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اثر پلاسمای تخلیه الکتریکی تابان بر بهبود جریان اتصال کوتاه در سلول های خورشیدی حساس شده با رنگینه

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چکیده- لایه های نازک ZnO از طریق روش سُل-ژِل آماده و تحت پلاسمای تخلیه الکتریکی تابان آرگون و نیتروژن قرار گرفتند. میدان الکتریکی در غلاف پلاسمای آرگون قوی تر از نیتروژن است بنابراین تغییرات در ساختار بلورین برای ZnO/Ar در قیاس با ZnO/N_2 بزرگتر بود. مطالعه دقیق پارامترهای پاشندگی و پذیرفتاری اپتیکی غیر خطی مرتبه سوم، تغییرات خواص شیمیائی در سطح این لایه های نازک را آشکار ساخت. پلاسما بطور قابل ملاحظه ای موجب افزایش جفت شدگی الکترونی Zn-N719، با کاهش کمپلکس Zn^{2+}/dye می شود. بررسی دانسیته های جریان اتصال کوتاه بهبود قابل توجه در جفت شدگی الکترونی را نمایش داد.

کلید واژه- اکسید روی، پلاسمای تخلیه الکتریکی تابان، رنگینه N719، سُل-ژِل، کمپلکس Zn^{2+}/dye

Effect of the Glow Discharge Plasma on the short circuit current improvement in DSSCs

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Abstract- The ZnO thin films were prepared via the sol-gel method and then treated in Ar and N_2 glow discharge plasma. The electric field in the Ar plasma sheath is stronger than the N_2 plasma, so the crystalline changes in the ZnO/Ar were larger in comparison to ZnO/N_2. A detailed study of the dispersion parameters and the third-order nonlinear optical susceptibilities represented alterations in the chemical properties of the thin films' surface. The plasma remarkably enhances the Zn-N719 electronic coupling via the reduction of the Zn^{2+}/dye complexes. The short circuit photocurrent densities showed the electronic coupling improvement.

Keywords: Glow discharge plasma, N719 dye, Sol-Gel, Zn^{2+}/dye complex, ZnO

1. Introduction

N-type semiconductors, zinc oxide (ZnO) is relatively inexpensive, non-toxic, and optically transparent in the visible wavelengths with high electron mobility. ZnO has direct band gap energy of about 3.3 eV [1]. The semiconductors are usually used in optical filters, gas sensors, biosensors, thin-film transistors, as a Photocatalyst, light-emitting diodes (LED), and dye-sensitized solar cells (DSSCs) [2]. Commercial dyes, such as N719 and N3 are widely used in the sensitization process of the ZnO-based DSSCs. Formation of the non-conductive Zn^{2+}/dye complex in the sensitization process and slow kinetics of the electron transfer in the ZnO-dye bonds result in low efficiency for the ZnO-based DSSC [3]. The electric field in the plasma sheath can change the physicochemical properties of the material's surface. In this work, the electric field effects of Ar and N_2 plasma sheath on the electronic coupling of the Zn-dye in the sensitization process have been studied for the thin films of ZnO.

2. Materials and methods

The thin films of ZnO were deposited on ITO (indium tin oxide) coated glass substrates by the means of the sol-gel method via spin-coating. N719 dye was supplied from Sigma Aldrich. Zinc acetate dihydrate, monoethanolamine, 2-propanol, ethanol, and sodium hydroxide, all were purchased from Merck (technical graded; 99 %,).

2.1. Glow discharge plasma and sheath effects

The thin films were under the plasma sheath to be treated with the glow discharge plasmas of Ar (ZnO/Ar) and N_2 (ZnO/N_2). The best-obtained results were at the pressure of 40 Pa and a time of 10 minutes. The N_2 and Ar glow discharge plasma systems operated at 800 V, 20 mA, and 13 kHz. The strength of electric field is directly related to the ion mass in the plasma sheath. So, the electric field in Ar plasma is stronger than N_2 plasma.

2.2. Sensitization of the thin films

The solution of 0.5 mM of the N719 dye was used to sensitize the thin films, for 24 hours, to obtain the photoanode. In the adsorption process of the N719 dye on the ZnO thin films the major product is the Zn^{2+}/dye complex.

2.3. Characterization of the thin films and the photoanodes

Scanning electron microscope (SEM) images for the thin films were obtained using Scanning Electron Microscope Leo 1430 Vp, to investigate the morphological changes due to the plasma treatments. To study the changes of thin films' surface structures a Siemens D5000 X-ray diffraction system (XRD) with a copper anode (λ=0.15406 nm) was used. The optical properties of the thin films were recorded using a Shimadzu UV-2450 ultraviolet-visible spectrum (UV-Vis) Spectrophotometer.

3. Results and Discussion

3.1. Surface morphology and Crystal structure

Based on the SEM images, all fabricated thin films have a homogeneous smooth surface. To study the changes in the crystalline structure of the thin films was used the XRD analysis. Fig. 1 represents the XRD spectra of the thin films.

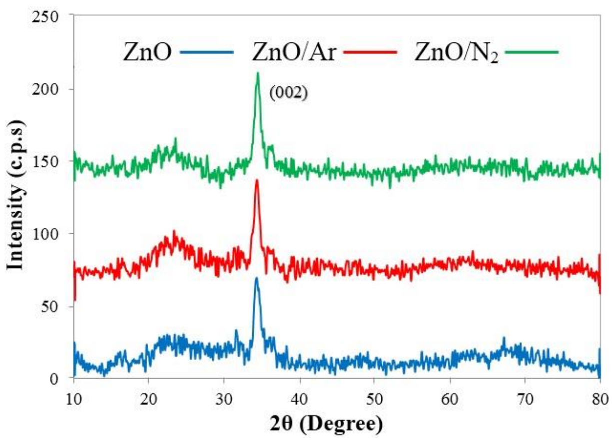

Fig. 1: The XRD spectrums for ZnO, ZnO/Ar, and ZnO/N_2 thin films.

The physical quantities of the crystalline structure of the thin films, such as; average crystallite size (*D*), lattice strain (ε), and dislocation densities (δ)

are obtained from the XRD spectra as shown in Table 1 [4].

Table 1. Parameters of the crystalline structure for the thin films of ZnO, ZnO/Ar, and ZnO/N_2.

	2*θ* (002)	***β* (002)**	***D* (nm)**	***ε* (10^{-3})**	***δ*(nm)$^{-2}$ (10^{-3})**
ZnO	34.32	1.01	9.1	4.2	12
ZnO/Ar	34.33	1.12	8.2	4.6	15
ZnO/N_2	34.34	1.07	8.6	4.4	13

3.2. Optoelectronic properties of the thin films

The optoelectronic properties of the thin films were determined via the spectroscopic method in the visible region. In the interaction of light with matter, the refractive index is a material property. In addition, the refractive index is a function of the wavelength of the incident light, a phenomenon called dispersion. The dispersion can be described by the Wemple DiDomenico single-oscillator model. Accordingly, the refractive index (n) obeys the incident photon energy (E) and the single-oscillator parameters via Equation 1.

$$n^2 - 1 = \frac{E_o E_d}{E_o^2 - E^2} \qquad (1)$$

In which, the oscillator energy (E_o) and the dispersion energy (E_d) are the dispersion (or the single-oscillator) parameters. The plots of $(n^2-1)^{-1}$ versus E^2 are presented in Fig.2. The dispersion parameters can be estimated from the slope ($1/E_oE_d$) and the intercept (E_o/E_d) of the plots. The values of E_o and E_d are reported in Table 2. Considering the following empirical equation, the nature of the chemical bonds and the electrons of the valence band affect the dispersion energy.

$$E_d = \beta N_c Z_a N_e \qquad (2)$$

Where N_c, Z_a, N_e, and β are the effective coordination number of the cation nearest-neighbor to the anion, the formal charge of the anion, the effective number of the valence electrons per anion, and a constant that depends on the interatomic bond, respectively. So, the plasma treatment changes the structure of the thin films, the charge distribution in the crystal unit cells, and ultimately, the chemical bonds. The results show an increment in the dispersion energies of about 19.74% and 11.16% for the thin films of ZnO/Ar and ZnO/N_2, respectively.

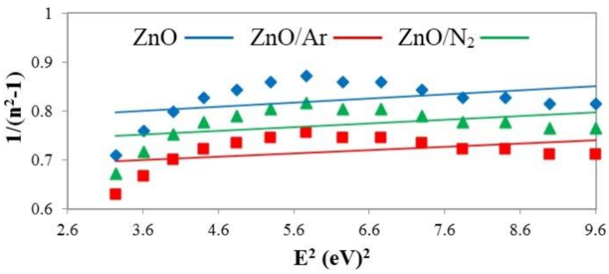

Fig. 2: The plots of $(n^2\text{-}1)^{-1}$ versus E^2 for ZnO, ZnO/Ar, and ZnO/N_2 thin films.

E_d/E_o is an important ratio in determining the third-order nonlinear optical susceptibility ($\chi^{(3)}$). Accordingly, Miller's empirical rule was employed, in form of Equation 3, for the visible and the near-IR spectra.

$$\chi^{(3)} = A(\chi^{(1)})^4 = A(\frac{n^2-1}{4\pi})^4 = C(\frac{E_d}{E_o})^4 \qquad (3)$$

Where $\chi^{(1)}$ and C are the linear optical susceptibility and a constant, respectively. The third-order nonlinear optical susceptibilities for the thin films are tabulated in Table 2.

Table 2. The optoelectrical parameters for the thin films of ZnO, ZnO/Ar, and ZnO/N_2.

	***E_g* (eV)**	***E_d* (eV)**	***E_o* (eV)**	**$\chi^{(3)}$ (m^2V^{-2})**
ZnO	3.3	12.36	9.52	2.84C
ZnO/Ar	3.3	14.8	10	4.80C
ZnO/N_2	3.33	13.74	9.77	3.91C

Due to the effect of the electric field in the plasma sheath, an increment of about 69% and 37.7% is seen in the nonlinear susceptibility of the thin films of ZnO/Ar and ZnO/N_2, respectively. In a material system, the dipole moment per unit volume (or polarization) directly depends on the susceptibility, whenever the wavelength of the applied light is a constant. The nonlinearity is strongly related to the polarization in the chemical bonds. So, the plasma treatment changes the nature of the chemical bonds on the surface of the thin films.

3.3. photocurrent-voltage characterizations

The density of photocurrent (J) versus voltage (V) was measured via the sunlight simulator, under the light intensity of 100 mW/cm^2 (AM 1.5), for the ZnO-based solar cells. The photovoltaic parameters of the solar cells are reported in Table 3. Changes in the density of the photocurrent for the ZnO-based solar cells are related to the difference in the chemical bonds of the Zn-dyes. The results show that the short circuit photocurrent density (J_{sc}) is increased by about 150% and 62% for the solar cells fabricated by the thin films of ZnO/Ar and ZnO/N_2, respectively. The chemical bond in Zn^{2+}/N719 is an ionic bond that makes a non-conductive layer. The electron injection kinetics dependent on the nature of the Zn-N719 bond, so to raise the density of the photocurrent one must increase the Zn-N719 electronic coupling. We believe the plasma treatment leads to variations in the chemical property of the ZnO thin film's surface and significantly improve the Zn-N719 electronic coupling.

Table 3. The photovoltaic parameters for the DSSCs of ZnO, ZnO/Ar, and ZnO/N_2.

	V_{oc} (mV)	J_{sc} (mA/cm^2)	R_{sc} Ω	R_{oc} Ω
ZnO	303	0.08	4678	5040
ZnO/Ar	280	0.20	1533	2177
ZnO/N_2	332	0.13	6433	3482

According to the results, the increment in the nonlinear susceptibility for the thin films of ZnO/Ar and ZnO/N_2 is about 69% and 37.7%, respectively. Since the electric field in the Ar plasma sheath is stronger than that of N_2, the polarization on the thin film of ZnO/Ar is higher than ZnO/N_2. Also, the results show that the plasma affects the J_{sc} (or the kinetics of electron injection). Increment the J_{sc} obeys the electric field of plasma sheath, so the plasma effects lead to the reduction of the Zn^{2+}/dye in the ZnO photoanodes.

4. Conclusions

Treatment with Ar and N_2 plasmas affect the crystalline structure of the ZnO thin films. The crystalline changes alter the optoelectronic properties of the thin films. The electric field in the plasma sheath for the Ar plasma is stronger than the N_2 plasma, so the changes are more severe in the Ar plasma. Changes in the optoelectronic quantities of the E_d and the $\chi^{(3)}$ show the effect of plasma on the chemical properties of the surface for the thin films. The N719 dye-sensitization process for the ZnO thin film is mainly achieved via the formation of non-conductive Zn^{2+}/dye complexes. The plasma considerably enhances the Zn-N719 electronic coupling. Enhancement of the Zn-dye electronic coupling in the ZnO-based photoanodes is a way to increase the photocurrent density in ZnO-based solar cells, and using plasma is an innovative manner to perform this strategy.

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