Effect of the Dielectric Barrier Discharge Plasma on the Optical Properties of SnO₂ 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 were deposed on cleaned glass substrates at 450°C using spray pyrolysis deposition technique prepared from $SnCl_4:5H_2O$ 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 190nm to 1100nm. The transmittance and reflectance spectra of the films in the UV-VIS region were also studied.

The transmittance T, the Reflectance R, absorption coefficient α, energy gap Eg, extinction coefficient K, refractive index n, dielectric constant ϵ 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**,** SnO₂ 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 [١]. 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 wetability or to improve adhesion, and manufacture of thin films, including diamond-like carbon (DLC), and films having desired metallic, dielectric, or other composite properties. SnO₂ thin films are one of transparent oxide semiconductors [3].

SnO₂ 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 (Eg=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 wer 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 cupper 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.


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

B. Materials and Preparing Methods

SnO2 thin films were Prepared on the glass substrates using the chemical spray pyrolysis. The sprayed solution prepared from disolved 3.305 gm of tin tetraclorid penthydrate $(SnCl_4 :5H_2O)$ 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
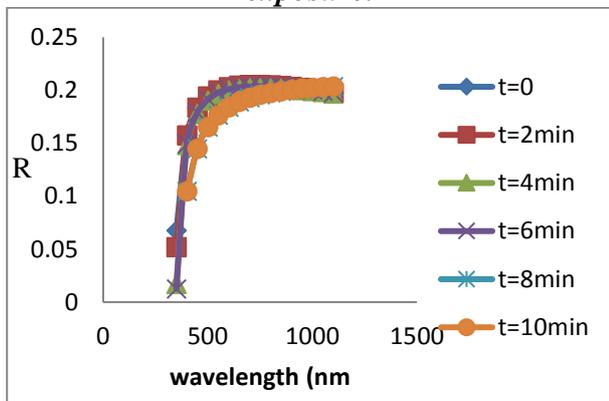
Fig.(2) show that absorption spectrum (A) in light region(300-1100)nm, for Sno2 thin film exposure to non-thermal plasma for different time (0,2,4,6,8and 10) min. From Fig.(2) we note that the absorption decreased with increased of wavelength for all samples, also is found that for a given wavelength 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.
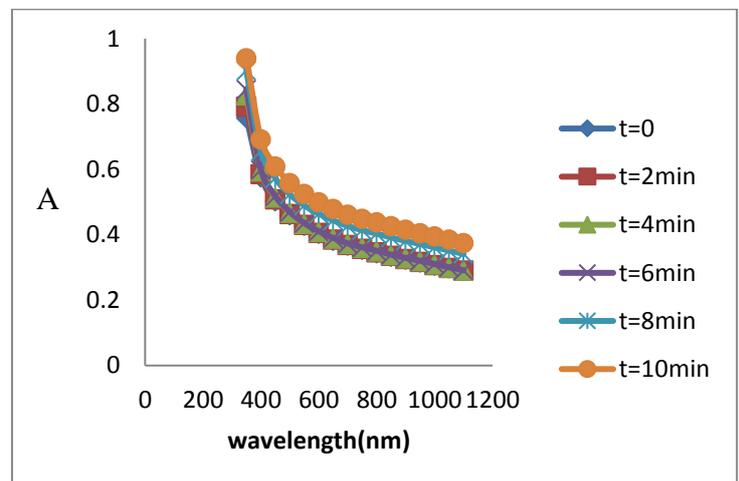
Fig.(2) Absorption spectrum (A) with wave length for different time exposure.
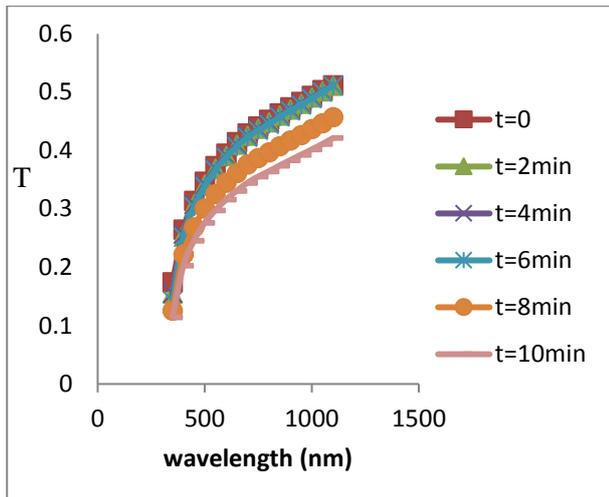
Fig.(3): Transmission spectrum of SnO₂ thin film with wave length for different time exposure.

Fig.(4): Reflectance spectrum of SnO₂ thin film with wave length for different time exposure.

Optical Constant
Extinction coefficient K

Can be calculated from the following [14]:

$$k=\alpha\lambda/4\pi \quad \text{.. (1)}$$

Where λ 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 SnO₂ thin film exposure to non-thermal plasma different time (0,2,4,6,8and10) min.

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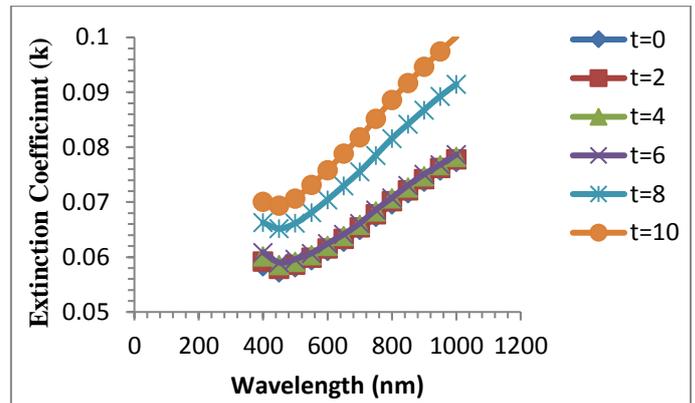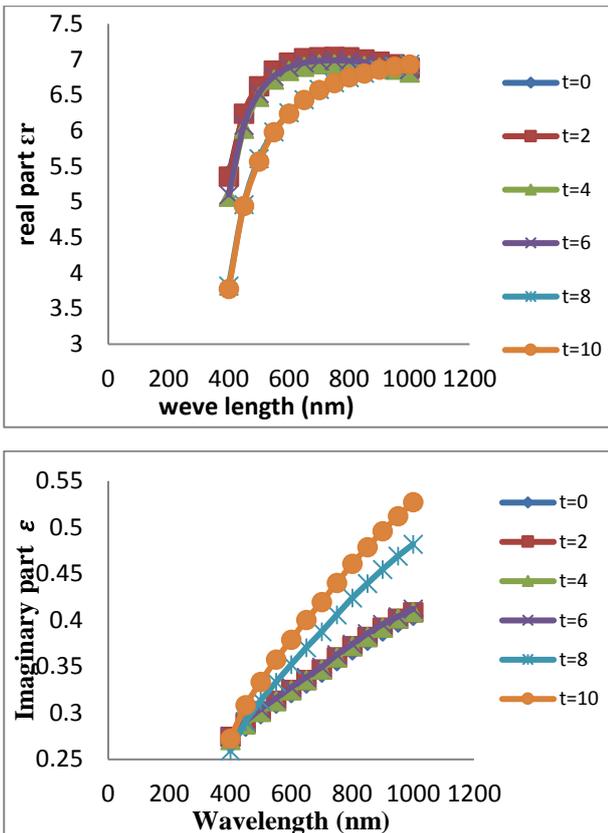

Fig.(3): show the relation between the extinction coefficient and the wave length in different time exposure.

Dielectric constant ε

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

$$\boldsymbol{\varepsilon}= \boldsymbol{\varepsilon}_r+i \boldsymbol{\varepsilon}_i \ , \ \boldsymbol{\varepsilon}_r =n^2- k^2 \ , \ \boldsymbol{\varepsilon}_i =2nk \quad \text{................ (2)}$$

Where ϵ_r is the real part and is the normal dielectric constant, ϵ_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 SnO₂ 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.(5): show that the refractive index as a function of wave length for different time exposure.

Fig.(4): the real and the imaginary part of dielectric constant SnO₂ different time exposure as function of wavelength.

Absorption coefficient (α)

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

$$\alpha = \frac{2.303\,A}{t}$$ .... (6)

Where A: absorption, t: thickness of film. Fig.(6) show that the absorption coefficient as wave length in light region (300-1100) nm for Sno2 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.

- Refractive index (n)

]16[We calculate the Refractive index as the following:

$$R = \frac{(n-1)^2}{(n+1)^2}$$ .... (3)
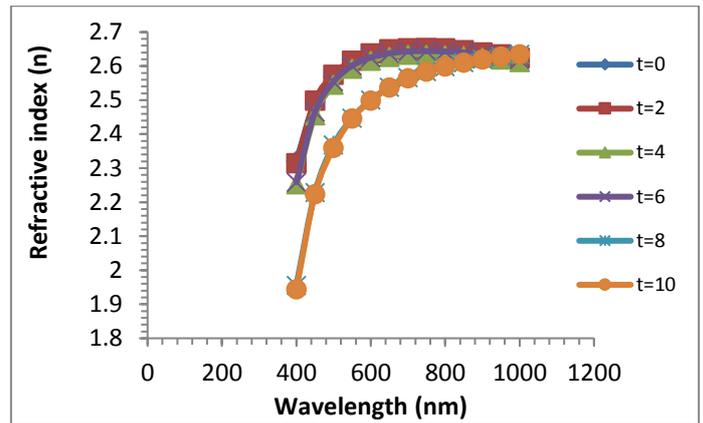
and we can make reformat as the following:

$$n = 1 + \sqrt{R}/1 - \sqrt{R}$$ .... (4)

Where R: Reflectance, we can calculate from the relation:

$$R + T + A = 1$$ .... (5)

Fig.(5) show that the refractive index for SnO₂ thin film as a function of wave length for different time (0,2,4,6,8and10)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.
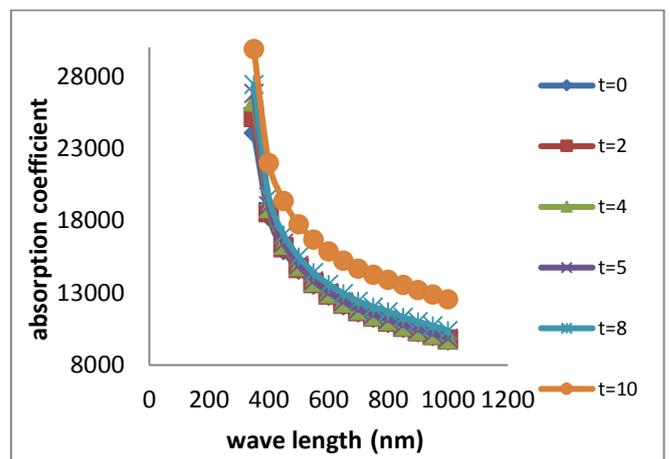

Fig.(6): show that the absorption coefficient as wave length in light region for different time exposure.

Energy gap E_g

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

$$\upsilon h\alpha = B(h\upsilon - E_g)^m \dots\dots\dots\dots\dots\dots (7)$$

Where: B: constant depends on the nature of the mater, E_g: energy gap $h\upsilon$,: 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 $(\alpha h\upsilon^2)$ versus photon energy $(h\upsilon)$,the energy gap Eg can obtain by extrapolating the linear portion of the graph to $(\alpha h\upsilon^2 = 0)$. Fig.(7) show that the relation between the $\alpha h\upsilon^2$ and photon energy $(h\upsilon)$ for 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.
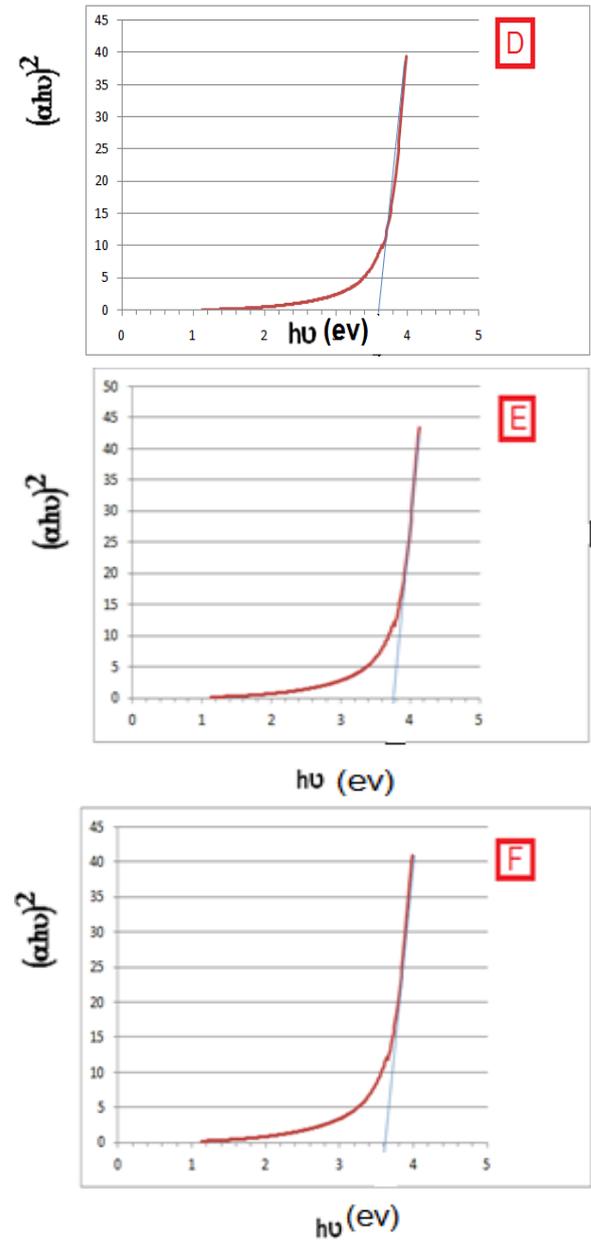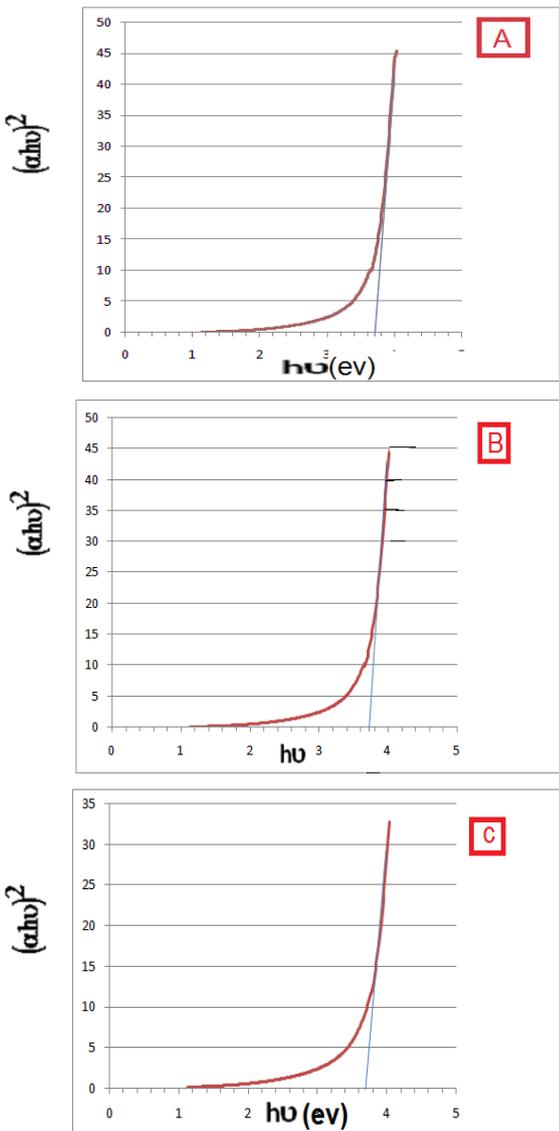
Fig.(7): aplot of $\alpha h\upsilon^2$ vs. photon energy ($h\upsilon$) for SnO$_2$ thin film for different time (A(t=0),B(t=2)min, C(t=4)min, D(t=6)min, E(t=8)min, F(t=10)min).
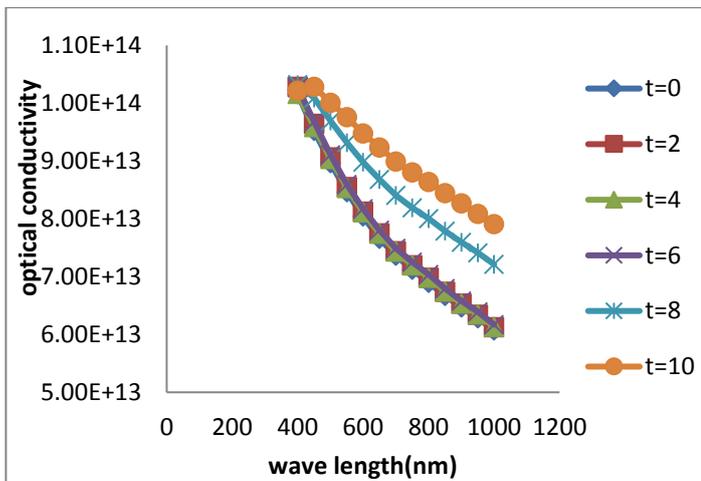
Optical conductivity

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

$$\sigma = \alpha n c \varepsilon_\circ \quad or \quad \sigma = \frac{\alpha n c}{4\pi} \dots\dots\dots (8)$$

Where c: velocity of ligth, Fig.(8) show that the optical conductivity for 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 ε and Refractive index n .we note that the Reflectance R, transmission T, real part of dielectric constant ε$_r$ and Refractive index n decreased with increasing the time of exposure while the absorption coefficient, imaginary part of dielectric constant ϵ_i , extinction coefficient K, Optical conductivity increasing with increased the time of exposure.

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الخلاصة

تم في هذا البحث استخدام منظومة الحاجز العازل للتأثير
على اغشية (SnO_2) الرقيقة, تعمل هذه المنظومة على إنتاج
البلازما غير الحرارية عند الضغط الجوي الاعتيادي, وتعمل
هذه المنظومة عادة عند الترددات 0.05 و 500kHz وعند
فولتية تصل الى 1500-100 kVolt. تحضير أغشية
اوكسيد القصدير (SnO_2) الرقيقة بطريقة الرش الكيميائي
الحراري من رش محمول مكون من كلوريدات القصدير
المائية ($SnCl_4: 5H_2O$) المذابة في الماء المقطر بتركيز
(0.1M) وعلى شرائح زجاجية مسخنة الى درجة حرارة
$450°C$.

درست اطياف الاشعة المرئية – فوق البنفسجية للاغشية
باستخدام حسابات الامتصاص البصري والتي اخذت في
المنطقة الطيفية (١١٠٠–١٩٠) نانومتر. كما درست ايضا
النفاذية والانعكاسية للاغشية في المنطقة المرئية – فوق
البنفسجية UV-VIS.

درس تاثير التعرض للبلازما لكل من النفاذية T,
الانعكاسية, الامتصاصية R, معامل الخمود K, معامل
الانكسار n و ثابت العزل Є. بينت النتائج ان كل من معامل
الخمود والجزء الخيالي من ثابت العزل تزداد مع زيادة زمن
التعريض للبلازما, بينما يقل كل من النفاذية والانعكاسية
والجزء الحقيقي من ثابت العزل ومعامل الانكسار مع زيادة
زمن التعريض للبلازما.