Effect of the Dielectric Barrier Discharge Plasma on the Optical Properties of SnO$_2$ Thin Film

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Abstract
In this paper, a dielectric barrier discharge DBD plasma system was used to study effects of the nonthermal plasma on the optical properties of the tin oxide (SnO$_2$) thin films. Tin oxide (SnO$_2$) thin films were deposited on cleaned glass substrates at 450˚C using spray pyrolysis deposition technique prepared from SnCl$_4$:5H$_2$O solution with concentration (0.1M).

The prepared films were exposure to different time intervals (0, 2, 4, 6, 8 and 10) min.

UV-VIS spectra of the films were studies using optical absorbance measurements which were taken in the spectral region from 190 nm to 1100 nm. The transmittance and reflectance spectra of the films in the UV-VIS region were also studied.

The transmittance T, the Reflectance R, absorption coefficient $\alpha$, energy gap $E_g$, extinction coefficient $K$, refractive index $n$, dielectric constant $\epsilon$ and optical conductivity were studied. It is found that the Reflectance, absorption coefficient, extinction coefficient and optical conductivity were increased with exposure time and the transmittance, energy gap, refractive index, dielectric constant were decreased with exposure time of DBD plasma.

Keywords: non-thermal plasma, SnO$_2$ thin film, optical properties.

Introduction
Plasma is one of the four fundamental states of matter (the others being solid, liquid, and gas), a plasma is a quasineutral gas of charged and neutral particles which exhibits collective behavior [1]. Plasma are generally classified as either thermal or non-thermal. Non-thermal plasmas are also frequently called, “non-equilibrium” plasmas because they are characterized by a large difference in the temperature of the electrons relative to the ions and neutrals. Since the electrons are extremely light, they move quickly and have almost no heat capacity. In these plasmas, Non-thermal plasmas (of low pressure glow, RF and microwave discharges) offer high selectivity and energy efficiency in plasma chemical reactions; they are able to operate effectively at low temperatures and without any special quenching. So far non-thermal atmospheric pressure plasmas have been studied for a variety of industrial applications such as pollution control applications, volatile organic compounds (VOCs) removal, car exhaust emission control and polymer surface treatment (to promote wettability, printability and adhesion). For decades, non-thermal plasmas have been used to generate ozone for water purification. Non-thermal plasmas have been extensively used for materials processing applications for the past 30 years [2]. Yet, these applications have generally been limited to select, high “value-added” uses, such as steps required for manufacture of semiconductor devices, magnetic media or deposition of energy-efficient films for architectural glass. In these applications, plasmas are used because they provide a rich source of chemically active species that react with a surface, or which react with each other to produce secondary, short-lived chemical precursors needed for thin film deposition. The success of plasma processing technology stems from its low temperature operation and the fact that no other method can provide the same nondestructive, materials treatment capability. As such, plasmas are typically used for selective film etching, surface treatment to enhance wettability or to improve adhesion, and manufacture of thin films, including diamond-like carbon (DLC), and films having desired metallic, dielectric, or other composite properties. SnO$_2$ thin films are one of transparent oxide semiconductors [3].

SnO$_2$ is a polycrystalline solid with a tetragonal crystal lattice. It is a wide gap $E_g > 3eV$, non stoichiometric, and as a degenerate n-type semiconductor. Tin oxide (TO) thin
films have been prepared by several methods; evaporation [4,5], reactive sputtering (RS) [6], pulsed laser deposition (PLD) [7], spray pyrolysis (SP) [8,9], sol-gel [10,11] and post oxidation of evaporated thin films of metal [12]. As SnO$_2$ film (E$_g$=3.5 eV) is transparent it can be applied to protecting film over materials with a narrow band gap as well as an electrode for photo electrochemical conversion. The high transparency of oxide films in the visible region, together with their high reflectivity in the infrared, make them very attractive for use as transparent heat-reflecting material [13].

In this work, SnO$_2$ films were prepared by using chemical spray pyrolysis, and then studying the Optical properties of it.

**Optical Properties of Semiconductors**

**Experimental work**

**A. Dielectric Barrier Discharge system**

A. The DBD system consist of two electrodes, made of copper with 90 mm diameter which is insulated by a Teflon of thickness 10 mm. The two electrode were insulated by glass plate with 2mm thickness, the SnO$_2$ films are placed on the ground electrode and the high voltage electrode is placed at 1 mm distance from the film surface.

The two electrodes of the DBD system were connected to high voltage transformer (input voltage 220V, 50Hz and output voltage 15kV)(sigurtrad, model :NT-15-OUT, 50Hz), the output voltage of transformer can be varied from (1-15)kV by varying input voltage.

**B. Materials and Preparing Methods**

SnO$_2$ thin films were Prepared on the glass substrates using the chemical spray pyrolysis. The sprayed solution prepared from dissolved 3.305 gm of tin tetrachlorid penthydrate (SnCl$_4$·5H$_2$O) in 100 ml of distilled water, the final concentration of the solution was 0.1 M. the spray parameter were fixed as follows; the distance between the nozzle of the spray device to the substrate is (30±1) cm, the substrate temperature is 450˚C, and the flow rate of the gas (1 l/min). Nitrogen was used as gas carrier.

**Results and Discussion**

Fig.(2) show that absorption spectrum (A) in light region(300-1100)nm, for SnO$_2$ thin film exposure to non-thermal plasma for different time (0,2,4,6,8and 10) min. From Fig.(2) we note that the absorption decreased with increased of wavelength for all samples, also is found that for a given wavelength the absorption increases with increasing exposure time to plasma. and Fig.(3) showing that the Transmission (T) Reflectance (R) spectral respectively. From figure we note that the Reflectance and Transmission increased with increased wave length.

![Fig.(2) Absorption spectrum (A) with wave length for different time exposure.](image)

*Fig.(1): Photographic picture of DBD system used to treat of films.*
Optical Constant

Extinction coefficient $K$

Can be calculated from the following [14]:

$$k = \frac{\alpha \lambda}{4\pi}$$ \hspace{1cm} (1)

Where $\lambda$ is the wavelength of the incident photons. Fig.(4) show the relation between the extinction coefficient and the wavelength in light region (300-1100) nm for SnO$_2$ thin film exposure to non-thermal plasma different time (0,2,4,6,8 and 10) min.

It is found that for a given wavelength the extinction coefficient increases by increasing the time exposure of plasma.

Dielectric constant $\varepsilon$

The real and the imaginary parts of the dielectric constant were determine using the relation [15]:

$$\varepsilon = \varepsilon_r + i \varepsilon_i, \varepsilon_r = n^2 - k^2, \varepsilon_i = 2nk$$ \hspace{1cm} (2)

Where $\varepsilon_r$ is the real part and is the normal dielectric constant, $\varepsilon_i$ is the imaginary part and represents the absorption associated of radiation by free carrier. Fig.(4) show the real and the imaginary part of dielectric constant for SnO$_2$ thin film exposure to non-thermal plasma at different time (0,2,4,6,8 and 10) min as function of wave length for lengths (300-1100)nm. For the curve of real part it was shown that the dielectric constant increases with increasing wave length, and for a given wavelength the real part of dielectric constant decreases with increasing the time of exposure. And in the imaginary part of the dielectric constant we note that increases by increasing wavelength and the increases of the imaginary part with increasing time exposure confirms the free carriers contribution to the absorption.
Fig. (4): the real and the imaginary part of dielectric constant SnO$_2$ different time exposure as function of wavelength.

- **Refractive index (n)**
  
  [16] We calculate the Refractive index as the following:
  
  \[
  R = \frac{(n-1)^2}{(n+1)^2}
  \]
  
  and we can make reformat as the following:
  
  \[n = 1 + \sqrt{R} / 1 - \sqrt{R}\]
  
  Where R: Reflectance, we can calculate from the relation:
  
  \[R + T + A = 1\]
  
  Fig. (5) show that the refractive index for SnO$_2$ thin film as a function of wave length for different time (0, 2, 4, 6, 8 and 10) min. It is found that the refractive index increases very fast with increasing wave length until about 600nm, then it stable with increasing wavelength, from the fig. it can be shown for a given wavelength the refractive index decreases with increasing time of exposure.

Absorption coefficient ($\alpha$)

To calculate absorption coefficient we used Lambert formal as the following [17]:

\[
\alpha = \frac{2.303A}{t}
\]


Fig. (6) show that the absorption coefficient as wave length in light region (300-1100) nm for Sn02 thin film exposure to non-thermal plasma different time (0, 2, 4, 6, 8 and 10) min. we note that the absorption coefficient increases with increasing of wavelength, also for a given wavelength the absorption coefficient increases with increasing of exposure time.

Energy gap $E_g$

We used the absorption coefficient is given by Tauc relation to calculate energy gap as the following [18]:

\[
E_g = \frac{2.303A}{t}
\]
\[ \alpha \propto B (h\nu - E_g)^m \] .......................... (7)

Where: B: constant depends on the nature of the mater, \( E_g \): energy gap, \( h\nu \): photon energy, m: a constant which have the values n=2 for allowed direct transition, n=1/2 for allowed indirect, n=1/3 for forbidden indirect and n=2/3 for forbidden indirect of optical transition. By plotting \( (\alpha h\nu^2) \) versus photon energy \( (h\nu) \), the energy gap \( E_g \) can obtain by extrapolating the linear portion of the graph to \( (\alpha h\nu^2 = 0) \). Fig.(7) show that the relation between the \( \alpha h\nu^2 \) and photon energy \( (h\nu) \) for \( \text{SnO}_2 \) thin film exposure to non-thermal plasma for different time (0,2,4,6,8 and 10) min and we found the value of energy for all carve are: (3.6838,3.6838,3.6549,3.6895,3.7872,3.6439) ev, respectively.

\( \text{Fig.}(7) \): aplot of \( \alpha h\nu^2 \)  vs. photon energy \( (h\nu) \) for \( \text{SnO}_2 \) thin film for different time \( (A(t=0),B(t=2)\text{min}, C(t=4)\text{min}, D(t=6)\text{min}, E(t=8)\text{min}, F(t=10)\text{min}) \).

**Optical conductivity**

The optical conductivity was determined using the relation [19]:

\[ \sigma = \alpha n c \epsilon \quad \text{or} \quad \sigma = \frac{\alpha n c}{4\pi} \] .......................... (8)

Where c: velocity of ligth, Fig.(8) show that the optical conductivity for \( \text{SnO}_2 \) thin film as a function of wavelength for different time (0,2,4,6,8 and 10) min. from Fig.(8) we note that the conductivity decreases with increasing wave length for all samples, it may be show that for given wavelength the conductivity
increases with increasing time of exposure. The increased optical conductivity is due increasing of the absorption coefficient of the SnO$_2$ thin film with exposure time.

**Fig.(8): Optical conductivity as a function of wave length for different time exposure.**

**Conclusion:**

In this work we study the effect of non-thermal plasma on the optical properties of tin oxide SnO$_2$ thin film prepared by chemical spray pyrolysis. we used non-thermal DBD plasma for this purpose. After exposure the prepared thin film for different time (0,2,4,6,8 and 10) min and calculating the Optical properties of the thin film the value of Reflectance R, absorption A, transmission T, extinction coefficient K, dielectric constant $\varepsilon_r$ and Refractive index n. we note that the Reflectance R, transmission T, real part of dielectric constant $\varepsilon_r$ and Refractive index n decreased with increasing the time of exposure while the absorption coefficient, imaginary part of dielectric constant $\varepsilon_i$ , extinction coefficient K, Optical conductivity increasing with increased the time of exposure.

**References:**

تم في هذا البحث استخدام منظومة الحاجز العازل للتأثير على أغشية (SnO2) الرقيقة. تعمل هذه المنظومة على إنتاج البلازما غير الحرارية عند الضغط الجوي الاعتيادي، وتعمل هذه المنظومة عادة عند الترددات 0.05 و 500kHz، وبعد فولتيت تصل إلى 1500-1000. تحضير أغشية أوكسيد القصدير (SnO2) الرقيقة بطريقة الرش الكيميائي الحراري من رش محصول مكون من كيبريدات القصدير المذابة في الماء المقطر تركز (SnCl4: 5H2O) على شرائح زجاجية مسخنة إلى درجة حرارة (0.1M) 450°C.

درست اطيفات الأشعة المرئية - فوق البنفسجية للأغشية باستخدام حسابات الامتصاص البصري والتي اخذت في المنطقة الطيفية (190-1100) نانومتر. كما درست أيضا النفاذية والانعكاسية للأغشية في المنطقة المرئية - فوق البنفسجية UV-VIS.

درس تأثير التعرض للبلازما لكل من النفاذية R، معامل الخزم K، معامل الإلكسارية، الامتصاصية R، المعامل الخمسي K، ثابت العزل ε، ثابت الالكسارية n، ثابت العزل ε، بينما يقل كل من النفاذية والانعكاسية والجزء الحقيقي من ثابت العزل ومعامل الاكسسارية زمن التعرض للبلازما.