EÜFBED - Fen Bilimleri Enstitüsü Dergisi Cilt-Sayı: 5-1 Yıl: 2012 13-24

# EFFECT OF NOZZLE-SUBSTRATE DISTANCE ON ELECTRICAL, STRUCTURAL AND OPTICAL PROPERTIES OF $SnO_2$ THIN FILMS PREPARED BY SPRAY PYROLYSIS

# PÜSKÜRTME YÖNTEMİ İLE HAZIRLANAN $SnO_2$ İNCE FİLMLERİN ELEKTRİKSEL, YAPISAL VE OPTİKSEL ÖZELLİKLERİNE BURUN-ALTLIK MESAFESİNİN ETKİSİ

**Güven TURGUT[1*], Demet TATAR [1] and Bahattin DÜZGÜN[1]**

[1]*K. K. Education Faculty, Department of Physics, Ataturk University, Erzurum 25240, Turkey*

**Geliş Tarihi:** 11 Mart 2011 **Kabul Tarihi:** 18 Ocak 2012

## ABSTRACT

The physical, electrical and optical properties of $SnO_2$ (TO) thin films deposited using spray pyrolysis technique at different nozzle-to-substrate distances were reported. The solutions consisted of diluted $SnCl_2.2H_2O$ were sprayed on hot glass substrate which temperature was in 400±5 ˚C. X-ray diffraction (XRD), Uv-vis spectrophotometer and van der Pauw configuration studies had been performed on TO films coated on optical glass substrates. X-ray diffraction pattern revealed the presence of tetragonal crystal structure with (301) preferential orientation for all films. The grain size of the films varied from 23.78 nm to 29.74 nm at different nozzle-substrate distances. The film deposited at 40 cm nozzle-substrate distance had minimum sheet resistance of 3.233 $\Omega/cm^2$ and had maximum transmittance at 550 nm of 59.55 %. The best films deposited with optimum nozzle-to-substrate distance (NSD) of 40 cm.

***Keywords:*** $SnO_2$; X-Ray diffraction; spray pyrolysis; nozzle-substrate distance

## ÖZET

Farklı burun-altlık arasındaki mesafelerde püskürtme tekniği kullanılarak büyütülen $SnO_2$ (TO) ince filmlerin fiziksel, elektriksel ve optiksel özellikleri araştırıldı. Filmler, 400±5 ˚C sıcaklığındaki cam altlıklar üzerine, seyreltilmiş $SnCl_2.2H_2O$ dan oluşan çözeltiler püskürtülerek elde edildi. X-ışını kırınımı, görünür bölge spektrometresi ve van der Pauw konfigürasyon çalışmaları, optik cam altlıklar üzerine kaplanan TO için yapıldı. X-ışını kırınım çalışmaları, tüm filmlerin (301) tercihli yönelimi olan

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[*] Sorumlu Yazar: guventrgt@gmail.com

tetragonal yapıdaolduğunu gösterdi. Burun ile altlık arasındaki mesafelerde elde edilen filmlerin tane boyutları 23.78 nm'den 29.74 nm'ye değiştiği görüldü. Püskürtme burnu ile altlık arasında 40 cm'lik mesafede büyütülen film, 3.233 Ω/cm$^2$'lik minimum yüzey direncine ve 550 nm de %59.55 ile maksimum geçirgenliğe sahip olduğu bulundu. En iyi filmler, burnu-altlık mesafesinin 40 cm olduğunda elde edildi.

**Anahtar Kelimeler :** $SnO_2$; X-Işını kırınımı; püskürtme metodu; püskürtme burnu-altlık mesafesi

## 1. INTRODUCTON

Among transparent conductive oxides, tin oxide (TO) have attracted the attention of many researchers due to its unique properties. Tin oxide ($SnO_2$) is widely used in solar cells, display devices, hybrid microelectronics (Ravichandran et al., 2009), stable resistors, touch-sensitive switches digital displays (Jain et al., 2004), electro-chromic displays and gas sensors (Kasar et al., 2008) architectural windows (Elengovan and Ramamurthi, 2003) etc. due to theirs low electrical resistivity, high optical transmittance in visible region, high optical reflectance in infrared region, chemically inert and mechanically hard (Elengovan et al., 2005). In earlier works, tin oxide thin films were prepared by variety of methods such as chemical vapor deposition(CVD) (Kim et al., 2001), sol-gel process (Dua et al., 2009, Zhang et al., 2006, Zhang et al., 2006), spray pyrolysis (Jain et al., 2004, Kasar et al., 2008, Elengovan et al., 2005, Elengovan et al., 2004, Thangaraju et al., 2002, Elengovan and Ramamurthi, 2005 ), hydrothermal method (Zhang and Gao, 2004) and pulsed laser deposition (Kim and Pique, 2004) and some physical properties of the films prepared were investigated. Among these techniques, the spray pyrolysis technique is an attractive method to obtain thin films because of its simple and inexpensive experimental arrangement (Elengovan et al., 2004), ease of adding doping materials, reproducibility (Serin et al., 2006).

Physical properties of thin films deposited by spray depend on the substrate temperature, spray duration and flow rate, ambient atmosphere, nozzle-substrate distance, carrier gas pressure and the cooling rate after deposition (Ilıcan et al., 2005). When a spraying solution emerges from an atomizer, the fine spherical droplets made up of solvent and solute experiences different temperature zones being transported through different substrate temperature or nozzle-substrate distances. The thin film formation depends on the thermal energy, heterogeneous reaction, solvent vaporization, perfect pyrolytic decomposition, and evaporation of the solvent molecules (Deokate, 2010).

In the spray pyrolysis, many processes occur simultaneously when a droplet hits the surface of the substrate: evaporation of residual solvent, spreading of the droplet, and salt decomposition. The film formation depends on the process of droplet landing, reaction and solvent evaporation, which are related to droplet size and momentum. An ideal deposition condition is when the droplet approaches the substrate just as the solvent is completely removed (Patil, 1999).

Assuming that the size distribution of all the droplets are the same and other spray deposition condition, with increasing nozzle-substrate distance, droplets will vaporize completely far away from substrate, consequently the solid particles are formed after the chemical reaction in the vapor phase. Then the solid precipitate melts and vaporizes without decomposition and the vapor diffuses to the substrate. This is a homogeneous reaction, because all the reactant molecules and product molecules are in the vapour phase. The molecules condense as micro crystallites, which form a powdery precipitate on the substrate. With decreasing nozzle-substrate distances, the droplet splashes onto the substrate and decomposes. At intermediate nozzle-substrate distances, the solvent evaporates before the droplet reaches the substrate. This is a heterogeneous reaction and good quality films can be obtained. In this study, we investigated the effect of nozzle-substrate distance on structural, electrical and optical properties of tin oxide thin films.

## 2. EXPERIMENTAL

Tin oxide thin films deposited at different nozzle-substrate distances were prepared by using a homemade spray pyrolysis apparatus. The schematic diagram of the experimental set-up is seen in Figure 1.

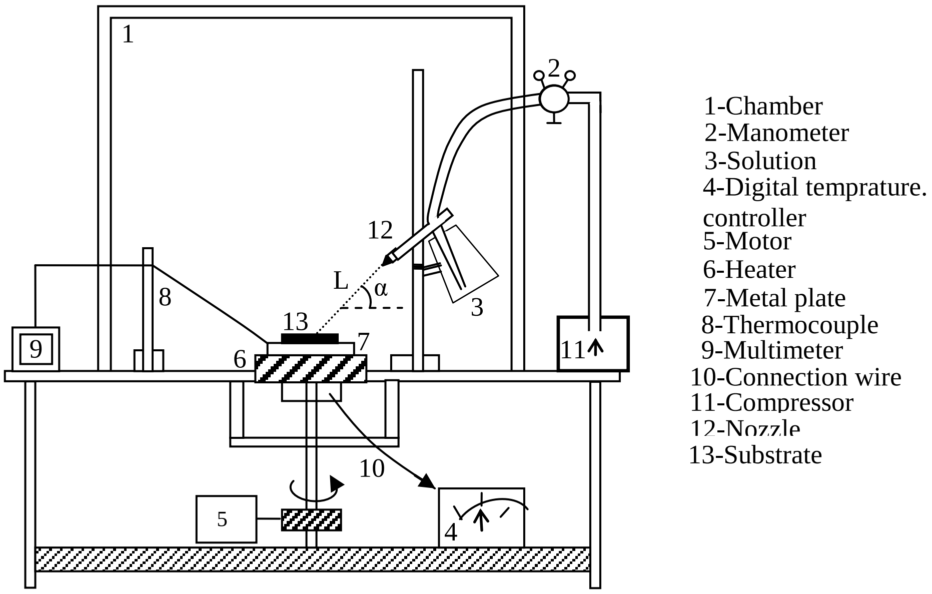

**Fig. 1.**Spray pyrolysis experimental setup.

For preparing spray solution, 15g stannous chloride ($SnO_2.2H_2O$ with 98% purity, Merck) was dissolved in 5 ml of diluted hydrochloric acid (HCl). This mixture subsequently was diluted with methanol served as starting solution. The addition of HCl was required in order to break down the polymer molecules that were formed when diluting with methanol (Elengovan and Ramamurthi, 2003, Elengovan et al., 2004). In each case, the amount of spray solutions prepared was 50 ml. All the spray solutions were magnetically stirred for 1h and finally these solutions were filtered by syringe filter with 0.2 µm pore size before spraying on substrate. The well-cleaned microscopic glasses with 1cm x1cm x 1mm dimensions were used as substrates.

The spraying parameters; L which is distance between the spray nozzle and substrate was varied from 25 to 45 cm at the interval of 5 cm, the spray angle (α) was $45^o$, the substrate temperature was 400 $^oC$. The substrate temperature was maintaine dusing a k-type thermo couple based digital temperature controller. Uniform coating was achieved by rotating the substrate with a speed of 20 rpm/min in its plane. The flow rate of air used as a carrier gas is about 1.25 ml/min. Hence, the duration of the film deposition was about 40 min. After film deposition, coated substrates were allowed to naturally cool down to room temperature.

The structural characterization of the films prepared was carried out by X-ray diffraction (XRD) measurements using a Rigaku D/Max-IIIC diffractometer with CuKα radiation (λ=1.5418 Å), at 30 kV, 10 mA. The electrical measurements were carried out by Hall measurements in van der Pauw configuration. Optical measurements of the films were studied in the UV-Visible spectrophotometer (Perkin Elmer, Lambda 35).

## 3. RESULTS AND DİSCUSSİON

### *3.1. Structural properties*

The XRD patterns of the films deposited at various nozzle-substrate distances were shown in Figure 2. The films deposited at 25 cm nozzle-substrate distance were almost amorphous in nature. XRD images showed that the films were polycrystalline and were prefentially oriented along (301) direction irrespective of the nozzle–substrate distance. Other orientations observed were (110), (101), (200), (211), (220), (310) and (321).

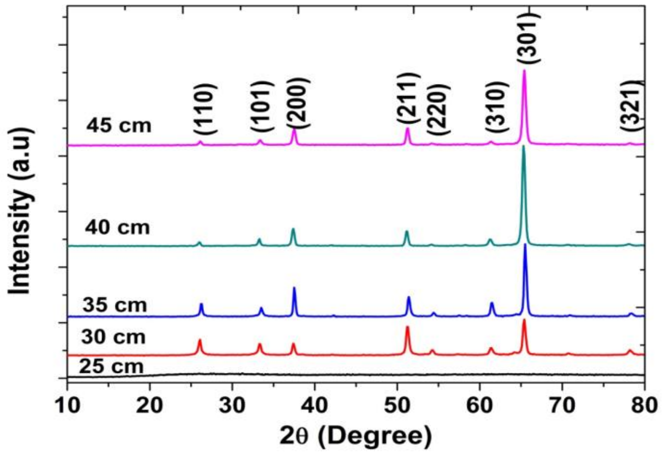

**Fig. 2.** XRD images of $SnO_2$ thin films deposited at different nozzle-substrate distance.(JCPDS card no: 41-1445)

The prefential orientation peak intensities and crystallinity of the films increased the increasing nozzle-substrate distance and reached maximum at 40 cm distance then decreased at 45 cm. The peak intensities of other orientations, except for (200) orientation, continuously decreased with increasing nozzle-substrate distance.

At low nozzle-substrate distances like 25cm, droplet in liquid phase sputters onto the substrate and decomposes without a good film growth. When the distance is increased up to 40 cm, decomposition increase and consequently, by evaporating the solvent before the droplet reaches the substrate, ideal deposition condition taken place and the crystallinity increases. But even with the increase to 45 cm in the nozzle-substrate distance, the solid precipitate melts in spray solution vaporizes without decomposition and the vapor diffuses to the substrate and the crystallinity worsens.

The observed 'd' values were presented in Table 1 and these values were compared with the Standard ones from JCPDS card no: 41-1445. The matching of the observed and standard 'd' values confirms that the deposited films are of $SnO_2$with tetragonal structure.

**Table 1.**Standard and calculated for $SnO_2$ films 'd' values.

| (hkl) | Standard d(Å) | Observed d(Å) | | | | |
|---|---|---|---|---|---|---|
| | | 5 cm | 30 cm | 35 cm | 40 cm | 45 cm |
| 110 | 33.470 | - | 34.144 | 33.902 | 34.239 | 34.093 |
| 101 | 26.427 | - | 26.868 | 26.718 | 26.901 | 26.815 |
| 200 | 23.690 | - | 24.017 | 23.948 | 24.031 | 23.963 |
| 211 | 17.641 | - | 17.818 | 17.761 | 17.835 | 17.804 |
| 220 | 16.750 | - | 16.887 | 16.847 | 16.933 | 16.894 |
| 310 | 14.984 | - | 15.089 | 15.067 | 15.125 | 15.091 |
| 301 | 14.155 | - | 14.258 | 14.235 | 14.275 | 14.258 |
| 321 | 12.147 | - | 12.213 | 12.189 | 12.237 | 12.211 |

The lattice constants for tetragonal crystal sturucture'a' and 'c' was determined by relation (Kasar et al., 2008)

$$\frac{1}{d^2} = \left(\frac{h^2 + k^2}{a^2}\right) + \left(\frac{l^2}{c^2}\right) \qquad 1.1$$

where ‘d’ is the interplaner distance and (hkl) miller indicies, respectively. The standardand calculated lattice constants were given in Table 2. The calculated ‘a’ and ‘c’ values agree with JCPDS card no: 41-1445. As seen from Table 2, nozzle-substrate distance did not affect much lattice constans of $SnO_2$.

**Table 2.** Structural parameters of films growth at different nozzle-substrate distance.

| **NDS (cm)** | **Lattice constants(Å)** | | **D(nm)** | $\delta$ **(x $10^{14}$ lines/ $m^2$)** |
|---|---|---|---|---|
| | **a** | **c** | | |
| 30 | 4.772 | 3.217 | 24.06 | 17.28 |
| 35 | 4.765 | 3.210 | 26.46 | 14.28 |
| 40 | 4.783 | 3.205 | 29.74 | 11.31 |
| 45 | 4.772 | 3.216 | 23.78 | 17.68 |

* JCPDS card no: 41-1445 (a*= 4,738 Å c*=3,187 Å)

The avarage grain size of the films was calculated using Scherrer Formula (Chacko et al., 2008),

$$D = \frac{K\lambda}{(\beta \cos\theta)} \qquad 1.2$$

where D is mean grain size of nanoparticles, K is a constant and value is 0.9 , $\beta$ is the full width at half of the peak maximum (FWHM) in radians and ‘$\theta$ ’ is Bragg’s angle. The dislocation density (δ) of the films prepared was estimated using the equation, $\delta = {}^{1}/_{D^2}$ ( lines /$m^2$) (Ravichandran et al., 2009). The variation of the grain size and dislocation density with nozzle-substrate distance is shown in Table 2.

The grain size ‘D’ firstly shows an increasing tendency wtih increasing nozzle-substrate distance and reaching a maximum value at around 40 cm nozzle-substrate distance and then shows a decreasing tendency after 40 cm nozzle- substrate distance. It is observed that (δ) decreases with nozzle-substrate up to 40 cm and there after increases. The dislocation density (δ), defined as the length of dislocation lines per unit volume and δ is the measure of the amount of the defects in a crystal. Since dislocation density of the films prepared at 40 cm nozzle-substrate distance is the lowest, the best crystallinity were observed at 40 cm nozzle-substrate distance.

### 3.2.Electrical and optical properties

Electrical properties of the films were investigated by van der Pauw configuration. Fig.3 shows sheet resistance (Rs) of TO films as a function of the nozzle-substrate distance. Sheet resistance (Rs) is a useful parameter in comparing electrical properties of the films. Therefore, we can put forward to ideas about conductivity of films by utilizing sheet resistance. When the sheet resistance of the films decreased, the conductivity increased. The sheet resistance of the films decreased by increasing nozzle-substrate distance and reached a minimum at 40 cm, then increased at 45 cm distance.

**Table 3.** Transmittance, sheet resistance and figure of merit for $SnO_2$ thin films at various nozzle-substrate distance

| NSD (cm) | T(%) (λ=550 nm) | Rs ($\Omega cm^{-2}$) | $\Phi_M$ ($\Omega^{-1}$) |
|---|---|---|---|
| 25 | 25.67 | 302.9 | $4.1x10^{-9}$ |
| 30 | 33.52 | 24.52 | $7.3x10^{-7}$ |
| 35 | 42.59 | 14.81 | $1.3x10^{-5}$ |
| 40 | 59.55 | 3.233 | $1.7x10^{-3}$ |
| 45 | 39.33 | 11.49 | $7.7x10^{-6}$ |

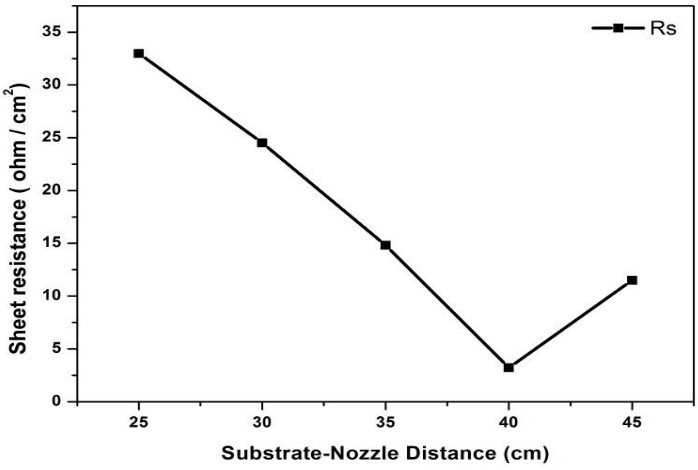

**Fig.3.** The sheet resistance variation of TO films as a function of nozzle-substrate distance

The optical properties of $SnO_2$ deposited at different nozzle-substrate distances were investigated by transmittance spectra (in Fig.4). The transmittance of the films increased by increasing nozzle-substrate distance and reached a maximum at 40 cm, then decreased at 45 cm distance. Because of an increasing crystallization, decreasing droplets in liquid phase sprayed onto the substrate surface with increasing nozzle-substrate distance up to40 cm, it is an increase in the transmittance. Due to the reactant molecules and product molecules in spray solution were in the vapour phase at 40 cm nozzle- substrate distance, ideal deposition condition completed and a good transparency films were obtained. After 40 cm of nozzle-substrate, the solid precipitate melts in spray solution vaporizes without decomposition and the vapour diffuses to the substrate and cause a decrease in the transmittance.

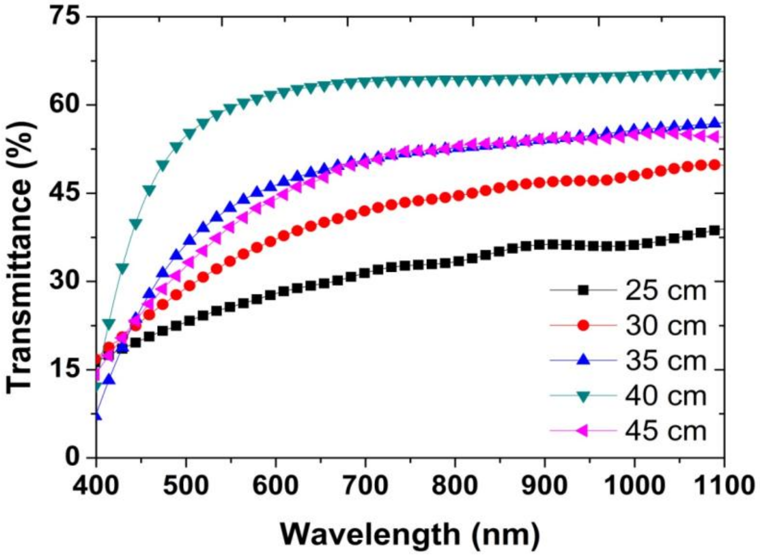

**Fig. 4.** Optical transmittance of $SnO_2$ thin films.

The figure of merit is an important parameter for evaluating TCO thin films for use in solar cells. Conductivity and transmittance are inversely proportional to each other and should be as possible for effective usage. The figure of merit as defined by Haacke is $\Phi_M=T^{10}/Rs$ (Haacker, 1976) where T is the transmittance at 550 nm and Rs is sheet resistance. This formula gives more weight to the transparency and thus is better adapted to solar cell technology. It is clear that figure of merit depend on the sheet resistance. The calculated figure of merit values are given in Table.3. When nozzle-substrate distance varied from 25 cm to 40 cm, value of the figure increased from $4.1x10^{-9}$ $\Omega^{-1}$to $1.7x10^{-3}$ $\Omega^{-1}$ and then decreased to $7.7x10^{-6}$ at 45 cm. It was found that the highest value obtained for the films at 40 cm nozzle- substrate distances was $1.7x10^{-3}$ $\Omega^{-1}$. Thus, the film prepared at 40 cm can be used solar cell and other optoelectronic devices.

The results obtained in present study have been compared with studies made by Kasar et al. 2008 and Chacko et al. 2007. The transmittance values in present study are less than theirs, but the lowest sheet resistance value we have achieved is much lower than the values of their achieved lowest sheet resistance values. Therefore, the largest figure of merit value obtained in our study greater than theirs.

## 4.CONCLUSION

Thin films were deposited onto optical glass substrates with substrate temperature of 400±5˚C by spray pyrolysis technique. We presented the results of the structural, optical, and electrical properties of $SnO_2$ films formed at 25, 30, 35, 40, and 45 cm nozzle-to-substrate distances. XRD studies revealed that the materials in the thin form were polycrystalline with tetragonal crystal structure. The crystallinity of the films was found increased at 40 cm. Further, when the films were prepared at 40 cm, the minimum sheet resistance, maximum transmittance and figure of merit were obtained, respectively. Hence, it was found that the film that was prepared at 40 cm showed better optical, electrical, and structural properties.

## REFERENCES

Chacko, S. Philip, N.S. and Vaidyan, V.K. (2007). Effect of substrate temperature on structural, optical and electrical properties of spray pyrolytically grown nanocrystalline $SnO_2$ thin films. Phys. Stat. Sol. (a)., 204, 3305–3315.

Chacko, S. Philip, N.S. Gophandran, K.G. Koshy, P. and Vaidyan, V.K. (2008). Nanostructural and surface morphological evolution of chemically sprayed $SnO_2$ thin films. Applied Surface Chemistry., 254, 2179.

Deokate, R.J. Moholkar, A.V. Agawane, G.L. Pawar, S.M. Kim, J.H. and Rajpure, K.Y. (2010), Studies on the effect of nozzle-to-substrate distance on the structural, electrical and optical properties of spray deposited $CdIn_2O_4$ thin films. Applied Surface Science., 256, 3522.

Dua, L. K. De, A. Chakraborty, S. and Biswas, P. K. (2009). Study of spin coated high antimony content Sn–Sb oxide films on silica glass. Materials charecterization. 59, 578.

Elangovan, E. and Ramamurthi, K. (2003). Studies on optical properties of polycrystalline $SnO_2$:Sb thin films prepared using $SnCl_2$ precursor. Cryst. Res. Technol., 38, 779.

Elangovan, E. Singh, M. P. Dharmaprakash, M. S. and Ramamurthi, K. (2004). Some Physical Properties of Spray Deposited $SnO_2$ Thin Films. Journal of Optoelectronics and Advanced Materials., 6, 197.

Elangovan, E. Ramesh, K. and Ramamurthi, K. (2004). Studies on the structural and electrical properties of spray deposited $SnO_2$:Sb thin films as a function of substrate temperature. Solid State Communications., 130, 523.

Elangovan, E. Shivashankar, S.A. and Ramamurthi, K. (2005). Studies on structural and electrical properties of sprayed $SnO_2$:Sb films Journal of Crystal Growth., 276, 215.

Elangovan, E. and Ramamurthi, K. (2005). A study on low cost-high conducting fluorine and antimony-doped tin oxide thin filmsApplied Surface Science., 249, 183.

Haacker, G. (1976). New figure of merit for transparent conductors. J. Appl. Phys., 47, 4086.

Ilıcan, S. Çağlar Y. and Çağlar, M. ( 2005). Spray Pyrolysis Yöntemi ile Elde Edilen CdZnS Filmlerinin Yapısal Özelliklerine Hazırlama Parametrelerinin Etkisi. C.Ü. Fen-Edebiyat Fakültesi Fen Bilimleri Dergisi., 26(2), 22.

Jain, G. and Kumar, R. (2004). Electrical and optical properties of tin oxide and antimony doped tin oxide films. Optical Materials., 26, 27.

Kasar, R.R. Deshpande, N.G. Gudage, Y.G. Vyas, J.C. and Sharma, R. (2008). Studies and correlation among the structural, optical and electrical parameters of spray-deposited tin oxide ($SnO_2$) thin films with different substrate temperatures. Physica B., 403, 3724.

Kim, H. and Pique, A. (2004). Transparent conducting Sb-doped SnO2 thin films grown by pulsed-laser deposition. Applied Physics letters., 84, 218.

Kim, K.S., Yoon, S.Y., Lee, W.J. and Kim, K.H. (2001). Aurface morphologies and electrical properties of antimony-doped tin oxide films deposited by plasma-enhanced chemical vapour deposition. Surface and Coating Technology., 138, 229.

Patil, P. S. (1999). Versatility of chemical spray pyrolysis technique (Review) Materials Chemistry and Physics., 59, 185.

Ravichandran, K. Muruganantham, G. and Sakthivel, B. (2009). Highly conducting and crystalline doubly doped tin oxide films fabricated using a low-cost and simplified spray technique. Physica B., 404, 4299.

Serin, T. Serin, N. Karadeniz, S. Sarı, H. Tugluoglu, N. and Pakma, O. (2006). Electrical, structural and optical properties of $SnO_2$ thin films prepared by spray pyrolysis. Journal of Non-Crystalline Solids., 352, 209.

Thangaraju, B. (2002). Structural and electrical studies on highly conducting spray deposited fluorine and antimony doped $SnO_2$ thin films from $SnCl_2$ precursor. Thin Solid Films., 402, 71.

Zhang, D. Deng, Z. Zhang, J. and Chen, L. (2006). Microstructure and electrical properties of antimony-doped tin oxide thin film deposited by sol-gel process .Materials Chemistry and Physics., 98, 353.

Zhang, D. Tao, L. Deng, Z. Zhang, J. and Chen, L. (2006). Surface morphologies and properties of pure and antimony-doped tin oxide films derived by sol-gel dip-coating processing. Materials Chemistry and Physics., 100, 275.

Zhang, J. and Gao, L. (2004). Synthesis and characterization of antimony-doped tin oxide (ATO) nanoparticles by a new hydrothermal method. Materials Chemistry and Physics., 87, 10.

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