Iraqi Journal of Physics, 2018 *Vol.16, No.37, PP. 7-14*

DOI: 10.20723/ijp.16.37.7-14

Spectroscopic and structural studies of cadmium oxide thin films prepared by D.C magnetron sputtering

Ahmed K. Al-Zubeidi[1], Ghuson H. Mohamed[2], Haider Kadhim Joudah[1], Kadhim A. Aadim[2]

[1]Department of Physics, College of Science, University of Wasit, Iraq

[2]Department of Physics, College of Science, University of Baghdad, Iraq

E-mail: ghuson1975@Gmail.com

Abstract

Cadmium oxide thin films were prepared by D.C magnetron plasma sputtering using different voltages (700, 800, 900, 1000, 1100 and 1200) Volt. The Cadmium oxide structural properties using XRD analysis for just a voltage of 1200 volt at room temperature after annealing in different temperatures (523 and 623) K were studied .The results show that the films prepared at room temperature have some peaks belong to cadmium element along the directions (002), (100), (102) and (103) while the other peaks along the directions of (111), (200) and (222) belong to cadmium oxide. Annealed samples display only cadmium oxide peaks. Also, the spectroscopic properties of plasma diagnostic for CdO thin films were determined and the results show that the electron temperature and electron density increase with increasing of sputtered voltage.

Key words

CdO, DC sputtering, optical emission spectroscopy, structural properties.

Article info.

Received: Sep. 2017
Accepted: Oct. 2017
Published: Jun. 2018

الدراسات الطيفية والتركيبية لاغشية أوكسيد الكادميوم الرقيقة المحضرة بطريقة الترذيذ المغناطيسي بالتيار المستمر

أحمد خضير الزبيدي[1]، غصون حميد محمد[2]، حيدر كاظم جودة[1]، كاظم عبدالواحد عادم[2]

[1]قسم الفيزياء، كلية العلوم، جامعة واسط، العراق

[2]قسم الفيزياء، كلية العلوم، جامعة بغداد، العراق

الخلاصة

تم تحضير أغشية اوكسيد الكادميوم الرقيقة بطريقة الترذيذ المغناطيسي بالتيار المستمر بأستخدام فولتيات ترسيب مختلفة V (700, 800, 900, 1000, 1100, 1200) حيث درست الخصائص التركيبية باستخدام تحليل حيود الاشعة السينية (XRD) عند فولتية الترسيب V (1200) فقط في درجة حرارة الغرفة وبعد التلدين في درجات حرارة مختلفة K (523، 623) وبينت النتائج أن الاغشية المحضرة في درجة حرارة الغرفة فيها قمم تنتمي الى عنصر الكادميوم على طول الاتجاهات للمستويات (002)، (100)، (102) و (103) وقمم أخرى تنتمي الى أوكسيد الكادميوم على طول الاتجاهات للمستويات (111)، (200) و (222) كذلك تم تشخيص البلازما من خلال تحديد الخصائص الطيفية لاغشية اوكسيد الكادميوم الرقيقة وبينت النتائج أن درجة الحرارة والكثافة العددية للألكترونات تزداد بزيادة فولتية الترسيب.

Introduction

Cadmium oxide is (n-type) semiconductor material. Its thin films can be prepared by physical and chemical methods such as spray pyrolysis, DC sputtering, Sol-Gel and Chemical bath methods etc [1]. It can also be obtained by heating cadmium with temperature less than its melting point [2]. It is used in various industrial applications such as diodes, transistors, detectors, solar cells and photovoltaic cells [3]. The wide band gap properties of CdO thin films are of interest particularly for applications such as solar cells and transparent electrodes [4]. These applications of CdO are based on its optical and electrical properties. Such as CdO films show a high transparency in the visible region of the solar spectrum, as well as a high conductivity [5, 6].

In this work pure CdO thin films were prepared on glass by D.C magnetron sputtering technique and the spectroscopic spectrum and structural properties at different sputtered voltage were investigated.

Experimental

Preparation of CdO thin films

DC magnetron sputtering plasma system consists of glass chamber of 18 cm diameter and 35 cm height, vacuumed by two stage rotary pump type Edward, with two disc electrodes of 7 cm radius, the anode electrode made of aluminum (Al) while the cathode electrode from cadmium (Cd) target with ring magnet above it to enhance and increase the sputtering, DC-power supply high voltage, voltmeter and ammeter devices. The gases were delivered into the chamber using needle valve controlled by two flowmeter, Pirani gauge type Edward and mixer to control Oxygen: Argon ratio (20 %) and gas pressure (3×10^{-1} mbar), sputtering time (3 min). The electrodes were polished before every run to clear it from deposited impurities. The CdO thin films were prepared on glass slides substrates dimensions (25.4×76.2) mm at different voltages from 700 to 1200 V at constant electrodes separation of 6 cm. The produced thin films annealed in oxygen at atmosphere pressure inside closed vessel at (523 and 623) K.

Plasma was diagnostic by optical emission spectroscopy (OES). The prepared films on glass slides substrates were examined by X-ray diffraction.

Measurements

The study of structural properties is very important "to know the type and nature of the thin film and crystalline development, used Scherrer equation to calculate rate of crystallite size [7, 8].

$$G.S = \frac{0.9\,\lambda}{\beta\,.cos(\theta)} \qquad (1)$$

where $G.S$ crystalline size, ϴ angle of diffraction and λ the XRD wavelength equal=1.5406 Å, (β) the full width at half maximum.

While, the distance between the adjacent atomic layers (d) using Bragg’s Law [9].

$$n\,\lambda = 2d\,\sin\theta \qquad (2)$$

where (n) rank reflection, (d) the distance interface between the levels of the crystal.

The microstrains ϒ in lattice was calculated by [10].

$$\Upsilon = \beta\,\cos\theta/4 \qquad (3)$$

where plasma diagnostic by Optical Emission Spectroscopy (OES) can used to calculate electron temperature (T_e) by using the intensity ratio between two emission lines in the following equation (depending on Boltzmann distribution)

$$\frac{I_1}{I_2} = \frac{A_1 g_1 \lambda_2}{A_2 g_2 \lambda_1}\exp\left(-\frac{E_1 - E_2}{KBT_e}\right) \qquad (4)$$

where I_1 and I_2 are the intensities of the two spectral lines, and A_1 and A_2 are the transition probabilities of the two spectral lines, g_1 and g_2 are the statistical weights of the upper level energy, λ_1 and λ_2 are the wavelength of the two emission lines, E_1 and E_2 are the upper level energies and (K_B) is the Boltzmann’s constant [11].

The electron density (n_e) can be calculated by Star broadening effect using the following equation [12],

$$n_e = \frac{\Delta\lambda}{2\omega} N_r \quad (5)$$

where ($\Delta\lambda$) the full width at half maximum for selected spectral line, (ω) Electron Impact Parameter (the value of the stark broadening), (N_r) constant $=10^{16}$.
And then extracted the Debye length (λ_D), plasma frequency (f_p), by the following equations.

$$\lambda_D = 69\sqrt{\frac{T_e}{n}} \quad (6)$$

$$f_p = 9\sqrt{n_e} \quad (7)$$

Results and discussion

Fig.1 Illustrates the XRD patterns for CdO films deposited with voltage (1200) volt by DC sputtering in Argon. Oxygen gas mixture at room temperature (RT). The XRD patterns shows polycrystalline structure with four peaks for cadmium element located at 2θ =31.8943°, 34.7262°, 47.8477° and 61.1580° matching with (002), (100), (102) and (103) directions in standard card No 96-901-2437 (JCPDS) and three peaks for cadmium oxide located at 2θ =32.8068, 38.3449 and 69.0560 matching with (111), (200) and (222) directions in standard card No 96-900-8610, and we can note through the data recorded in Table1 XRD peaks, standard and experimental d_{hkl}, microstrains ϒ for CdO, Cd films deposited by voltage (1200) Volt at room temperature.

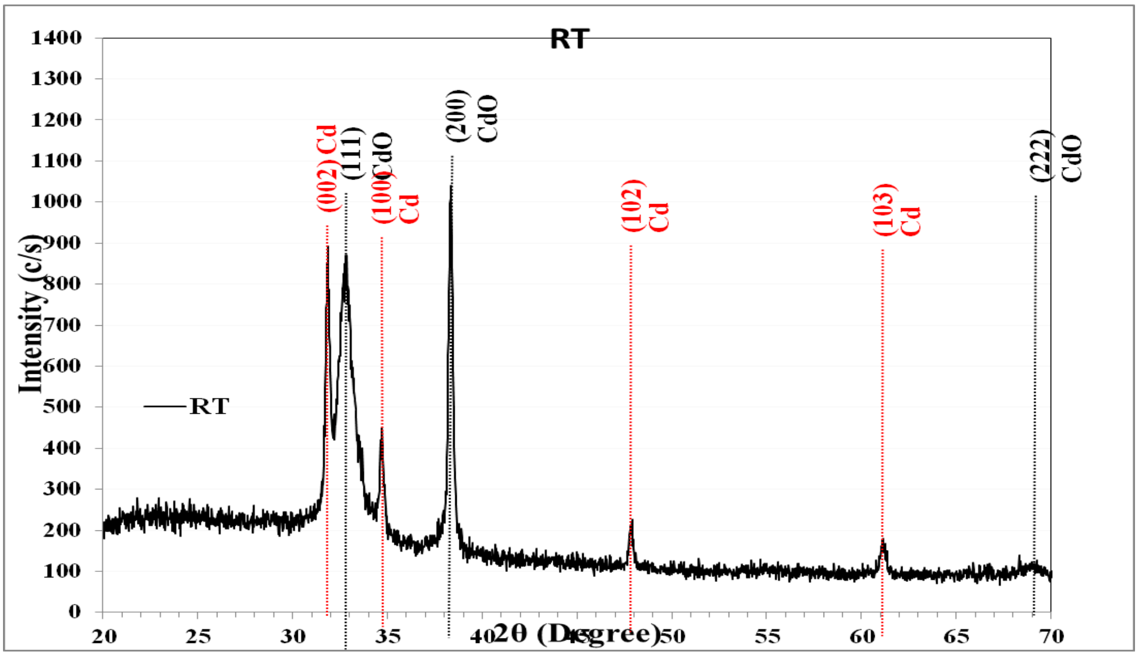

Fig. 1: X-ray diffraction curves CdO, Cd thin films deposited by voltage (1200) Volt at room temperature.

Table 1: XRD peaks, standard and experimental d_{hkl}, microstrains ϒ for CdO, Cd films deposited by voltage (1200) Volt at room temperature.

2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	hkl	d_{hkl} Std.(Å)	Phase	Card No.	ϒ
31.8943	0.2832	2.8036	29.19	(002)	2.8088	Cd	96-901-2437	0.0018
32.8068	0.8496	2.7277	9.75	(111)	2.7108	CdO	96-900-8610	0.0062
34.7262	0.2832	2.5812	29.40	(100)	2.5798	Cd	96-901-2437	0.0005
38.3449	0.2517	2.3455	33.43	(200)	2.3477	CdO	96-900-8610	0.0009
47.8477	0.2832	1.8995	30.70	(102)	1.9000	Cd	96-901-2437	0.0002
61.1580	0.4405	1.5142	20.96	(103)	1.5154	Cd	96-901-2437	0.0008
69.0560	0.9754	1.3590	9.89	(222)	1.3554	CdO	96-900-8610	0.0027

Fig. 2 Illustrates the XRD patterns for CdO films deposited with voltage (1200) V by DC sputtering in Argon: Oxygen gas mixture annealing at (523 and 623) K. The XRD patterns shows polycrystalline structure with cubic type [9], The preferred orientation along (111) direction. with five peaks for cadmium oxide (CdO), located at 2θ=32.8942, 38.1749, 55.1836, 65.8423 and 69.1793 matching with (111), (200), (202), (311) and (222) without any peaks for cadmium element due to annealing in oxygen, make the cadmium peaks hide[13], and regarded it one method to prepare cadmium oxide, and we are note through the data recorded in Table 2 the full width at half maximum for preferred orientation (111) direction increase, i.e. decrease the crystallite size (G.S), and microstrain ϒ increase with increase annealing temperature [14].

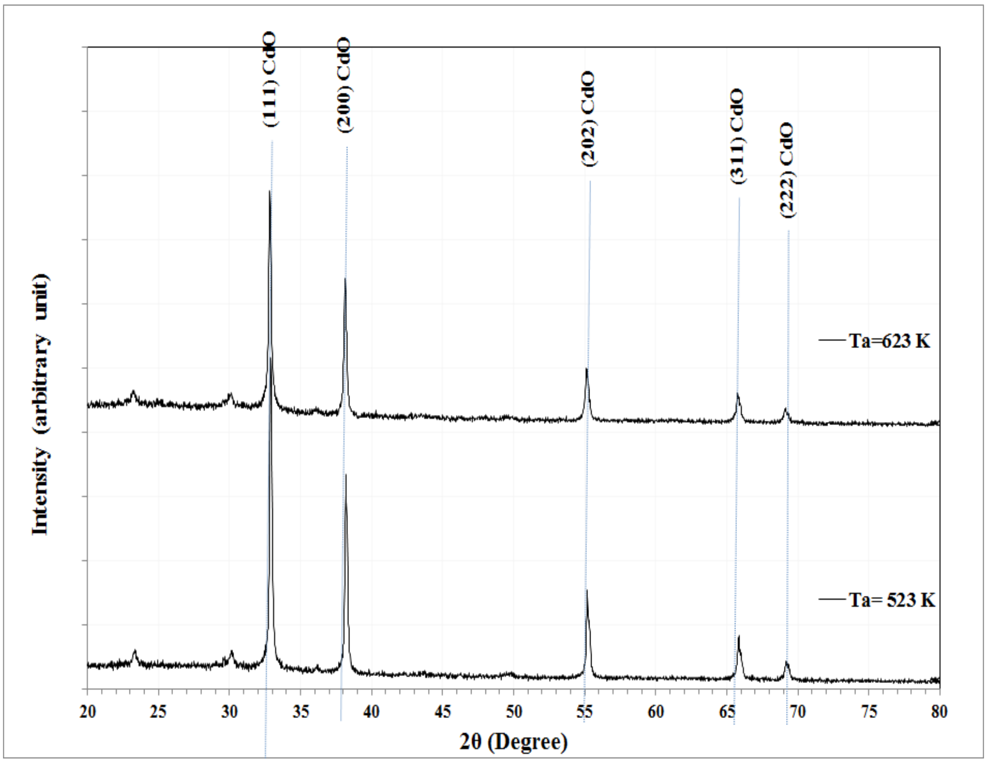

Fig. 2: X-ray diffraction curves CdO thin films deposited by voltage (1200) Volt at (523 and 623) K.

Table 2: XRD peaks, standard and experimental d_{hkl}, microstrains ϒ for CdO films deposited by voltage (1200)Volt annealed at (523 and 623) K.

Ta(K)	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	hkl	d_{hkl} Std.(Å)	card No.	ϒ
523	32.8942	0.1620	2.7207	51.1	(111)	2.7108	96-900-8610	0.0036
	38.1749	0.1943	2.3556	43.3	(200)	2.3477	96-900-8610	0.0033
	55.1836	0.2916	1.6631	30.7	(202)	1.6600	96-900-8610	0.0018
	65.8423	0.2916	1.4173	32.5	(311)	1.4157	96-900-8610	0.0011
	69.1793	0.324	1.3569	29.8	(222)	1.3554	96-900-8610	0.0010
623	32.8446	0.2210	2.7247	37.5	(111)	2.7108	96-900-8610	0.00511
	38.1483	0.222	2.3572	37.9	(200)	2.3477	96-900-8610	0.00402
	55.1152	0.2521	1.6650	35.5	(202)	1.6600	96-900-8610	0.00301
	65.7478	0.253	1.4191	37.4	(311)	1.4157	96-900-8610	0.00243
	69.1412	0.221	1.3575	43.7	(222)	1.3554	96-900-8610	0.00158

Fig.3 illustrates the optical emission spectrum (OES) of the plasma used during this research, shows different voltages (800, 900, 1000, 1100, 1200) Volt showing the atomic and ionic spectrum behavior of each (Ar, Cd, O).

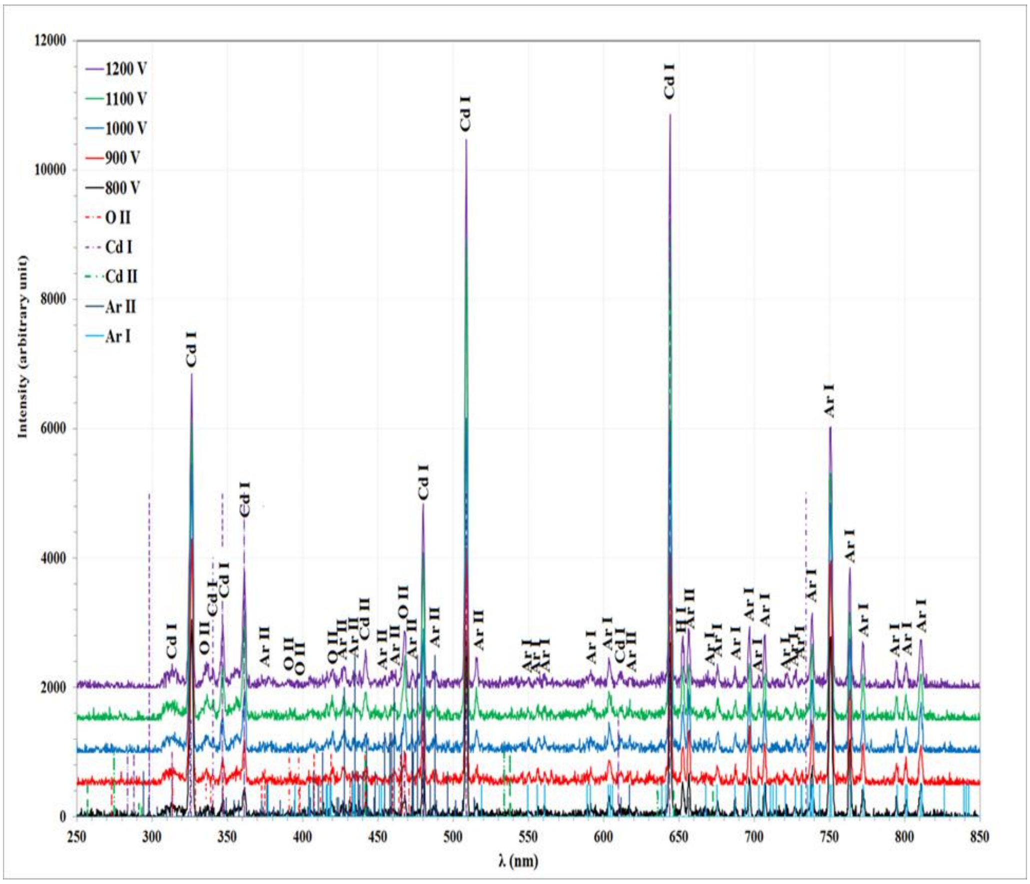

Fig. 3: OES to plasma diagnostic between intensity as a function of wave length for different voltage (800-1200) Volt.

Fig.4 illustrates the calculation of full width at half maximum ($\Delta\lambda$) by Gaussian Fitting to argon atom (Ar1) for wavelength (750.38) nm. It can be noted that the ($\Delta\lambda$) increase with increase voltage from 800 to 1200 V as shown in Table 3.

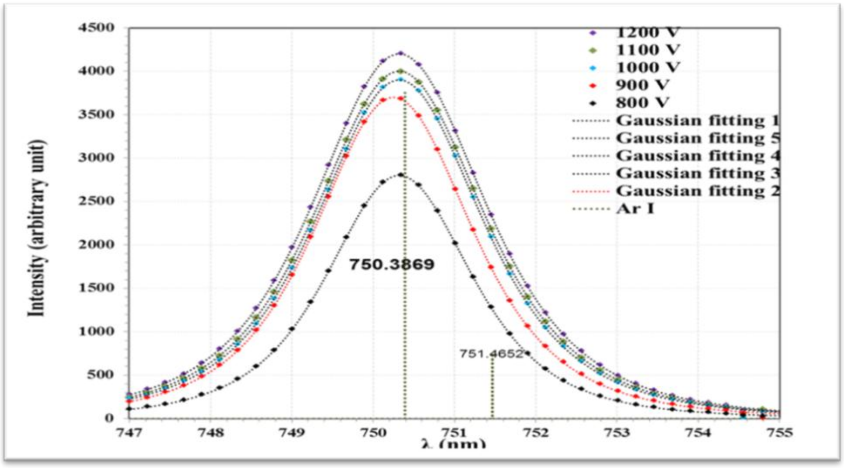

Fig. 4: The full width at half maximum (Δλ) by Gaussian fitting to argon atom (Ar1) for wave length (750.38) nm.

Table 3: The full at half maximum (Δλ) increase with increase voltage from 800 to 1200 V.

Voltage(V)	Δλ
800	2.100
900	2.280
1000	2.400
1100	2.450
1200	2.500

Table 4 shows The temperature of the electron T_e was increased by increasing the voltages between the cathode (Cd) and the anode up to (1.135) eV at (1200) volt, which is a large temperature, but it was considered a position (the thermal capacity was small) The increase in the numerical density of the electrons was caused by the increase in the ionization probability (the cross-section of ionization), which was related to the increase in the energy of the electrons (Fig.5). The length of the debye decreases with increasing voltages and increasing the electronic temperature and electronic density according to Eq. (6), while the plasma frequency values are increased by increasing the voltages and numerical density of the electrons according to Eq. (7).

Table 4: Plasma parameters (T_e, n_e, λ_D and f_p) for different voltage from 800 to 1200 V.

V(Volt)	T_e(eV)	n_e *10^{18}(cm)$^{-3}$	λ_D(cm)*10^{-7}	f_p(Hz)*10^{15}
800	1.125	1.235	7.092	1.0003
900	1.127	1.341	6.811	1.0423
1000	1.131	1.412	6.650	1.0694
1100	1.134	1.441	6.590	1.0804
1200	1.135	1.471	6.526	1.0914

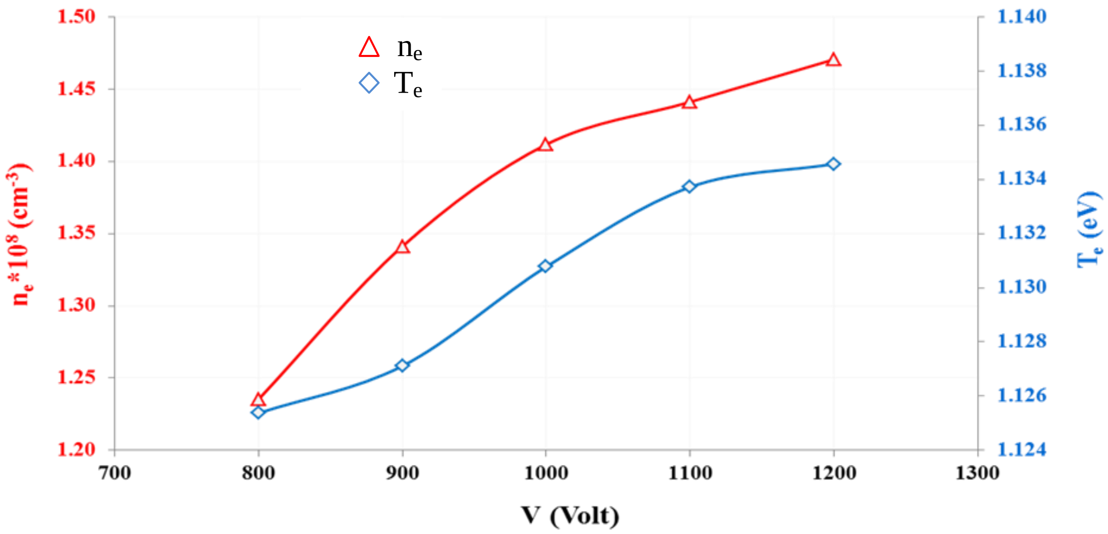

Fig. 5: The variation of electron temperature and electron density with DC voltages.

Conclusions

The cadmium oxide films prepared by D.C plasma magnetron sputtering with the voltage (1200) V, at the temperature of (523, 623) K, are polycrystalline and cubic type and the preferred orientation along (111) direction matching with standard card No 96-900-8610 (JCPDS).and also the peaks for cadmium element hide due to annealing in oxygen and which regarded it one of method prepare cadmium oxide.

Also, the microstrain increases by increasing the temperature of the annealing and the reason was the growth of the film, and thus the expansion of the lattice, which leads to a change in the vertical distance between the atoms.

Plasma diagnosis in the spectral analysis showed that electronic temperature and electron density increase by increasing voltages, and that the increase in the electrons density is caused by the increase in ionization probability, (The cross-collision of ionization), which is related to the increase in the energy of the electrons, and that the length of the debye decreases while the frequency of the plasma becomes more directly proportional "with the electronic density.

References

[1] R. H. Bari and S. B. Patil, Int. Lett. Chem. Phys. Astron., 37 (2013) 31-46.

[2] T.L. Chu and S.S. Chu, Journal of Electronic Material, 19 (1990) 1003-1005.

[3] Z. M. Jarzberzki, "Oxide Semiconductors", Pergamon Press, London, (1973).

[4] D.B. Chrisey and G.K.Hublereds Pulsed Laser Deposition of thin films". Chap.1. John Wiley & SonsNewYork", 1994.

[5] F.I. Ezema, and P.E. Ugwuoke, The Pacific J. of Science and Technology (2003) 33-38.

[6] C.H. Bhosale, A.V. Kambale, A.V. Kokate, K.Y. Rajpure, Materials Science and Engineering. B122 (2005) 67-71.

[7] F.A. Cotton, G. Willkinson, C.A. Murillo, M. Bochman, "Advance Inorganic Chemistry", John Wiley and Sons, 1999.

[8] Patnaik, Handbook of Inorganic Chemical Compounds, McGraw- Hill, 2003.

[9] B. D. Cullity, “Elements of X-ray Diffraction.”Addison-Wesley Reading, MA, 1970.

[10] W. L. Bragg, Nature, 95 (1915) 561-561.
[11] M. A. Hassouba and N. Dawood, Life Science Journal, 11, 9 (2014) 656-666.
[12] D.Kieran, "Design and Application of a plasma Impedance Monitor for RF Plasma Diagnostics "2000.
[13] S. S. Harilal, "Optical Emission Diagnostics of Laser Produced Plasma from Graphite and $YBa_2Cu_3O_7$. Ph.D. Thesis, International School of Photonics, University of Science and Technology, India, 1997.
[14] F.Bayansal. B.Şahin and T. Taşköprü, Ceram. Int., 40 (2014) 8709-8714.