: -www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)

Article DOI:10.21474/IJAR01/7653
DOI URL: http://dx.doi.org/10.21474/IJAR01/7653

RESEARCH ARTICLE

STUDY OF ANNEALING INFLUENCE ON IRO_2 THIN FILMS USING ULTRASONIC TECHNIQUE.

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Manuscript Info

Manuscript History

Received: 03 July 2018
Final Accepted: 05 August 2018
Published: September 2018

Keywords:-
IrO_2; Annealing; Ultrasonic; Mechanical properties; Band gap energy; Micro-harness.

Abstract

Iridium oxide (IrO_2) thin films were prepared using sol-gel technique. The prepared films subjected to different annealing temperatures (300^0C, 400^0C, 500^0C, 600^0C and 700^0C). By using ultrasonic pulse echo technique, ultrasonic attenuation coefficient (α), ultrasonic velocities (longitudinal, C_L and shear, C_S) and thin film thickness (X) measured. Then elastic moduli (Young's (E), longitudinal (L), shear (G) and bulk (K)), Poisson's ratio (v) and micro-hardness (H) were calculated. By optical method, band gap energy (E_g) of the prepared thin films measured. Films' densities (ρ) had known from weights difference. The study showed that the ultrasonic attenuation coefficient, films' densities and Poisson's ratio increased as the annealing temperature increased while ultrasonic velocities, elastic moduli, thickness, micro-hardness and band gap energy did the contrast. It may be due to molecules mobility and voids variation with respect to annealing temperatures. Therefore, the mechanical properties, band gap energy, density, micro-hardness and thickness of IrO_2 thin films were changed.

Introduction:-

Iridium oxide thin films have attracted attentions as an excellent bottom electrode and a good thermal barrier layer between Si wafers and capacitor dielectrics such as $(Ba,Sr)TiO_3$ or $(Pb,Zr)TiO_3$ thin films in memory devices [1]. IrO_2 nanostructures also used widely as the electrocatalysts for the oxygen evolution reaction (OER) in proton exchange membrane (PEM) water electrolysis, solid polymer electrolyte (SPE) electrolyzer, photocatalytic and electrolysis of water oxidation, etc. Apart from the electrocatalysis, IrO_2 nanostructures involved in several other applications including sensing, field emission, Li-air battery, electrical properties, etc [2]. Dioxides of Ru, Ir, Os, and Rh, all crystallizing in the tetragonal rutile structure, have bulk metallic resistivities ranging from 30 to 100 mWcm [3]. Among these conductive oxides, IrO_2 has the lowest bulk resistivity (~30 mWcm) [4]. Crystalline IrO_2 considered as the anode catalyst, since it shows better stability and rather tolerable activity [5]. Since the high activity of amorphous iridium oxide compared to crystalline IrO_2 is in the focus of research. Minguzzi et al. [6] pointed out that hydrous oxide approaches complete utilization of the material, while in crystalline oxide films only 1–2% of the iridium atoms participate in the reaction.

Among several non-destructive test, ultrasonic regarded as one of most easy and accurate technique. Thin film's study was firstly held by a modified ultrasonic technique using delay lines [7] and results showed ultrasonic was a useful technique to make such study. Ultrasonic investigation of SnO_2 thin films mechanical properties and

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thickness firstly discussed by Barakat *et al* [8]. For studying CuO doped thin films, Barakat ameliorated the ultrasonic transducer using wedges [9].

Ultrasonic attenuation coefficient (α) gives valuable information about microstructure features of materials that can be variated with material's temperature, concentration, etc. From the transmitted (L_1) and the reflected (L_2) echoes, ultrasonic attenuation coefficient (α) can be determined.

$\alpha = [20\text{Log}(L_2/L_1)] / 2X$ (1)

Where X is thin film thickness.

Ultrasonic can investigate the mechanical properties of thin films using the following formulas [8]:

$L = \rho (C_L)^2$ (2)

$G = \rho (C_S)^2$ (3)

$K = L - [(4/3) G]$ (4)

$E = 2\rho (C_S)^2 (1+v)$ (5)

$v = ((1 - 2(C_S/C_L)^2) / (2-2(C_S/C_L)^2))$ (6)

Where: L is longitudinal modulus, ρ is the density, C_L longitudinal velocity, G is shear modulus, C_S shear velocity, K is bulk modulus, E is Young's modulus and v is Poisson's ratio.

Materials and methods:-

IrO_2 thin film preparation:

IrO_2 thin films were prepared using sol-gel technique, 0.3 g $IrCl_3$ dissolved in 10 ml ethanol. Using hot stirrer, the prepared solution stirred for about 3 hours at constant temperature (60^0C). We added drops of acetic acid gradually to the solution after 15 min from stirring until a dense gel formed, the percentage of acetic acid to the solution is about 1:1. The gel solution left in room temperature for 24 h. Glass pieces acted as host substrate. They were cleaned using distilled water, methanol and acetone. Then they dried using an oven at 120^0C for 25 min. A few drops (about 8 drops) poured carefully on the glass piece. Spin coater used for 20 min, until a homogeneous thin film distributed on the glass surface. Five groups of the prepared thin films annealed in an oven. The annealing temperatures were 300^0C, 400^0C, 500^0C, 600^0C and 700^0C.

Ultrasonic equipment:

Ultrasonic echoes were generated using ultrasonic longitudinal and shear transducers of 2 MHz (Karl Deutsch, S12, HB2 and B2S- Krautkramer). The echoes displayed on the CRT screen of flaw detector (USIP 20 – Krautkramer Branson). The transit time (t) traveling through specimen were obtained using Oscilloscope (54615B - hp). To calibrate the used transducers, Vector Signal Analyzer (89441A - hp) was used to display echo signal profile, Table 1. To calculate thickness accuracy, step blocks (VI and VII) used as reference blocks that had known thickness. The coupling material was water gel.

Table 1:-Centre frequency (f_o), lower frequency (f_l), upper frequency (f_u) and bandwidth (BW) of used transducers after calibration.

Transducer type	Transducer code	Nominal frequency (*f*), MHz	Centre frequency (f_o), MHz	Deviation percentage between *f* and f_o	Lower frequency (f_l), MHz	Upper frequency (f_u), MHz	Bandwidth (BW), MHz
Normal	Karl Deutsch, S12, HB2	2	1.71	14.5%	1.4	1.9	0.5
Shear	B2S-Krautkramer	2	2.08	4%	1.78	2.57	0.79

NB: BW = f_u - f_l

The accuracy of transducers calibration measurements was about 0.04%. The deviation percentage between nominal and central frequencies was taking into consideration when doing measurements.

As ultrasonic mode of operation, pulse echo technique used to study IrO_2 thin films. The ultrasonic transducer coupled from one side to the specimen. Small delay line (from glass) used for well define the echoes reflected from

the very thin films. The fabricated delay line was flat circular shape, it had the diameter of the used transducers (12mm) and it had the thickness of the near field of the used transducers (~0.5mm and ~1.1mm for S12-HB2 and B2S transducers respectively), Fig. 1.

Knowing that near field, NF was determined using the following formula [9]:

$$NF = (D_{eff})^2 (f_o/4C) \quad (7)$$

Where D_{eff} is the transducer's effective diameter, f_o is the operating frequency of the used transducer and C is the ultrasonic velocity in the prepared IrO_2 thin films.

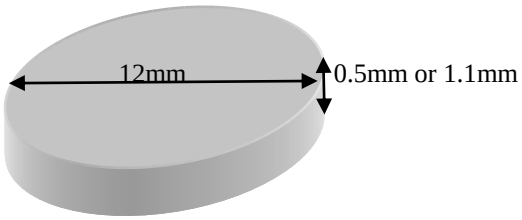

Fig. 1:-Sketch showing the shape and the dimensions of the fabricated delay line**.**

Optical equipment:

Band gap energy (E_g) of thin films measured by using spectrophotometer apparatus (UV-3101PC– Serial No. A13 - 29030002 – Shimadzu) [10].

Results and Discussion:-

Effect of annealing temperature on ultrasonic attenuation coefficient (α)

The ultrasonic attenuation coefficient (α), measured with respect to annealing temperatures, increased with the increment of annealing temperatures from 300°C to 700°C, Fig. 2.

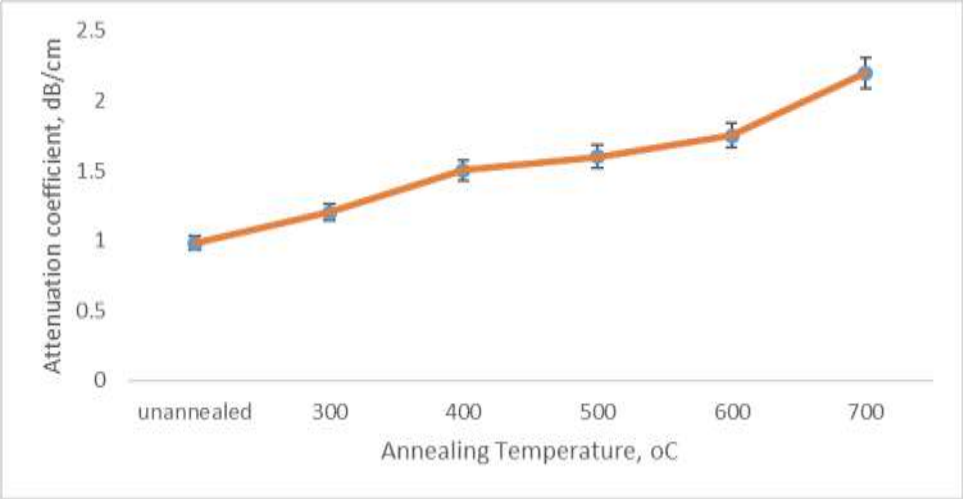

Fig. 2:-Ultrasonic attenuation coefficient varation with annealing temperatures in IrO_2 thin films specimens.

From ultrasonic attenuation, we can estimate the molecular chains mobility of IrO_2 specimens. When these specimens subjected to annealing temperatures: 300 and 400°C, the chains' motion increased. Consequently, the waves' path through the specimens became difficult, because hysteresis state increased in the specimens. Therefore, the attenuation increased. By further increment of temperature (500°C), the waves counteract more difficulty to pass through the specimens. It may postulated that the increment of chains' motion caused more resistance to ultrasonic waves [11].

Ultrasonic velocities variation under the effect of annealing temperatures

Ultrasonic longitudinal and shear velocities measured with respect to annealing temperatures. Fig. 3.

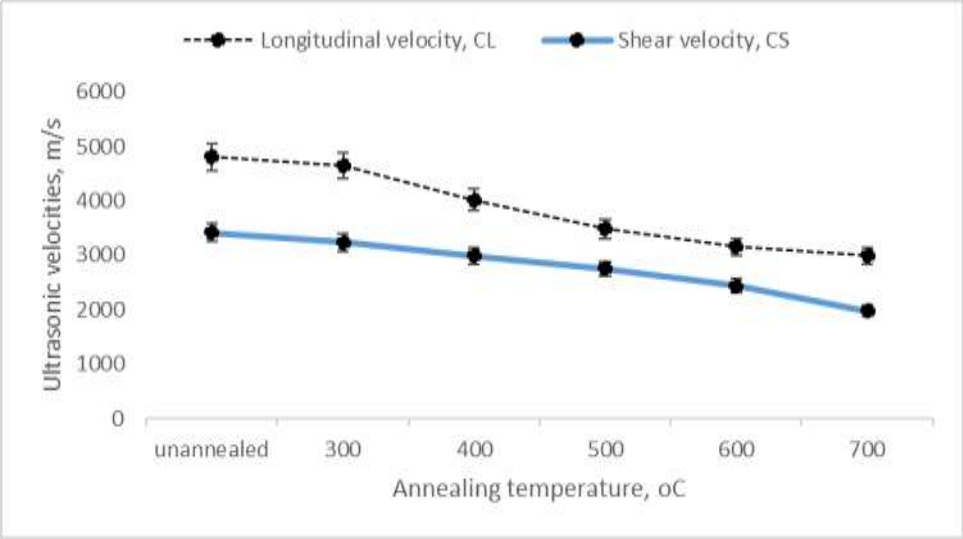

Fig. 3:-Ultrasonic velocities versus annealing teperature variation in IrO_2 thin films**.**

When the annealing temperatures increased from 300^{o}C to 700^{o}C there are more dissipation of ultrasonic waves, due to increment in molecules' motion. The dissipation of waves could decrease the ultrasonic waves' motion in the specimens. This means that the ultrasonic energy conduction in the specimens decreased. Therefore, Fig. 3 showed the decrement of either longitudinal and shear ultrasonic velocities with respect to annealing temperature increment.

Film's density, ρ

From the results, films' densities (ρ) increased with temperature, Table 2. As per Archimedes principle, the density measured by the difference in weights that were measured in air and in water [9].

$\rho = \rho_w [W_a / (W_a - W_w)]$ (8)

Where ρ_w is the density of water, W_a and W_w are specimen weights in air and in water respectively.

Table 2:-IrO_2 thin films' density versus annealing temperatures.

IrO_2 thin films	**Density (ρ), gm/cm^3**
Unannealed IrO_2 thin films	5.89
Annealed at 300 ^{o}C	5.97
Annealed at 400 ^{o}C	6.31
Annealed at 500 ^{o}C	6.58
Annealed at 600 ^{o}C	6.72
Annealed at 700 ^{o}C	6.86

As seen from Table 2, a slight increment in the density (ρ) with respect to the increment in annealing temperature of IrO_2 thin films. This may refer to IrO_2 thin films undergo volume decrement as the temperature increased, due to decrement in growth rate of the films. Knowing that the density is inverse proportional to the volume, so when the films' volume decreased the density did the contrast. Therefore, we can say that raising temperature may cause grain growth inhibition of IrO_2 thin films.

Relation of the mechanical properties with the annealing temperature

Using formulae 2-5, longitudinal (L), shear (G), bulk (K) and Young's (E) moduli were calculated.

Results showed that the elastic moduli (longitudinal, shear, bulk and Young's moduli) behaved like the ultrasonic velocities, i.e. they decreased as the annealing temperatures increased, Fig. 4. This inverse relation may be due to IrO_2 specimens' microstructure changed with temperature, the gaps inside the specimens moved with raising temperature, or they may disappear in some points so causing specimens to be more rigid. We can say that the thin films' flexibility lowered and the films became more rigid.

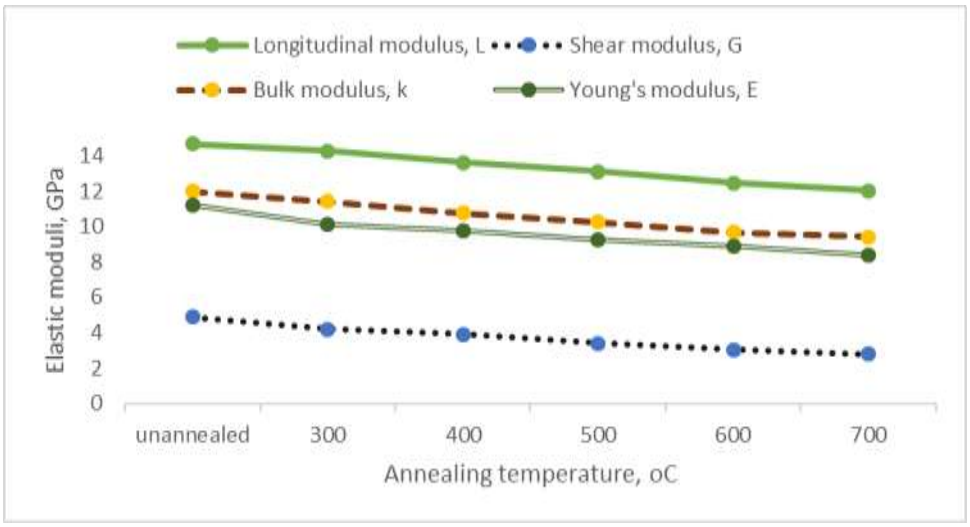

Fig. 4:-Elastic moduli versus annealing temperature of IrO_2 thin films specimens.

As a conclusion, the mechanical properties of the prepared IrO_2 thin films greatly influenced by the annealing temperatures.

Using formula 6, Poisson's ratio (v) was determined, Fig. 5. Poisson's ratio (v) measurements carried out several times for each prepared specimen and then the average value taken. The deviation of measurements was about ± 0.009.

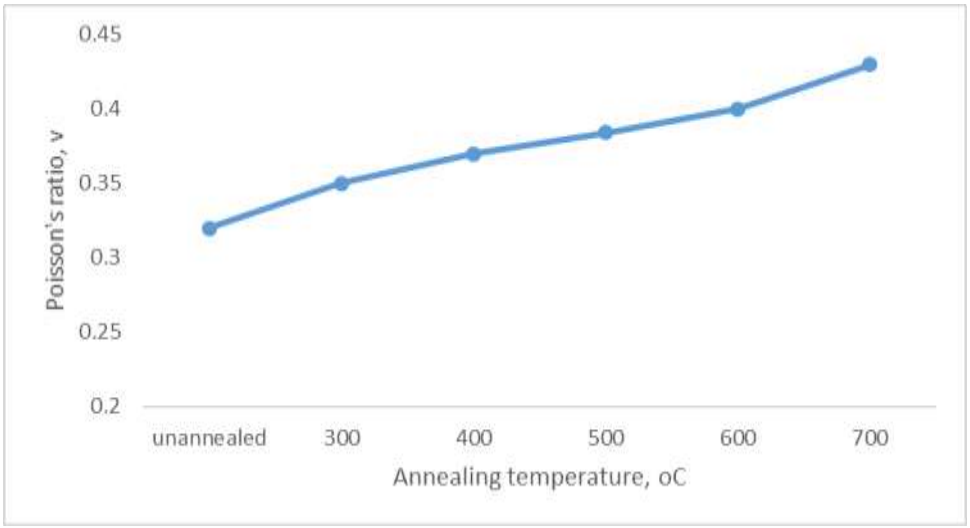

Fig. 5:-Poisson's ratio variation with respect to different annealing temperature in IrO_2 thin films**.**

Poisson's ratio (v) affected by the changes in the cross-link density of the molecular network [12]. The unannealed IrO_2 thin films had Poisson's ratio (v) smaller than the annealed ones. Poisson's ratio increased as the annealed temperature increased. This direct relation may refer to the variation of cross-link density of the molecular network in the prepared films. The temperature changed the intermolecular distance between the molecules, which moved continuously. Thus, the cross-link density increased also.

Thickness measurement by ultrasonic

Measuring thickness can give valuable information about the microstructure of the prepared IrO_2 thin films and their influenced by the annealing temperatures. Thickness known from computing the distances difference of the echoes reflected from the specimen. The echoes displayed on the CRT screen of the USIP 20 Flaw detector. Thin films thicknesses were in order of few nanometers, therefore they needed repeated measurements and high specimen handling. The uncertainty of measurements estimated to be ± 0.02nm.

Table 3:-IrO_2 thin films thicknesses variation with respect to annealing temperatures.

IrO_2 thin films	**Thickness (X), nm**
Unannealed IrO_2 thin films	125
Annealed at 300 ^oC	116
Annealed at 400 ^oC	112
Annealed at 500 ^oC	106
Annealed at 600 ^oC	104
Annealed at 700 ^oC	100

From Table 3, unannealed IrO_2 thin film had the greatest thickness, while the thickness undergoes decrement behavior with raising annealing temperatures. Temperature may decrease gap and voids in the prepared IrO_2 thin films, leading to thickness shrinkage. More temperature raising, more thickness decrement occurred.

Film's micro-hardness, H

Mathematically, micro-hardness, H calculated from the following formula [13]:

$$H = ([(1-2v)E]/ [6(1+v)]) \quad (9)$$

Where v is Poisson's ratio and E is Young's modulus.

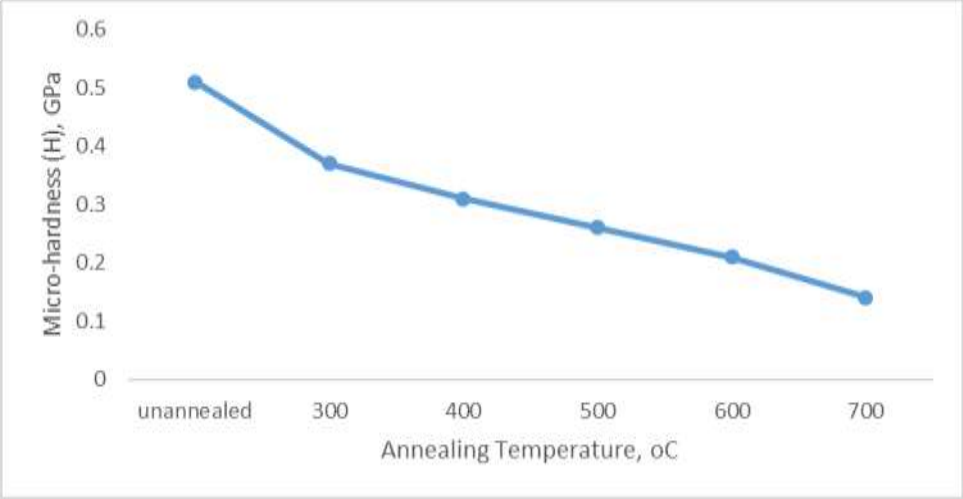

Fig. 6:-Micro-hardness variation in IrO_2 thin films of different annealing temperatures.

Results, represented in Fig. 6, showed a remarkable decrement of the micro-hardness as a function of temperatures' increment. This could interpret the great influence of IrO_2 thin films by the temperature: the texture configuration of the prepared thin films changed leading to weak bonds between molecules, thus the micro-hardness decreased by raising annealing temperatures.

Band gap energy (E_g) determination for IrO_2 thin films

Band gap energy, E_g was determined by optical method, different specimens of unannealed and annealed IrO_2 thin films were measured in the wavelength range of 400 to 1100 nm. E_g was calculated using the following formula [9]:

$$E_g = hf \quad (10)$$

Where f is the frequency and h is the Planck's constant.

Table 4:-Band gap energy, E_g measurements for unannealed and annealed IrO_2 thin films.

IrO_2 thin films	**Band gap energy (E_g), eV**
Unannealed IrO_2 thin films	1.35
Annealed at 300 ^oC	1.27
Annealed at 400 ^oC	1.16
Annealed at 500 ^oC	1.14
Annealed at 600 ^oC	1.08
Annealed at 700 ^oC	1.01

The knowledge of band gap energy E_g is very useful to have information about specimen's microstructure [14]. In previous study [12], band gap energy E_g calculated for thin films can give information about their improvement, i.e. decrement in E_g reflects increment in thin films' improvement. Table 4 shows the decrement of band gap energy E_g with the increment of annealing temperatures in the prepared IrO_2 thin films. E_g decreased from 1.35 eV to 1.01 eV. The temperature removed gaps and voids from the molecular network of the prepared IrO_2 causing the decrement in the band gap energy. Therefore, annealing temperature upgraded the prepared IrO_2 thin films.

Conclusion:-

Ultrasonic attenuation was highly influenced by the increment of the annealing temperatures in the prepared IrO_2 thin films. More temperature increment caused more chains mobility and attenuated the ultrasonic waves. Thus, the ultrasonic energy conduction in the specimens decreased. This lead to decrement of either longitudinal and shear ultrasonic velocities.

Raising temperature may cause grain growth inhibition of IrO_2 thin films, the films' volume decreased while their densities increased. In addition, it may cause voids disappearance, leading to decrement in the elastic moduli (longitudinal, shear, bulk and Young's moduli). Therefore, the thin films' flexibility lowered and the films became more rigid. Contrary, Poisson's ratio increased due to increment in crosslink density. We can said also that raising temperature caused thickness shrinkage and weak bonds between molecules in annealed specimens resulted decrement in both micro-hardness and band gap energy, E_g. Finally, we concluded that annealing temperature upgraded the prepared IrO_2 thin films to have less gaps and voids and to become more rigid for several applications that need these characteristics.

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