International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.9, pp 625-632, 2017

Study the Structural and Electrical Properties of PbO Thin Films Deposited by Chemical Spray Pyrolysis Technique

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Abstract : Chemical spray pyrolysis(CSP) method has been successfully employed for the deposition of nanocrystructured lead oxide (PbO) thin films. The films changes in the structural, topographical, and electrical properties were studied. The structural properties of (PbO) films were studied by means of X-ray diffraction (XRD) and atomic force microscopy (AFM). XRD analysis shows that all the films are polycrystalline in the tetragonal phase and present a random orientation. Surface topography of the lead oxide film consists of nanocrystalline grains with uniform coverage of the substrate surface with randomly oriented topography. The electrical measurements such as the Hall effect and D.C conductivity for all films. The results showed that (PbO) has conductivity about of [5.17×10^{-6} $(\Omega.cm)^{-1}$] at room temperature, and this conductivity increased with increasing of thickness, as well as the results showed throughout the study that all films have two activation energy and this energy increase with increasing of thickness.

1. Introduction

Lead Oxide (PbO), an important industrial material, has been widely applied in gas sensors, pigments and paints [1]. PbO has two polymorphic forms and a wide band gap: red α - PbO, stable at low temperature, and yellow β - PbO, stable at high temperature [2]. Because of its applications, considerable progresses have been made on the synthesis of lead (II) monoxide polymorphs (α - PbO and β - PbO) over the years. Methods such as thermal evaporation, sputtering ,and spray deposition [3] have been adopted for the synthesis of PbO. The available methods, precipitation, hydrothermal and solvothermal methods have gained importance due to the fact that they are simple, employ low synthesis temperature and ensure pure single and multi products. Among them, chemical spray pyrolysis technique has been a major focus in the preparative investigations due to the advantages over other techniques, such as low-cost, mild temperature, potential controllability over size and morphology, which play key roles in tailoring the properties of nanomaterials. Under low temperature conditions, many starting materials can undergo quite unexpected reactions, which are often accompanied with the formation of nanoscopic morphologies that are not accessible by traditional routes. Lead (II) monoxide (PbO) is a photo active semiconducting metal oxide and has gained industrial importance due to its potent application in diversified fields. It plays a vital role in the formation of electrode active mass in lead acid batteries that are used in a variety of areas due to its high power density, wide application temperature range, complete recycling system and relatively low price [4]. Despite the methods available in the literature for the preparation of PbO and nanoPbO, finding an efficient method to produce PbO with size control and orientation by simple methods is still a challenge to material scientists today. Recently, the synthesis of PbOnano structures has gained importance owing to their unusual physicochemical properties leading to outstanding applications as humidity sensors [5]. The output response of polycrystalline compound (when plotted in a complex plane) represents grain, grain boundary and electrode properties with different time constants leading to successive semicircles [6]. The mechanism of electrical conductivity in ion conducting solid is also an important problem. The conductivity is generally studied as a function of temperature, and it may also depend on structural changes in the material [7]. The aim of this paper is study, structural andelectrical properties and characterization of lead oxide.

2. Experimental Work

Lead Oxide thin films have been prepared by chemical spray pyrolysis (CSP) technique onto highly cleaned glass substrate with the dimensions (35× 25 ×1.35) mm^3. A homogeneous solution of (0.03M) was prepared by dissolving lead chloride compound ($PbCl_2.2H_2O$) by re-distilled water and a few drops of glacial acetic acid were then added to stabilize the solution. The solution was stirred for (1hr) with a magnetic stirrer. The carrier gas was (compressed nitrogen) and the solution is fed into a sprayer nozzle at a pre-adjusted constant atomization pressure (4.5 bar) and we use different number of spray (5, 10, and 20 No.of spray) that corresponding to the different thichness (55, 95, and 185) nm, respectivily at a constant temperature 400˚C for all samples.The crystal structure of the PbO thin film was determined by (XRD) using Shimadzu (6000) diffractometer with CuKα X-ray source. Their surface morphology was studied with an (AFM).The electrical conductivity has been measured as a function of temperature for films in the range (313 – 338) K by using the electrical circuit. The measurements have been done using sensitive digital electrometer type Keithley (616) and electrical oven.The Hall effect was carried out according to the electrical circuit which contains a D.C. power supply with (0 – 40) V, and two digital electrometers (HMS-3000) to measure the current and voltage.

3. Results and Discussion

We discuss in this section some properties that descripe characterization of (PbO) thin film deposited by (CSP) technique :

3.1 Structural Measurements (XRD)

XRD patterns of PbO thin films deposit on glass substrate at different thicknesses (different no. of spray (5, 10, and 20)) are shown in Fig.(1).

The intensities of the peaks increases with increasing the PbO thin film thickness for all substrates sample. This is due to the crystallinity of the films being improved and crystallite size become larger when elevating the thin film thickness. A similar behavior was observed by Öztaş and M.Bedir [8], and B. Deng *et al*. [9].All peaks appeared in the XRD spectra are consistent with the International Centre for Diffraction Data (JCPDS) card No. 85-1739 and revealing the tetragonal phase of PbO thin films. It can be concluded therefore,that the thickness plays a vital role in the growth mechanism of lead oxide thin films prepared by the spray pyrolysis technique. The crystallite size of the films for the (002) peak, calculated using Debye Scherrer's formula,C. S. Barrett and T.B. Massalski[10] :

$$G_S = \frac{0.94\,\lambda}{\beta \cos\theta} \quad (1)$$

Where (β) is the full width at half maximum of characteristic spectrum in units of radians. The average grain size that we found increased with increasing thickness , the values of (G_s)equal to (21.38, 23.03, and 26.69) nm corresponding to the following different thickness (55, 95, and 185) nm respectively

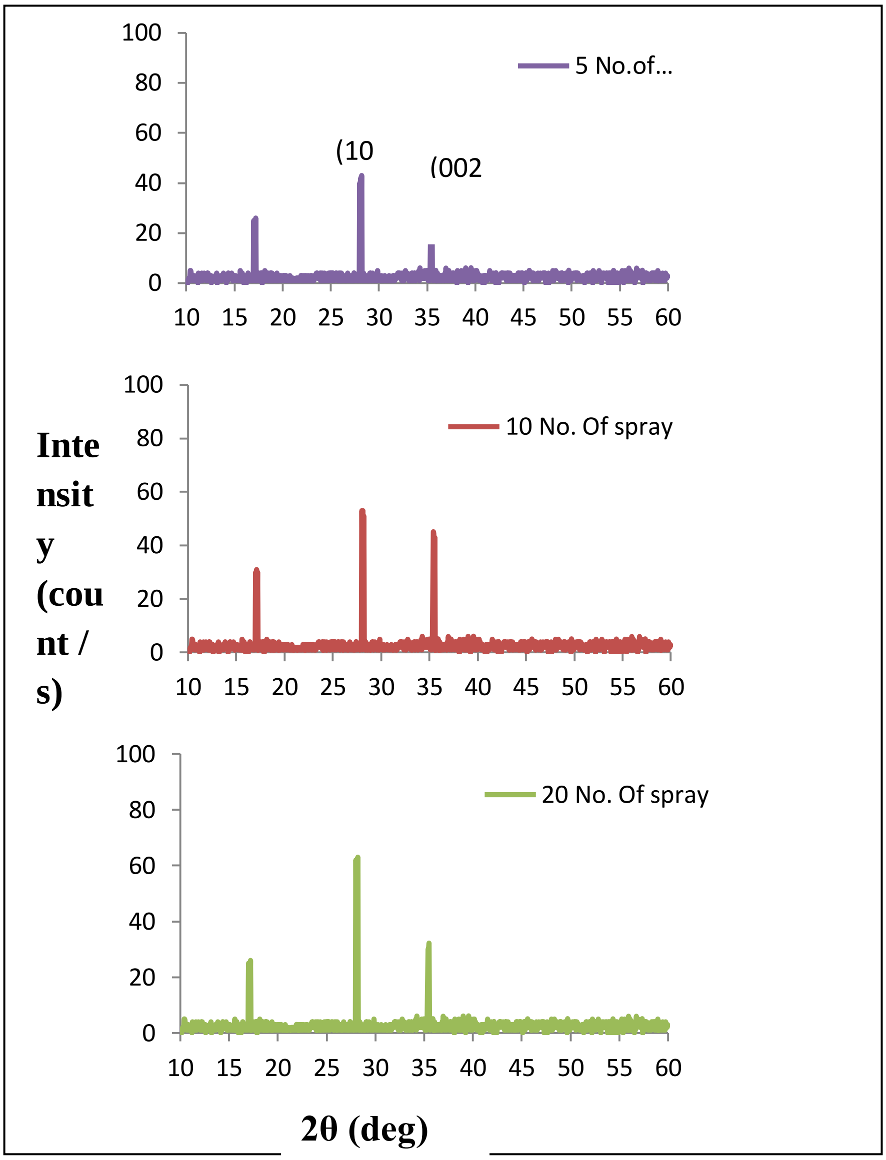

Fig. (1): XRD patterns for PbO thin films deposited on glass substrate with different No. of spray (5,10, and 20)

3.2 Surface Topography(AFM)

The 3-D AFM images and granularity accumulation distribution charts for PbO thin films deposited on glass substrate with different thickness {different no. of spray (5, 10, and 20)} shown in Fig.(2). The PbO have ball-shaped with good dispensability, homogenous grains and aligned vertically. By using special software imager, the estimated values of root mean square (r.m.s) of surface roughness average and average grain size are listed in Table (1). It is found that the grain size and the (r.m.s) of surface roughness increases when thickness increases. A similar behaved of B. Godbole*et al.* [11]. This phenomenon can be attributed to the nucleation and island as PbO grains were growing[12]. The compactness and homogeneity of the films was improved as the film thickness increased, which resulted in the formation of large PbO aggregates on the surface. Our results were a good agreement with S.M. Park *et al.*[12].

Table (1): The grain size, roughness average and root mean square for PbO thin films deposited on glass substrate with different thickness (No. of spray).

No. of spray	Thichness (nm)	Grain size (nm)	Roughness average (nm)	Root mean square (nm)
5	55	91.70	0.63	0.44
10	95	96.12	0.91	0.92
20	185	104.10	2.33	1.53

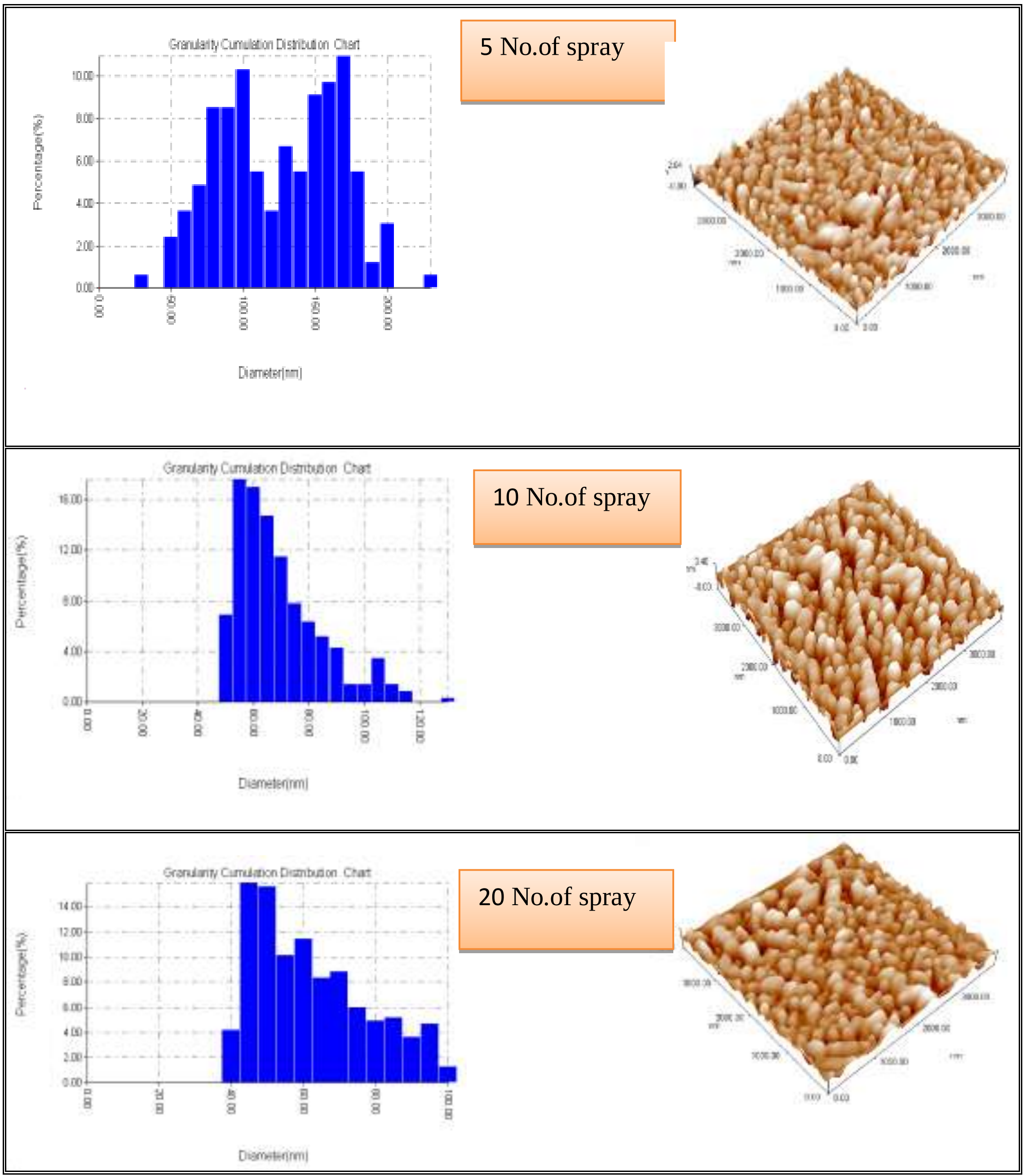

Fig.(2): 3-D AFM image and granularity accumulation for PbO with different thickness [No. of spray (5,10, and 20)].

The particle size found from AFM is different than XRD, this could be due to the techniques as AFM gives surface topography while X-ray penetrates inside and gives the average picture, and AFM give the grain size while XRD give the crystallite size. These results are agreement with [13].

Table (1) shows AFM topographies of the PbOthinfilms deposited onglass at different thickness. It has been observed that a minimum surface roughness has been found for the thickness (55) nm and the maximum value for the thickness (185) nm that are deposited with (5 and 20 No. Of spray) respectivily.

3.3 Electrical Properties of PbO Thin Films (Hall Effect)

As grown PbO usually exhibits n-type conductivity with a wide band gap. The n-type conductivity might be cause by intrinsic defects, interstitial lead and oxygen vacancies. From the Hall effect measurements, the resistivity (ρ), carrier concentration (N_H) and carrier mobility (μ_H) values were calculated and listed in Table (2). The negative sign of Hall coefficient indicates the conductivity nature of the film is n-type [14].

Figs. (3) and (4) show a plot of the variations of N_H andμ_H with thickness for thin pbO films deposition on glass substrate. Hall measurement indicates that the as-grown films are high resistance, which is usually attributed to poor crystal quality. We can notice from Figures the carrier concentration and mobility ofPbO thin films monotonically increased with increasing thickness. This is attributed to the improved crystallinity and increase grain sizes that weakens intercrystallite boundary scattering and increases carrier lifetime, these result agreement with M.Okutan *et al.*[15]. Also, the PbO film deposited with less thickness had the highest resistivity, which resulted from the lowest product of carrier concentration and mobility. These results are in agreement with other researches [8].

Table (2): Hall parameters for (PbO) films at different thickness [No. of spray (5,10, and 20)]

No. of spray	Thichness (nm)	R_H (cm^3 / C)	n_H (1 / cm^3)	$\sigma_{R.T}$ $(\Omega.cm)^{-1}$	$P_{R.T}$ (Ω.cm)	μ_H (cm^2/ V.s)
5	55	-8.56×10^6	-7.293×10^{11}	5.176×10^{-6}	2.632×10^5	4.430×10^1
10	95	-7.189×10^6	-8.683×10^{11}	7.766×10^{-5}	1.988×10^5	5.583
20	185	-3.219×10^1	-1.939×10^{17}	3.443×10^{-1}	1.205×10^5	1.108×10^{-1}

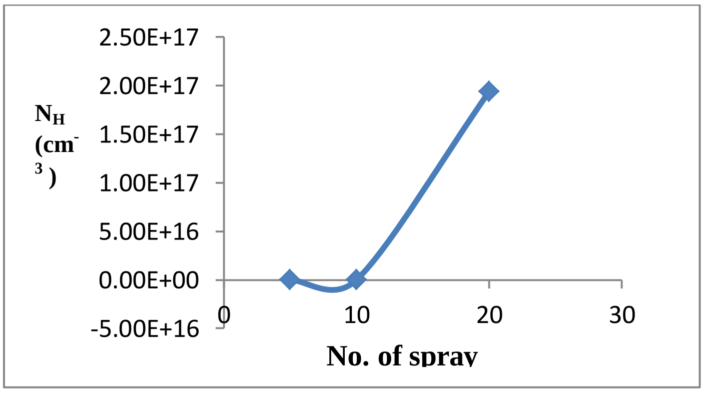

Fig.(3): Variation of carrier concentration as function of No. of spray for PbO thin film.

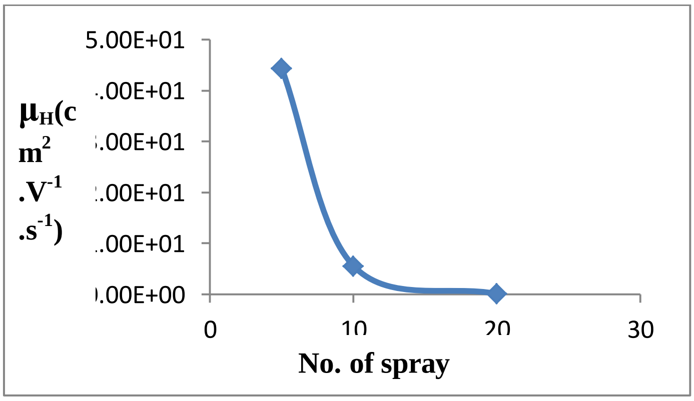

Fig.(4): Variation of mobility as function of No. of spray for PbO thin film.

The electrical resistivity as a function of thickness for of PbO thin films as shown in Fig.(5) for PbO films deposition on glass substrate . This curve consist of the resistivity is decrease with thickness increase.

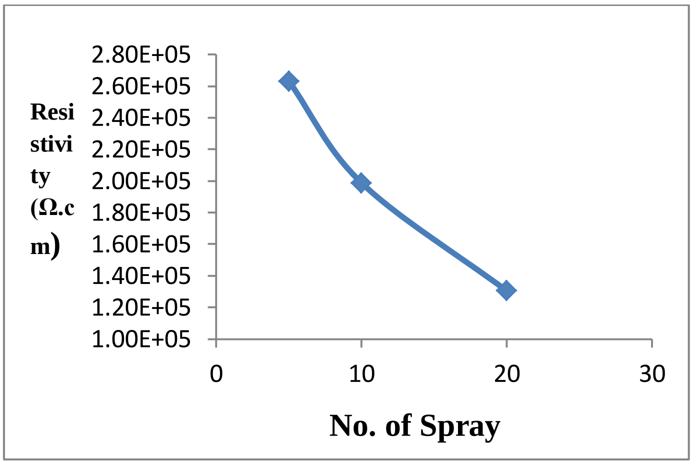

Fig. (5): Electrical resistivity as a function of No. of spray for PbO thin films.

3.4 D.C Electrical Conductivity

The direct electrical conductivity(D.C) curve of PbO thin film is shown inFig.(6). The electrical conductivity of the sample canbe analyzed by the well-known Arrhenius relation:

$$\sigma = \sigma_o \exp(-E_a/k_B T) \qquad (2)$$

Where(σ_o) is the pre-exponential factor and E_a is the activation energy for conduction. The conductivity curve indicates two conductivity regions corresponding to various conductivity mechanisms. These mechanisms may be distinguished experimentally in the investigated temperature ranges. It is evaluatedthat at the lower temperatures region ($313 \leq T \leq 323$ K) the conductivity takes place by means of variable-range hopping of thecharge carriers in the localized states near the Fermi level [16]. Thus, the conduction mechanism for thefirst conductivity region (I) is called variable-range hopping as the hopping length varies for each hop. The hopping conductivity is associated with charge carrier hopping between localized state.

The conduction mechanism in the second region (II) of Fig.(6),is mainly determined by hopping of thermally activated carriers into the band tails. In fact, the variable-range hopping regime dominating at region (I) should change to the constant-rangeregime with increasing temperature because the hopping distancewill reach its minimum possible value when the carriersjump between the nearest neighbouring sites [16]. Thus, athigher temperatures, the conductivity exhibits thermally activatedprocess and can be described by Eq. (2). The activationenergy was found as 0.0597 eV from the slope of second region of Fig.(6). This suggests a change to fixed range hopping charge transport at higher temperatures. From the fact that the temperature dependence of conductivity for the higher temperatures, we conclude that the semiconducting behavior is due to theactivation of a single energy state [17].The activation energy (E_a) obtained for these films is given in the Table (3).

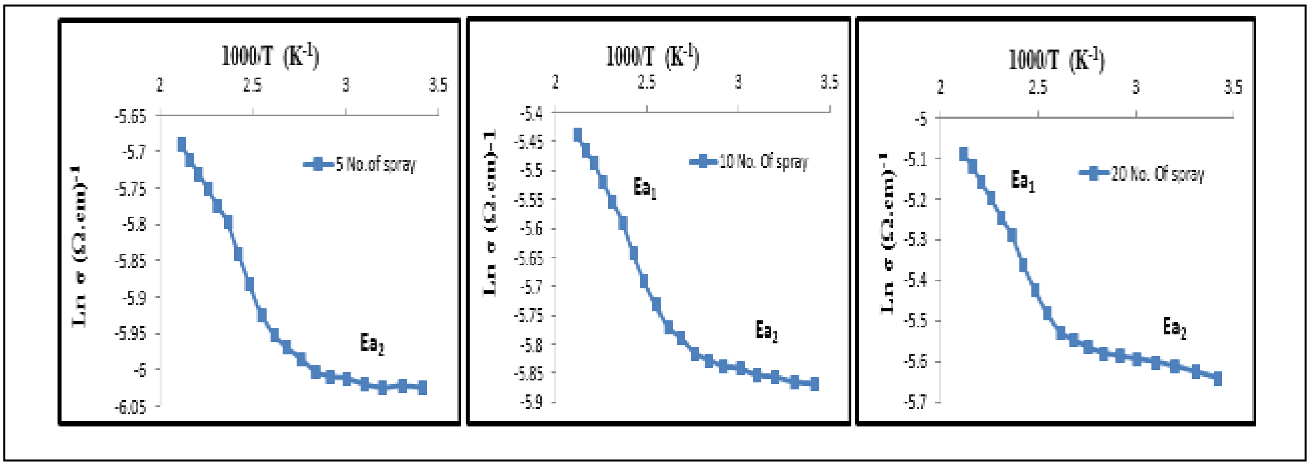

Fig.(6): Lnσ versus 1000/T for (PbO) thin films at different thickness(5, 10, and 20 No.of spray)

Table (3): D. Celectrical conductivity parameters for (PbO) thin films at different thickness(5, 10, and 20 No.of spray)

No. of spray	Thickness (nm)	Ea_1 (eV)	Temp.Range (K)	Ea_2 (eV)	Temp.Range (K)	$\sigma_{R.T}\times10^{-5}$ $(\Omega.cm)^{-1}$
5	55	0.00274	(313-323)	0.04035	(328-338)	241
10	95	0.00685	(313-323)	0.05985	(328-338)	282
20	185	0.00984	(313-323)	0.07918	(328-338)	355

Fig. (7) shows the variation of D.C conductivity (σ) vs. temperature (T), this figure shows that (σ) at different thicknness increased with T, this seems to be a normal behavior as one of semiconductor properties, due to the increasing of carrier concentration with temperature. When we increase No. Of spray (5, 10, and 20) noticd that $\sigma_{D.C}$ was increased with increasing T.

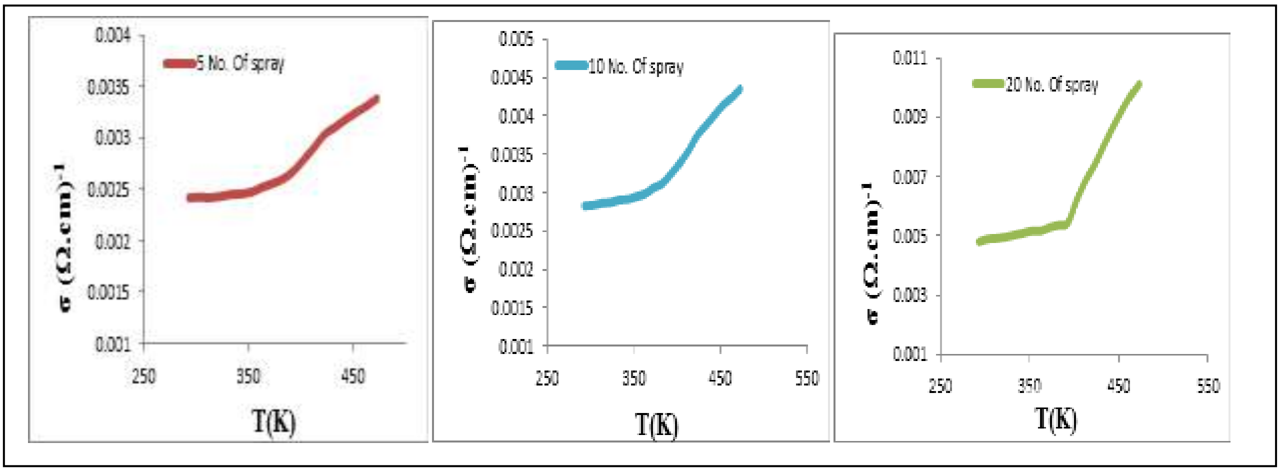

Fig.(7): Variation of $\sigma_{D.C}$ versus temperature for PbO films at different thichness (5, 10, and 20 No.of spray)

Conclusions

In summary, PbO thin films have been deposited by chemical spray pyrolysis method on glass substrates. The films have been deposited in a furnace at different thichness.The XRD results reveal that the deposited thin film has a goodpolycrystalline tetragonal structure. The size of (grains) that be from AFM for thichness (95 nm)[10 no. of spray] is about 96.12 nm. From the measurements of Hall effect conclude that the (PbO) thin films had n-type, and low conductivity. Also, have two activation energy. Mobility decrease with increasing of substrate temperatures. $\sigma_{D.C}$ was increased with increasing of thichness.Finally, we can say that we haveprepared samples of

PbO of good structural and electrical properties which can be usedin many electrical applications and mainly in the field of photovoltaic cells.

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