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Errata

The editor would like to announce the retraction of this paper from this journal for the reason of copyright infringement.

This article was identified as having a similarity index of 79% with papers listed in the annex.

The editorial staff of the journal would like to apologize for the misunderstanding and technical error that led to the publication of the article in this journal.

Editor in Chief

Prof. Dr. Mihai Popescu

Annex to errata

TEMPERATURE AND THICKNESS EFFECT ON THE CHARACTERIZATION OF THE SPRAYED MnO FILMS

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Digest Journal of Nanomaterials and Biostructures Vol. 12, No. 2, April - June 2017, p.
565 - 570 TEMPERATURE AND THICKNESS EFFECT
ON THE CHARACTERIZATION OF THE SPRAYED MnO FILMS M. ÖZTAŞa*, M. BEDİRb, M.
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cUniversity of Gaziantep, Department of Metallurgical and Materials Engineering, Gaziantep/Turkey d Higher Educational School, Yalova University, Yalova, Turkey eEngineering Faculty, Energy Systems Engineering, Yalova University, Yalova, Turkey MnO films have been deposited by spray pyrolysis technique using aqueous solutions of MnCl2 and deionized water. The MnO films were obtained at held substrate temperature of 375 oC on glass substrates using deposition times 2.0, 4.0, 6.0, 8.0 and 10.0 hour. The structural properties of the samples have been determined by using X-ray diffraction (XRD). It was found that the crystal structure of the MnO films is polycrystalline. The orientations forall the obtained films are along the c-axis perpendicular to the substrate. The electrical measurements of samples were obtained by DC four-probe technique on rectangular-shape samples. The effects of temperature on the electrical properties of the MnO films were studied in details. (Received March 22, 2017; Accepted June 6, 2017) Keywords: MnO, electrical conductivity, spray pyrolysis, X-ray diffraction

1. Introduction Manganese oxide particles are used as electrode materials and catalysts [1– 6]. Manganese oxide has crystal structures of MnO, MnO2, Mn2O3, and Mn3O4 according to the preparation conditions. The characteristics of manganese oxide particles such as mean size, crystal structure, morphology, and surface area are important to their applications. Nanosized manganese oxide particles are expected to exhibit good performance because of their large surface area and high reactivity. Nano-sized manganese oxide particles with various crystal structures were prepared using the liquid phase and gas phase reaction methods [1–3]. The liquid phase reaction method had advantages in the preparation of manganese oxide particles with narrow size distributions and spherical shapes.

The gas phase reaction method too resulted in the preparation of manganese oxide particles with high crystallinity because of their high preparation temperatures

Spray pyrolysis has several advantages in the preparation of nano-sized particles [7-9]. A variety of inexpensive metal salts can be used as precursors. Large-scale production is possible due to simple equipment and mild operating conditions. Nano-sized particles with low aggregation degrees are normally prepared at low temperatures in spray pyrolysis. To be able to prepare particles with high crystallinity and purity, however, a high processing temperature is required.

The electrical conductivities, are valuable tools for the study of transport mechanisms, and may also be obtained to give better insight into the electrical transport of compound semiconductors. The four-point probe method has proven to be a convenient tool for the measurement of electrical conductivities. The electrical conductivity measurements can be determined by a standard four-point probe measurement technique, which is one of the best methods to obtain electrical conductivity.

To our knowledge, there is no data available in the literature on electrical resistivity and conductivity of MnO films prepared by pyrolysis spray technique. The main aim of this study is to investigate the general feature of the

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temperature and thickness effect on the characterization of MnO films in the temperature range of 300 K–820 K.

2. Experimental details Spray pyrolysis involves the spraying of a fine mist of very small droplets containing reactants onto hot substrate. The droplets undergo evaporation, solute condensation, and thermal decomposition of volatile by products which result in film formation. In this technique, MnO films were deposited on heated clean glass (about 1 cm2 of geometric area) substrates by spraying an aqueous solution in air atmosphere at the fixed substrate temperature of 375 °C. The spray solutions are comprised MnCl2 (0.5 M, Merck, 99%) in the deionized water. The spray flow rate was adjusted to about 0.3 ml/min and the distance between the nozzle (head of the sprayed source) and the substrate was kept at 20 cm in all cases.The four-point probe method is the most widely used technique for electrical profile measurement of materials. Two of the probes are used to source current and the other two probes are used to measure voltage, using four probes eliminates measurement errors due to the probe resistance, the spreading resistance under each probe, and the contact resistance between each metal probe and material. The electrical measurements of samples were obtained by DC four-probe technique on rectangular-shape samples with area of 0.5 cm x 1.0 cm.

A Keithley 6500 source meter was used to provide constant current and the potential drop was measured by a Keithley 2700 multimeter through interface card, which are controlled by a computer. Platinum wires with diameter of 1 mm were employed as current and potential electrodes. The measurements have been done at 300-820 K temperature range. The temperature of sample has been changed by controllable Nabertherm type P 320 heater and measured using a standard thermocouple. The structural properties of the films were studied by X-ray analysis with a Rigaku D/Max-IIIS

model X-ray diffractometer (λ=1.5405 Å). The film thicknesses were determined by an interferometric method (using multiple-beam Fizeau fringe method at reflection of monochromatic light, λ=550 nm). Films of different thicknesses were produced using deposition times 2.0, 4 .0,
6.0, 8.0 and 10
.0 h. 3. Results and discussions The MnO films
were characterized by the X-ray diffraction (XRD) technique scanned in the 2θ range of 20–50°
as shown in Fig.1.
Figure 1 shows that all films are polycrystalline and formed with
different thickness exhibit a
strong peak [10]. No other diffraction peak around other planes of the MnO films was observed.
These results indicate an improvement in the degree of crystallinity of the films with increasing film thickness up to 495 nm. The improvement in crystallinity is due to increased ability of adatoms to move towards stable sites in the lattice.
It is observed from figure 1 that the film thickness mostly affects the
crystallinity and degree of orientation of the MnO films.
In this study, the films have good quality of crystallinity with increasing film thickness and deposition time
up tp 495 nm.
Also the trend of increase in crystallite size may be interpreted in the terms of a columnar grain growth in the structure. The
growth in grains with film thickness as explained earlier leads to reductions in grain boundary scattering due to charge carriers, thus increases the mobility for the obtained films[11] and eventually reduces the film resistivity, which is consistent with XRD observations. Then, increasing the
film thickness
results in a change of preferred growth. The
decrease in XRD peak intensity with the increasing of the film thickness may be due to the sufficient increase in supply of thermal energy for recrystallization and the grain boundary growth with
deposition times. The variation of the structural parameters of MnO
films at room temperature is shown in Table 1 as a function of thickness. Just as it was expected, all films showed a decrease in the electrical resistivity as the films thickness increases
up to 495 nm.
Increased film thickness leads to better stacking of the film with resultant increase in grain size thus reducing grain defects and grain boundary scattering.
This resistivity behavior agreed with that reported by Yu et al. for ZnO:Ga films deposited by rf magnetron sputtering[12]. Also, this behavior may be due to increase of carrier concentration and mobility. A similar characteristic has been observed in ZnO:Cu films by Oztas et al.[13]. Thus it can be said that as the films get poor crystallinity, the resistivity is markedly increased, whichwas primarily due to the 567 decrease in carrier concentration
and also
the presence of neutral impurity centers, grain boundary discontinuities, presence of surface
states for higher thickness of the film.
These observations may be due to size effects that are arising because of
quantum confinement of charge carriers within the particles. Generally in semiconductors the conduction mechanism is highly influenced by the intercrystalline grain boundaries and strain fields associated dislocation network.
As deposition time increases, amount of solute (i.e. manganese chloride) reaching on the surface of the substrate increases to form film and therefore the electrostatic interaction between solute particles becomes larger thereby increasing the probability of more solute particles to be gathered together forming a grain.
Moreover,
the samples prepared by the spray pyrolysis method in air atmosphere, it is found that oxygen becomes one of the most important background impurities that are easily diffusing into the crystal lattice during the production of the samples in air at elevated temperatures. The oxygen impurities are first physically adsorbed at the grain boundaries and on the surface of the films[
14].
As a result, the resistivity of the films are high. This may be due to the grain boundary effects since the films are polycrystalline in nature. Since air was used as the carrier gas it is quite likely that a large number of the oxygen molecules are chemisorbed in the film both at the grain boundaries and on the surface. The chemisorption of the oxygen will produce potential barrier, which hinders the electrical transport causing a reduction in conductivity.
(
(e) (d) (c) (b) (a) 20 25 30 35 40 45 50 Fig. 1.
X-ray diffraction
patterns of MnO films grown at 375 °C substrate temperature with different film thicknesses: (a) 235 nm,
(b) 335 nm, (c) 495 nm, (d) 525 nm, (e)565 nm Table 1. The variation of

the structural properties of MnO films deposited at 375 °C substrate temperature Sample no Deposition time (Hour) Thickness (nm) Grain Size (nm) Resistivity (x107 Ohm- cm) Carrier Mobility(cm2/V.s) Carrier Concentrations
(x1016 cm-3) 1 2.0 235 89 45 120 25 2 4.0 335 125 32 140 32 3 6.0 495 175 25 155 55 4 8.0 525 155 30 138 48 5 10.0 565 130 38 130 40
Fig. 2. Plot of log(σ) vs. (1000/T) of MnO films of thicknesses.
900 800 Activation Energy (meV) 700 600 500 400 300 200 300 400 500 600 Thickness (nm)
Fig. 3. Plot of activation energy vs. thickness. It is known[15,16] that between the electronic transport properties of polycrystalline semiconducting films and their structural characteristics there is a strong correlation. Particularly, both the values and the variation of the electrical conductivity of such films are in connection with their structure and its changes. On this basis, the study of the temperature dependence of the electrical properties of the films, may offer useful information about the possible changes of the structural characteristics of the films. The conductivity (σ)measurements were carried out in the temperature range 300–
820K
using dc four -point probe method. Since our experimental data fit to the relation; ? ? ? 0 exp(? Ea) (1)
kT where σ is the measured electrical conductivity, T the absolute temperature, σ0 the conductivity pre-exponential factor, Ea the activation energy and k is the Boltzmann's constant.
The
ln σ versus 1000/T plots in Fig. 2 is linear for different thicknesses which confirm
that the conduction in the concerned range of temperature is through thermally activated process and the conductivity increasing with temperature is exponential. Maity et al.[17] also observed a similar type of observation of conductivity behavior in transparent conducting oxides. It is seen that conductivity increases with temperature indicating semiconducting nature of films[18]. The increase in conductivity with
temperature depends on the decrease in grain boundary concentration and the increase in ionized defects, which increases the carrier concentration and movement ofthe charge carriers.The activation energies are calculated from the local gradients of the ln σ versus inverse temperature
plots. A graph
of the activation energy versus different thickness for the two representative MnO films (FIG. 3) confirms the reduction in activation energy as the thickness
increases, thus re-proving the semiconductivity
of the sprayed MnO films. In films, certain structural changes resulting from imperfections and
defects can occur and conductivity is 569 increased and
high temperature conductivity is attributed to the thermal stimulation of the
grains
of the charge carriers to the neutral regions of the grains. The
decrease in the
activation energy also suggests that is attributed to the decrease in defect levels, and the grain boundary scattering contribution reduces significantly as the thickness increases. A similar characteristic has been observed in As2S3 thin
films by Mane et al.[19]. In general, the electron transport properties are affected by the presence of a number of defects such as structural disorders, dislocations and surface imperfections, and the variation of the grain size could also influence the activation energy
[20]. Activation energy was found to depend on the thickness and decrease with increasing
thickness. This can be explained due to the polycrystalline nature of the films as explained by Seto's model[21]. A polycrystalline film material includes a plurality of microcrystals with grain boundaries between them. At the grain boundary, incomplete atomic bonds can act as trap centers. These trap centers hold the charge carriers at the grain boundary and
for this reason an area
charge can be generated locally. This field charge inhibits the passage of charge carriers from one crystallite to another. Hence, the
values of Ea are different for different
applied voltages depending on the different holding levels
between the valence and the conduction band.
4. Conclusions MnO
films have been prepared by the spray pyrolysis method on glass substrates heated at 375 °C using different deposition times. XRD analysis of the films as a function of film thickness show that crystallinity improves with film thickness up to 495 nm. Then the
crystallization is deteriorating.
It is observed that temperature dependence of electrical conductivity
exhibits a semiconducting behavior. The calculation of activation energy suggests that thermally activated conduction mechanism plays a significant role in conduction processes. The Arrhenius graphs of MnO films confirm the mechanism of high temperature conduction as grain boundary distributionmechanism.
For this reason,

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MnO films have been deposited by spray pyrolysis technique using aqueous solutions of $MnCl_2$ and deionized water. The MnO films were obtained at held substrate temperature of 375 ^oC on glass substrates using deposition times 2.0, 4.0, 6.0, 8.0 and 10.0 hour. The structural properties of the samples have been determined by using X-ray diffraction (XRD). It was found that the crystal structure of the MnO films is polycrystalline. The orientations for all the obtained films are along the *c*-axis perpendicular to the substrate. The electrical measurements of samples were obtained by DC four-probe technique on rectangular-shape samples. The effects of temperature on the electrical properties of the MnO films were studied in details.

(Received March 22, 2017; Accepted June 6, 2017)

Keywords: MnO, electrical conductivity, spray pyrolysis, X-ray diffraction

1. Introduction

Manganese oxide particles are used as electrode materials and catalysts [1–6]. Manganese oxide has crystal structures of MnO, MnO_2, Mn_2O_3, and Mn_3O_4 according to the preparation conditions. The characteristics of manganese oxide particles such as mean size, crystal structure, morphology, and surface area are important to their applications. Nanosized manganese oxide particles are expected to exhibit good performance because of their large surface area and high reactivity. Nano-sized manganese oxide particles with various crystal structures were prepared using the liquid phase and gas phase reaction methods [1–3]. The liquid phase reaction method had advantages in the preparation of manganese oxide particles with narrow size distributions and spherical shapes. The gas phase reaction method too resulted in the preparation of manganese oxide particles with high crystallinity because of their high preparation temperatures

Spray pyrolysis has several advantages in the preparation of nano-sized particles [7-9]. A variety of inexpensive metal salts can be used as precursors. Large-scale production is possible due to simple equipment and mild operating conditions. Nano-sized particles with low aggregation degrees are normally prepared at low temperatures in spray pyrolysis. To be able to prepare particles with high crystallinity and purity, however, a high processing temperature is required. The electrical conductivities, are valuable tools for the study of transport mechanisms, and may also be obtained to give better insight into the electrical transport of compound semiconductors. The four-point probe method has proven to be a convenient tool for the measurement of electrical conductivities. The electrical conductivity measurements can be determined by a standard four-point probe measurement technique, which is one of the best methods to obtain electrical conductivity. To our knowledge, there is no data available in the literature on electrical resistivity and conductivity of MnO films prepared by pyrolysis spray technique. The main aim of this study is to investigate the general feature of the

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temperature and thickness effect on the characterization of MnO films in the temperature range of 300 K–820 K.

2. Experimental details

Spray pyrolysis involves the spraying of a fine mist of very small droplets containing reactants onto hot substrate. The droplets undergo evaporation, solute condensation, and thermal decomposition of volatile by products which result in film formation. In this technique, MnO films were deposited on heated clean glass (about 1 cm^2 of geometric area) substrates by spraying an aqueous solution in air atmosphere at the fixed substrate temperature of 375 °C. The spray solutions are comprised $MnCl_2$ (0.5 M, Merck, $\geqslant$99%) in the deionized water. The spray flow rate was adjusted to about 0.3 ml/min and the distance between the nozzle (head of the sprayed source) and the substrate was kept at 20 cm in all cases. The four-point probe method is the most widely used technique for electrical profile measurement of materials. Two of the probes are used to source current and the other two probes are used to measure voltage, using four probes eliminates measurement errors due to the probe resistance, the spreading resistance under each probe, and the contact resistance between each metal probe and material. The electrical measurements of samples were obtained by DC four-probe technique on rectangular-shape samples with area of 0.5 cm x 1.0 cm. A Keithley 6500 source meter was used to provide constant current and the potential drop was measured by a Keithley 2700 multimeter through interface card, which are controlled by a computer. Platinum wires with diameter of 1 mm were employed as current and potential electrodes. The measurements have been done at 300-820 K temperature range. The temperature of sample has been changed by controllable Nabertherm type P 320 heater and measured using a standard thermocouple. The structural properties of the films were studied by X-ray analysis with a Rigaku D/Max-IIIS model X-ray diffractometer (λ=1.5405 Å). The film thicknesses were determined by an interferometric method (using multiple-beam Fizeau fringe method at reflection of monochromatic light, λ=550 nm). Films of different thicknesses were produced using deposition times 2.0, 4.0, 6.0, 8.0 and 10.0 h.

3. Results and discussions

The MnO films were characterized by the X-ray diffraction (XRD) technique scanned in the 2θ range of 20–50° as shown in Fig.1. Figure 1 shows that all films are polycrystalline and formed with different thickness exhibit a strong peak [10]. No other diffraction peak around other planes of the MnO films was observed. These results indicate an improvement in the degree of crystallinity of the films with increasing film thickness up to 495 nm. The improvement in crystallinity is due to increased ability of adatoms to move towards stable sites in the lattice. It is observed from figure 1 that the film thickness mostly affects the crystallinity and degree of orientation of the MnO films.In this study, the films have good quality of crystallinity with increasing film thickness and deposition time up tp 495 nm. Also the trend of increase in crystallite size may be interpreted in the terms of a columnar grain growth in the structure. The growth in grains with film thickness as explained earlier leads to reductions in grain boundary scattering due to charge carriers, thus increases the mobility for the obtained films[11] and eventually reduces the film resistivity, which is consistent with XRD observations. Then, increasing the film thickness results in a change of preferred growth. The decrease in XRD peak intensity with the increasing of the film thickness may be due to the sufficient increase in supply of thermal energy for recrystallization and the grain boundary growth with deposition times. The variation of the structural parameters of MnO films at room temperature is shown in Table 1 as a function of thickness. Just as it was expected, all films showed a decrease in the electrical resistivity as the films thickness increases up to 495 nm. Increased film thickness leads to better stacking of the film with resultant increase in grain size thus reducing grain defects and grain boundary scattering. This resistivity behavior agreed with that reported by Yu et al. for ZnO:Ga films deposited by rf magnetron sputtering[12]. Also, this behavior may be due to increase of carrier concentration and mobility. A similar characteristic has been observed in ZnO:Cu films by Oztas et al.[13]. Thus it can be said that as the films get poor crystallinity, the resistivity is markedly increased, which was primarily due to the

decrease in carrier concentration and also the presence of neutral impurity centers, grain boundary discontinuities, presence of surface states for higher thickness of the film. These observations may be due to size effects that are arising because of quantum confinement of charge carriers within the particles. Generally in semiconductors the conduction mechanism is highly influenced by the intercrystalline grain boundaries and strain fields associated dislocation network. As deposition time increases, amount of solute (i.e. manganese chloride) reaching on the surface of the substrate increases to form film and therefore the electrostatic interaction between solute particles becomes larger thereby increasing the probability of more solute particles to be gathered together forming a grain. Moreover, the samples prepared by the spray pyrolysis method in air atmosphere, it is found that oxygen becomes one of the most important background impurities that are easily diffusing into the crystal lattice during the production of the samples in air at elevated temperatures. The oxygen impurities are first physically adsorbed at the grain boundaries and on the surface of the films[14]. As a result, the resistivity of the films are high. This may be due to the grain boundary effects since the films are polycrystalline in nature. Since air was used as the carrier gas it is quite likely that a large number of the oxygen molecules are chemisorbed in the film both at the grain boundaries and on the surface. The chemisorption of the oxygen will produce potential barrier, which hinders the electrical transport causing a reduction in conductivity.

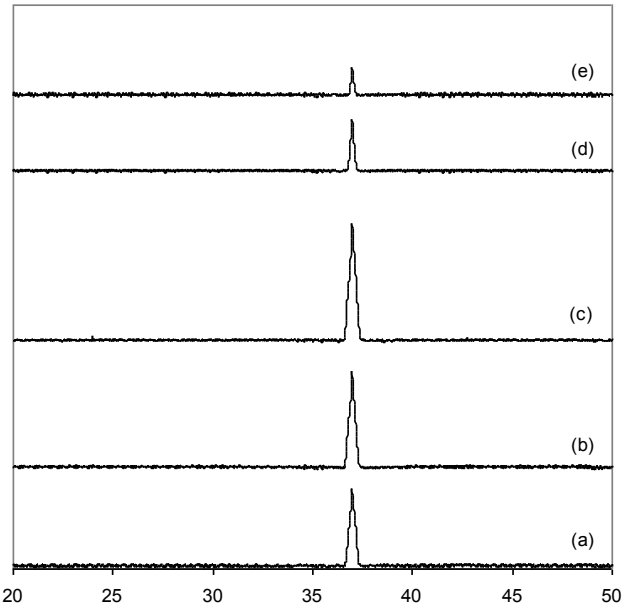

Fig. 1. X-ray diffraction patterns of MnO films grown at 375 °C substrate temperature with different film thicknesses: (a) 235 nm, (b)335 nm, (c) 495 nm, (d) 525 nm, (e)565 nm

Table 1. The variation of the structural properties of MnO films deposited at 375 °C substrate temperature

Sample no	Deposition time (Hour)	Thickness (nm)	Grain Size (nm)	Resistivity ($x10^7$ Ohm-cm)	Carrier Mobility ($cm^2/V.s$)	Carrier Concentrations ($x10^{16}$ cm^{-3})
1	2.0	235	89	45	120	25
2	4.0	335	125	32	140	32
3	6.0	495	175	25	155	55
4	8.0	525	155	30	138	48
5	10.0	565	130	38	130	40

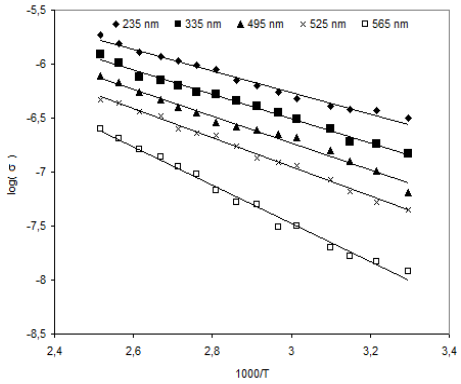

Fig. 2. Plot of log(σ) vs. (1000/T) of MnO films of thicknesses.

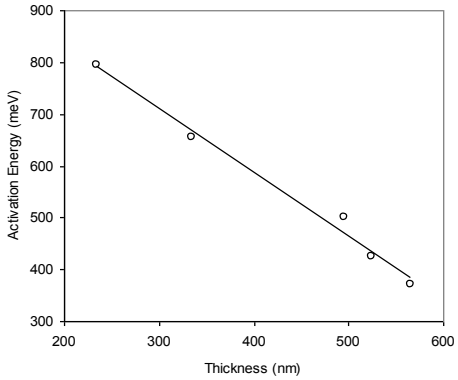

Fig. 3. Plot of activation energy vs. thickness.

It is known[15,16] that between the electronic transport properties of polycrystalline semiconducting films and their structural characteristics there is a strong correlation. Particularly, both the values and the variation of the electrical conductivity of such films are in connection with their structure and its changes. On this basis, the study of the temperature dependence of the electrical properties of the films, may offer useful information about the possible changes of the structural characteristics of the films. The conductivity (σ) measurements were carried out in the temperature range 300–820K using dc four-point probe method. Since our experimental data fit to the relation;

$$\sigma = \sigma_0 \exp(\frac{-E_a}{kT}) \tag{1}$$

where σ is the measured electrical conductivity, T the absolute temperature, σ_0 the conductivity pre-exponential factor, E_a the activation energy and k is the Boltzmann's constant. The ln σ versus 1000/T plots in Fig. 2 is linear for different thicknesses which confirm that the conduction in the concerned range of temperature is through thermally activated process and the conductivity increasing with temperature is exponential. Maity et al.[17] also observed a similar type of observation of conductivity behavior in transparent conducting oxides. It is seen that conductivity increases with temperature indicating semiconducting nature of films[18]. The increase in conductivity with temperature depends on the decrease in grain boundary concentration and the increase in ionized defects, which increases the carrier concentration and movement of the charge carriers.The activation energies are calculated from the local gradients of the ln σ versus inverse temperature plots. A graph of the activation energy versus different thickness for the two representative MnO films (FIG. 3) confirms the reduction in activation energy as the thickness increases, thus re-proving the semiconductivity of the sprayed MnO films. In films, certain structural changes resulting from imperfections and defects can occur and conductivity is

increased and high temperature conductivity is attributed to the thermal stimulation of the grains of the charge carriers to the neutral regions of the grains. The decrease in the activation energy also suggests that is attributed to the decrease in defect levels, and the grain boundary scattering contribution reduces significantly as the thickness increases. A similar characteristic has been observed in As_2S_3 thin films by Mane et al.[19]. In general, the electron transport properties are affected by the presence of a number of defects such as structural disorders, dislocations and surface imperfections, and the variation of the grain size could also influence the activation energy [20]. Activation energy was found to depend on the thickness and decrease with increasing thickness. This can be explained due to the polycrystalline nature of the films as explained by Seto's model[21]. A polycrystalline film material includes a plurality of microcrystals with grain boundaries between them. At the grain boundary, incomplete atomic bonds can act as trap centers. These trap centers hold the charge carriers at the grain boundary and for this reason an area charge can be generated locally. This field charge inhibits the passage of charge carriers from one crystallite to another. Hence, the values of Ea are different for different applied voltages depending on the different holding levels between the valence and the conduction band.

4. Conclusions

MnO films have been prepared by the spray pyrolysis method on glass substrates heated at 375 °C using different deposition times. XRD analysis of the films as a function of film thickness show that crystallinity improves with film thickness up to 495 nm. Then the crystallization is deteriorating. It is observed that temperature dependence of electrical conductivity exhibits a semiconducting behavior. The calculation of activation energy suggests that thermally activated conduction mechanism plays a significant role in conduction processes. The Arrhenius graphs of MnO films confirm the mechanism of high temperature conduction as grain boundary distribution mechanism. For this reason, it has been observed that the electrical conductivity and the activation energy depend on the thickness. The thickness dependence of the activation energy is attributed to the grain size and grain boundary potential change according to the Seto's model.

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