

# Nanostructured dye films of 4-tricyanovinyl-N,N-diethylaniline (TCVA) for optoelectronic applications: microstructure change and electrical conductivity improvement under UV irradiated effect

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Received 18 October 2019, revised 9 December 2019

Accepted for publication 16 December 2019

Published 13 February 2020



CrossMark

## Abstract

This article was committed to synthesizing thin films of 4-tricyanovinyl-N,N-diethylaniline (TCVA) by the thermal evaporation technique. The UV light then irradiated these films for different exposure times. Infrared spectroscopy demonstrated that the evaporation method is a good one to get un-dissociated TCVA films, and these films have excellent radiation stability. The x-ray diffraction pattern at room temperature confirms TCVA films have a nanocrystalline structure. These films are transformed into the amorphous structure after UV irradiation, indicating the increase of the disorder in these films. The optical spectroscopy of TCVA films was recorded before and after irradiation. It was found that the optical band gap decreases from 1.56 to 1.49 eV, and Urbach's energy increases after UV irradiation. The electrical studies showed that the value of electrical conductivity increases and the value of activation energy decreases after UV irradiation.

Keywords: dye films, spectroscopy, conductivity, UV irradiation

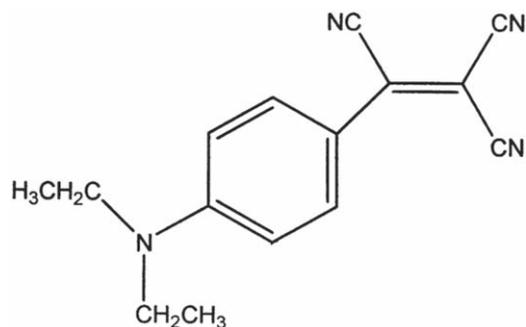
(Some figures may appear in colour only in the online journal)

## 1. Introduction

Monetarily, the organic materials assume an indispensable part in the organic electronics field. These materials pick up its remarkable properties given of organic semiconductors with the small molecule as in the organic light-emitting diodes, field-effect transistor, and organic photovoltaic application [1–5].

Tricyanovinyl derivative dyes have the height charge transport capacity in the electronic ground state; also, they have strong attention as promising conductive organic

materials [6, 7]. Additionally, these dyes are a conceivable contender for application in optical sensors because of their tricyanovinyl groups, which are vulnerable to nucleophilic offensive [6, 7]. The organic dye of 4-tricyanovinyl-N,N-diethylaniline (TCVA) has acceptor-donor disubstituted benzenes. The chemical structure of the TCVA compound is shown in scheme 1. In addition, TCVA compound classified as organic molecular rotors compounds and demonstrates excellent possibility applications in the nonlinear optics and optoelectronic gadgets [6–8]. Besides, it has an incredible significance for shading engineered polymer strands. TCVA



Scheme 1. The chemical structure of TCVA.

compound was utilized as an excellent dye in heat-transfer and recording materials photoconductive [7, 9].

Photoinduced optical anisotropy in organic dyes is the subject of intensive care (study) and investigations [10–14]. The importance of these optical materials for applications is quite apparent in many fields of modern optics, among which, optical data storage, photonics, optoelectronics, and all-optical modulation [11, 12]. The present study points to highlight the preparation and optical characterization of TCVA nanostructure films. So, the point of this investigation is to examine the impact of UV irradiation on the physical properties of TCVA nanostructured films.

## 2. Experimental details

The synthetic of the TCVA compound was previously reported, and the direct reaction between tetracyanoethylene and N, N-diethylaniline was used [6]. By thermal evaporation method, films of TCVA were fabricated utilizing a coating unit (Edwards E306A), onto an ultrasonically cleaned different substrate such as flat glass, quartz and cleaved KBr single crystal. The substrate put at room temperature, and it was fixed onto a spin holder to obtain uniform produced. The film of TCVA was manufactured in a vacuum of  $2.5 \times 10^{-4}$  Pa. The film thickness (315 nm) and the deposition rate ( $5 \text{ nm s}^{-1}$ ) were controlled by a quartz crystal monitor. Then, the thickness of the film has been checked by using the interferometric technique. For the study the influence of UV irradiation on these films, the as-deposited samples were exposed for a different time, in the air and at room temperature, to UV light using a UV lamp (UVP Mineralight UVGL-25 UV (wavelength 254 nm and 4 W power). The infrared cut filter was used to repress any influence of temperature.

X-ray diffraction (XRD) of TCVA films deposited on glass substrates was made using Philips diffractometer 1710 with Ni-fitter  $\text{CuK}\alpha$  source ( $\lambda = 0.154 \text{ nm}$ ). Atomic force microscopy (AFM) NT-MDT (Type Next, Russia) model used to get the image of surface morphology for the films before and after UV irradiation. The Fourier-change infrared (FTIR) has been utilized to examine the molecular structures of TCVA films deposited on KBr substrates. The absorbance (A) of TCVA films deposited on quartz substrates was measured utilizing a double beam spectrophotometer. Samples in

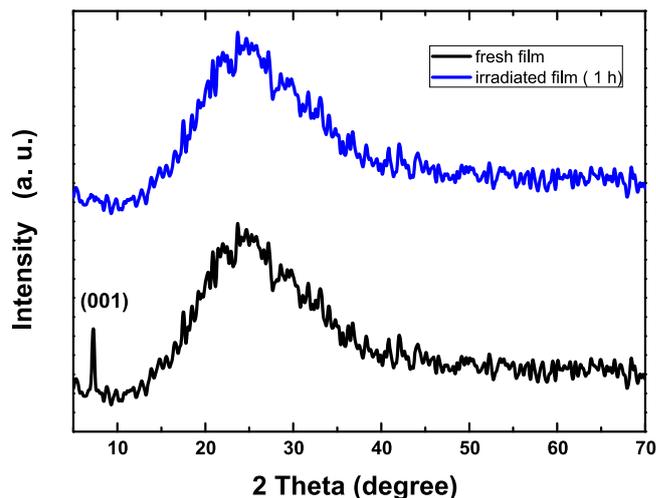


Figure 1. XRD of TCVA films before and after UV irradiation.

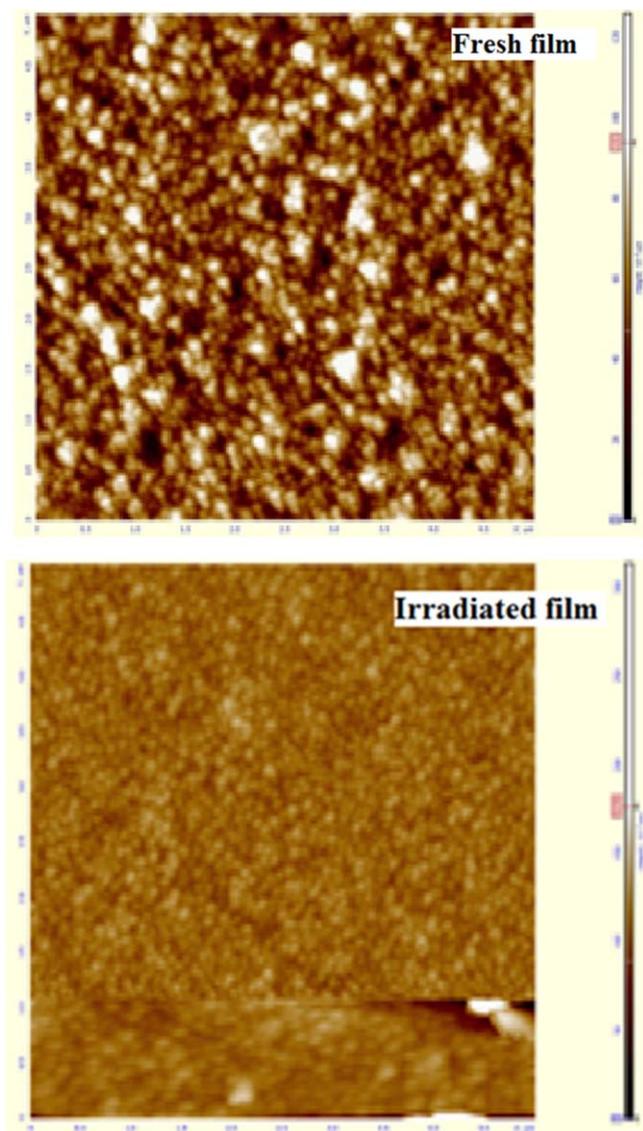
the planar design were used for the electrical estimations. The films deposited on glass substrates and Au electrodes were deposited in a high vacuum as Ohmic contacts on TCVA films. The Keithley mode 610 with a high impedance electrometer was used to measure the electrical resistance of TCVA films by two probe technique. The estimations had been done at different temperatures.

## 3. Results and discussion

### 3.1. Structural studies

Previously, XRD was used to investigate the crystal structure of TCVA powder, and it is found that TCVA has a triclinic structure [15]. The thermal evaporation of TCVA led to films with a certain degree of crystallinity [15]. Figure 1 shows the XRD of as-deposited and UV irradiated thin films. The fresh film has only one peak (001) at  $2\theta = 7.25^\circ$  with the hump of amorphous in  $17^\circ$ – $35^\circ$ . The crystallite size was calculated by Scherrer's equation [15], and it is found to be 45 nm. That means TCVA films are belonging to the nano-sized structure. A nano-film of 6-(3,4 Dimethoxyphenyl)-1-methyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazolo[4,3-b]-5-carbonitrile (DMOPC) was get by thermal evaporation [16]. Zeyada *et al* concluded that DMOPC film has nanocrystals embedded in the amorphous medium [16]. Exposure of the as-deposited TCVA film to UV irradiation for 1 h produces nanocrystalline to amorphous phase transformation in the studied sample, as shown in figure 1. This behavior could be referred to as the UV irradiation-induced disorder in the films.

The surface investigation has been done using an AFM system for TCVA films before and after UV irradiation. The 2D images of fresh TCVA films and that irradiated were illustrated in figure 2. The image for the fresh film shows that the grains are uniformly distributed within the scanning area. The grain size and roughness of the fresh film were calculated and equal to 75.3 and 84.2 nm, respectively. For the irradiated film, the surface becomes smoother with uniform grains.

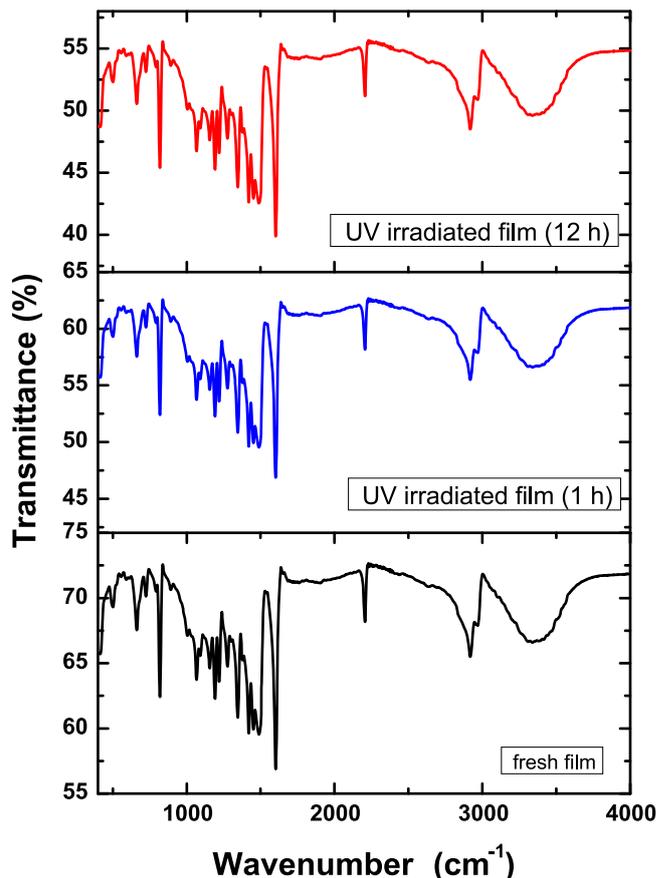


**Figure 2.** AFM of TCVA films before and after UV irradiation.

Also, it is found that the grain size and roughness of the irradiated film equal to 45 and 60.4 nm, respectively.

### 3.2. Infrared spectroscopy studies

Previously, a correlation of FTIR spectra for the powder of TCVA and its prepared film demonstrates that the evaporation method is a decent one to get undissociated films of TCVA [15]. FTIR spectra of TCVA films before and after UV irradiated in the most important range 4000–400  $\text{cm}^{-1}$  are shown in figure 3. It displays that the spectrum of the as-deposited thin film is like the spectra of the UV irradiated film, which indicates that TCVA films have excellent radiation stability. Similar results were obtained for DMOPC [16] and Rose Bengal films [17]. As illustrated in figure 3, a wide intensity band at 3368  $\text{cm}^{-1}$  because of extending vibration of the O–H hydroxyl group for fresh and UV illuminated TCVA films. The band absorption of the C–H aromatic has shown up at 3000  $\text{cm}^{-1}$ . The two bands at 2974 and 2920  $\text{cm}^{-1}$  are set to



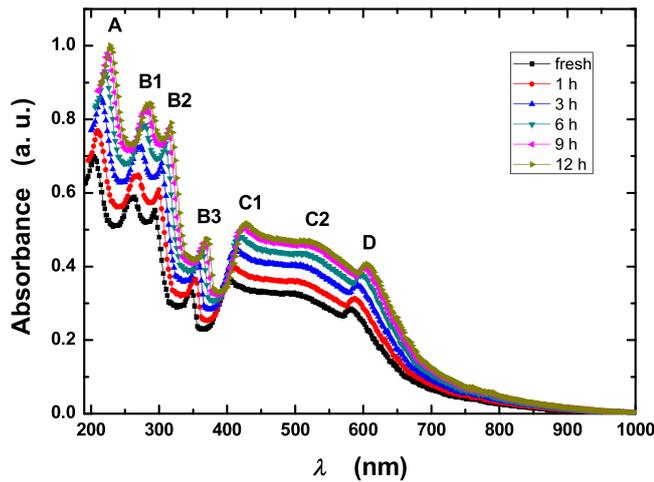
**Figure 3.** Infrared spectra of TCVA films before and after UV irradiation.

C–H asymmetric extending in  $\text{CH}_3$  and  $\text{CH}_2$ , separately. At 2202  $\text{cm}^{-1}$ , a sharp absorption band showed up is set to the expansion vibration of  $\text{C}\equiv\text{N}$ . Because of the  $\text{C}=\text{C}$  extending vibration, a sturdy band showing up at 1601  $\text{cm}^{-1}$ . The tops at 1450 and 1367.8  $\text{cm}^{-1}$  showing to the  $\text{CH}_3$  bending modes. The bands in 820 and 793  $\text{cm}^{-1}$  can be allocated to the C–H deformation bands. The C–C and C–H vibrations are watched at 792.7–679  $\text{cm}^{-1}$ .

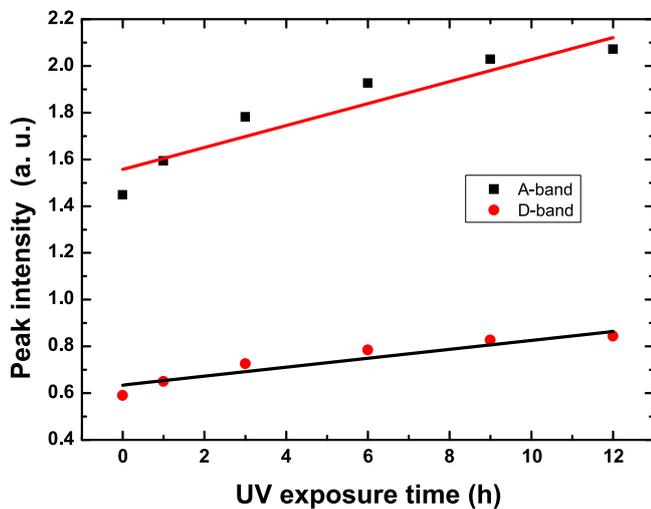
From FTIR spectra, only the intensity of the peaks bands decreased when exposed to UV light. Therefore, FTIR and XRD, illustrate that the nanocrystalline phase of TCVA film has the same chemical bonds like that of the amorphous phase and this indicates that the change occurred when atoms in the crystal front change to disordered state and those clusters change their order.

### 3.3. Absorption spectroscopy studies

The absorbance spectra of TCVA films before and after UV irradiated with various exposure times appear in figure 4 and show four principal bands. First, A-band at 230–200 nm is allotted to the transitions of  $n\text{-}\sigma^*$  transitions from the  $N,N$ -diethylaniline group. The second B-band at 265–335 nm is appointed to the transition of  $\pi\text{-}\pi^*$  from the aromatic rings and this band shows up splitting. The third C-band at 370–565 nm includes the transition of  $n\text{-}\pi^*$  from the  $\text{C}\equiv\text{N}$



**Figure 4.** Absorbance spectra for TCVA films before and after UV irradiation.



**Figure 5.** The dependence of peak intensity on UV exposure time for TCVA films.

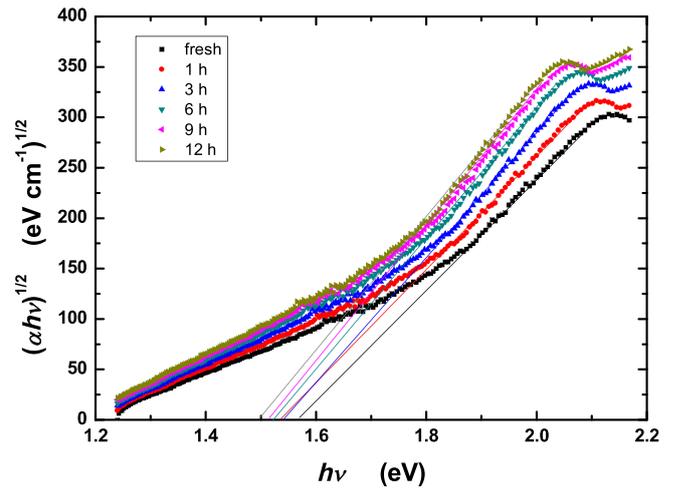
groups. The last one D-band at 900–570 nm is allotted to charge transport interaction in intermolecular.

The intensities of these bands are increasing with rising illumination time, while its positions moved towards long wavelengths as appeared in figure 5. It is uncovered that intensity increments directly with rising exposure time. These got results can efficiently be connected to radiation dosimeter estimations [18]. Also, it is clear that the main absorption edge characterizes the absorption spectrum of fresh TCVA film. This edge is moved towards longer wavelengths upon UV irradiation, which shows the energy gap diminishes with rising the exposure time of UV irradiation.

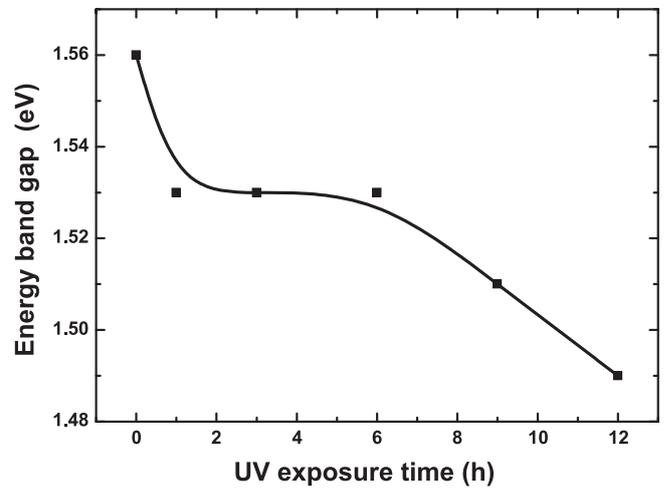
The absorption coefficient,  $\alpha$ , of a film characterizes the attenuation of light intensity with space in the film, which is calculated from the absorbance spectrum using the relation [6]

$$\alpha = 2.303 \times \frac{A}{d}, \quad (1)$$

where  $d$  is the thickness of the film in cm. Moreover, the energy gap was calculated from the analysis of the absorbance



**Figure 6.** The dependence of  $(\alpha h\nu)^{1/2}$  on photon energy for TCVA films before and after UV irradiation.



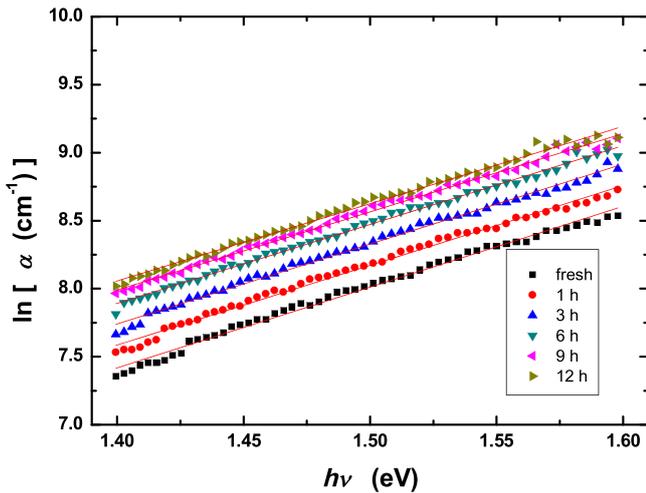
**Figure 7.** The relation between the energy band gap and UV exposure time for TCVA films.

spectrum near the absorbance edge. According to the band-to-band transitions theory [19], the absorbance pursues a power relation as:

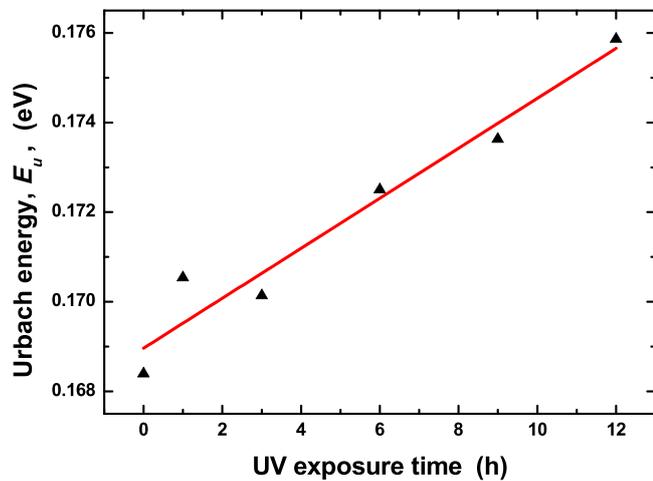
$$(\alpha h\nu)^r = H(h\nu - E_g), \quad (2)$$

where  $h\nu$  is the energy of the incident photon,  $H$  is a parameter depending on transition probability, and  $E_g$  is the energy gap. The factor  $r$  is the power, which describes the transition procedure. The electronic transitions in the organic materials happen between the highest occupied molecular orbital and lowest unoccupied molecular orbital.

The normal technique for the assurance of the estimation of  $E_g$  includes plotting  $(\alpha h\nu)^r$  versus  $h\nu$  utilizing diverse estimations of  $r$ . The best fit was gotten for  $r = 1/2$ , which demonstrates that the transition energy for electrons is indirect. The plots of  $(\alpha h\nu)^{1/2}$  against  $h\nu$  for TCVA films with different exposure UV irradiation were illustrated in figure 6. The estimations of  $E_g$  for as-deposited and irradiated TCVA films are calculated from this figure, and the variation of the optical energy gap with the UV exposure time was shown in



**Figure 8.** The dependence of  $\ln(\alpha)$  on  $h\nu$  for TCVA film before and after UV irradiation.



**Figure 9.** The relation between the Urbach energy and UV exposure time for TCVA films.

figure 7. It is clear that  $E_g$  decreased with increasing the UV exposure time, which is a result of defect and disorder in TCVA films. This defect produces localized states in the forbidden band, and the energy gap will be decreased [20]. Similar observations were obtained for DMOPC [16] and Rose Bengal films [17].

In the structure of a solid, the disorder beneath the absorbance edge can be determined by the Urbach relation [19]. This rule relates the Urbach energy of the tail of the localized state,  $E_u$ , with the absorption coefficient,  $\alpha$ , as [19]

$$\alpha = \alpha_o \exp\left(\frac{h\nu}{E_u}\right), \quad (3)$$

where  $\alpha_o$  is a constant. Figure 8 illustrated a graph of  $\ln(\alpha)$  against  $h\nu$  for TCVA films before and after UV irradiation. The values of  $E_u$  were calculated from the reciprocal of the slope of the linear portion, and its dependence on the UV exposure time was represented in figure 9. It is clear that the values of  $E_u$  increased with increasing UV exposure time indicating an increase in disorder in TCVA films [21].

### 3.4. Electrical conductivity studies

The graph is shown in figure 10(a) depicts the variation of electrical conductivity of TCVA films with UV exposure time. It is clear that the conductivity increments with UV exposure time. This improvement could be a result of the disorder in the structure of TCVA films. The UV irradiation produces the defects when it is going through the thin film as seen by XRD, which motioned above. This defect produces localized states in the forbidden band.

Figure 10(b) shows the electrical conductivity of TCVA films before and after UV irradiation in the temperature range from 309 to 370 K, which can be expressed by Arrhenius relation [22]

$$\sigma = \sigma_o \exp\left(\frac{-\Delta E}{K_B T}\right), \quad (4)$$

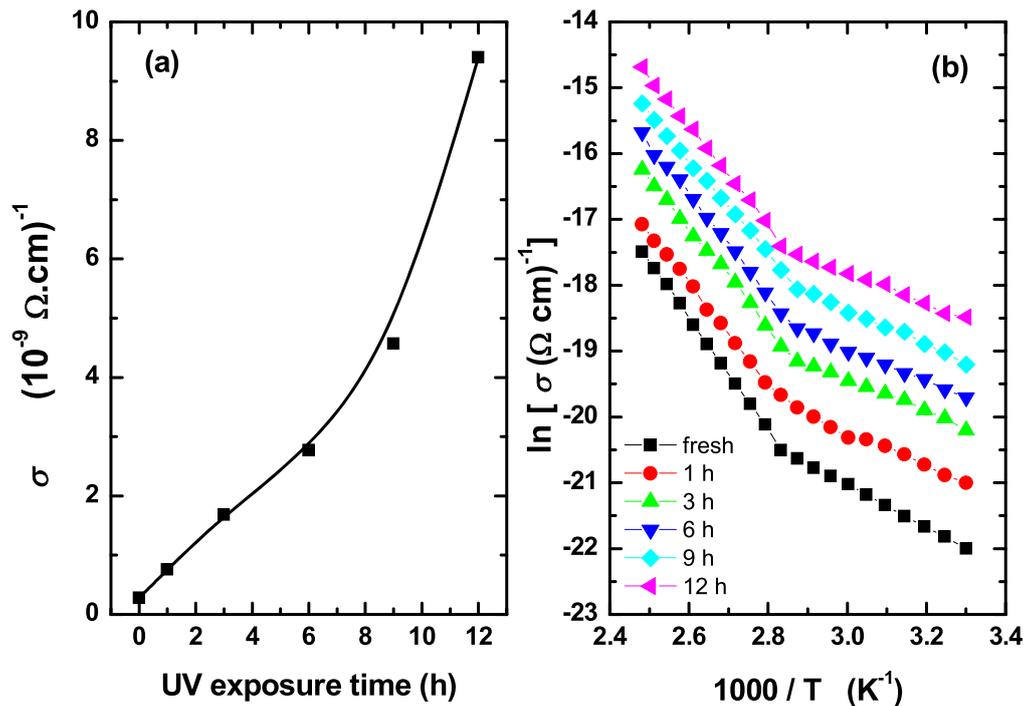
where  $T$  will be the temperature,  $K_B$  will be the Boltzmann's constant,  $\Delta E$  will be the activation energy, and  $\sigma_o$  will be the pre-exponential factor. The results (figure 9(b)) show that TCVA films are a semiconductor material and that the conduction process is thermally activated with two conduction mechanisms. The direct lines of the two-component identified as (I) and (II). Then, equation (4) can be written as:

$$\sigma = \sigma_{o1} \exp\left(\frac{-\Delta E_1}{K_B T}\right) + \sigma_{o2} \exp\left(\frac{-\Delta E_2}{K_B T}\right), \quad (5)$$

where  $\sigma_{o1}$  and  $\sigma_{o2}$  are the pre-exponential factors,  $\Delta E_1$  and  $\Delta E_2$  are the electrical activation energies in regions (I) and (II) respectively. Table 1 records the values of  $\sigma_{o1}$ ,  $\sigma_{o2}$ ,  $\Delta E_1$  and  $\Delta E_2$  in the two temperature districts at different exposure times. The activation energies for these two regions have been found to be:  $\Delta E_1 = 0.28$  eV and  $\Delta E_2 = 0.74$  eV. Therefore, the two separate conductivity mechanisms, for each region are extrinsic and intrinsic conductions, respectively. Also, it is found that the values of activation energies decrease after UV irradiation. This behavior can be a result of the adjustment in the structure of TCVA films.

## 4. Conclusion

TCVA films were prepared by an evaporation method to have a nanostructured nature. It was found that these films have excellent radiation stability. XRD investigation demonstrates that UV irradiation changed these films to an amorphous structure. UV irradiation increased the absorption spectra and the intensity increments directly with rising exposure time. These got results can efficiently be connected to radiation dosimeter estimations. Also, it was found that the energy gap decreased with increasing the UV exposure time, which is a result of defect and disorder in TCVA films. However, the conductivity of TCVA films increments with UV exposure time due to the disorder in the structure of TCVA films. Also, it was found that the conduction is through the expanded states.



**Figure 10.** (a) The dependence of electrical conductivity on UV exposure time for TCVA films (b) the dependence of electrical conductivity on temperature for TCVA films before and after UV irradiation.

**Table 1.** The pre-exponential constant of conductivity and thermal activation energy of TCVA films before and after UV irradiation.

Sample	Region I		Region II	
	$\sigma_{o1} (\times 10^{-5} \Omega^{-1} \text{cm}^{-1})$	$\Delta E_1$ (eV)	$\sigma_{o2} (\Omega^{-1} \text{cm}^{-1})$	$\Delta E_2$ (eV)
As-deposited	1.13	0.28	43.97	0.74
1 h	0.39	0.22	5.58	0.65
3 h	0.50	0.21	10.87	0.65
6 h	0.89	0.21	28.12	0.66
9 h	2.94	0.21	8.81	0.61
12 h	1.71	0.20	53.12	0.61

## Acknowledgments

This work was supported by the Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah, under grant No. (D-061-363-1437). The authors, therefore, gratefully acknowledge the DSR technical and financial support.

## Conflict of interest

The authors declare that they have no conflict of interest.

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## References

- [1] Anthony J E, Facchetti A, Heney M, Marder S R and Zhan X W 2010 *Adv. Mater.* **22** 3876
- [2] Goetz K P, Li Z, Ward J W, Bougher C, Rivnay J, Smith J and Conrad B R 2011 *Adv. Mater.* **23** 3698
- [3] Al Garni S E and Darwish A A A 2017 *Sol. Energy Mater. Sol. Cells* **160** 335
- [4] Lehnher D, Waterloo A R, Goetz K P and Payne M M 2012 *Org. Lett.* **14** 3660–3
- [5] Mei Y, Loth M A, Payne M, Zhang W, Smith J and Day C S 2013 *Adv. Mater.* **25** 4352
- [6] El-Nahass M M, Zeyada H M, Abd El-Rahman K F, Farag A A M and Darwish A A A 2008 *Spectrochim. Acta A* **69** 205
- [7] El-Nahass M M, Abd-El-Rahman K F and Darwish A A A 2009 *Eur. Phys. J. Appl.* **48** 20402
- [8] El-Nahass M M, Zeyada H M, Abd-El-Rahman K F and Darwish A A A 2009 *Sol. Energy Mater. Sol. Cells* **91** 1120
- [9] Deshpande A V, Beidoun A, Penzkofer A and Wagenblast G 1990 *Chem. Phys.* **142** 123
- [10] Ivanov M, Nikolova L, Todorov T, Tomova N and Dragostinova V 1994 *Opt. Quantum Electron.* **26** 1013
- [11] Abbas B and Alshikh Khalil M 2010 *Acta Phys. Pol. A* **117** 904
- [12] Sekkat Z, Wood J, Aust E F, Knoll W, Volksen W and Miller R D 1996 *J. Opt. Soc. Am. B* **13** 1713
- [13] Dumont M 1996 *Mol. Cryst. Liq. Cryst.* **282** 437
- [14] Ueda M, Kim H-B, Ikeda T and Ichimura K 1993 *J. Non-Cryst. Solids* **163** 125
- [15] El-Nahass M M, Zeyada H M, Abd-El-Rahman K F and Darwish A A A 2013 *Eur. Phys. J. Appl.* **62** 10202
- [16] Zeyada H M, El-Ghamaz N A, Youssif M I and Gaml E A 2017 *Opt. Mater.* **69** 392–400
- [17] Zeyada H M, Youssif M I, El-Ghamaz N A and Aboderbala M E O 2017 *Physica B* **506** 75–82
- [18] Migahed M D and Zidan H M 2006 *Curr. Appl Phys.* **6** 91–6

- [19] El-Nahass M M, Abd El-Rahman K F, Farag A A M and Darwish A A A 2004 *Int. J. Mod. Phys. B* **18** 421
- [20] Chaudhuri S and Biswas S K 1985 *Solid State Commun.* **53** 273
- [21] Dow J D and Redfield D 1972 *Phys. Rev. B* **5** 594
- [22] Darwish A A A, El-Nahass M M and Bahlol M H 2013 *Appl. Surf. Sci.* **276** 210