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Synthesis of Photodetectors Based on CdS Nanostructures by SILAR Method without Using Ammonia as a Catalyst

Zainab S. Hussain*[1], Hussein A. Alshamarti[1]

[1]Department of Physics, Faculty of Science, University of Kufa, Najaf-Iraq

*Corresponding Author E-mail: [a]zainabsh309@gmail.com

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ABSTRACT

In this paper, photodetectors based on CdS thin films were successfully prepared and deposited on glass substrates using the SILAR method without using ammonia as a catalyst and with the presence of ammonia. The previously mentioned samples were named as Z3 and Z4, respectively. The structural, morphological, and optical properties were studied. XRD data revealed a crystal phase and a cubic structure of CdS with peaks corresponding to planes (111), (022), and (131). Also, the measured crystal size of plane (111) was 20.506 and 54.661 nm for samples Z3 and Z4 respectively. FESEM images showed homogenous nanosized grains for prepared samples. The absorption spectra and energy band gap of CdS were measured with UV-Vis spectroscopy, which showed that $E_g = 2.3$ eV for sample Z3 and $E_g = 2.35$ eV for sample Z4 and both were seen to be tended toward redshift. The (I-V) properties of Z3 and Z4 photodetectors revealed a weak response under visible light, but a much higher response to UV light. At 5V bias, the photocurrent was increased from 4.09×10^{-8} to 3.7×10^{-7} μA for Z3, while increased from 1.8×10^{-8} to 1.4×10^{-7} μA for Z4. Photosensitivity investigation demonstrated that Z4 had a higher response than Z3. The rise time of samples Z3 and Z4 were 3.4 s and 3.21 s, respectively, while the decay time for Z3 was 3.2 s and for Z4 was 3.2 s.
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تحضير المستشعرات الضوئية المعتمدة على هياكل نانوية من CdS باستخدام طريقة SILAR دون استخدام الأمونيا كعامل محفز

زينب سلام حسين[1]، حسين عبدالله الشمري[1]

قسم الفيزياء، كلية العلوم، جامعة الكوفة، النجف ـ العراق [1]

الكلمات المفتاحية:

الـــخُـــلاصـــة

(CdS) حُضِرَ في هذا البحث مستشعرات ضوئية تعتمد على أغشية رقيقة من كبريتيد الكادميوم مع وجود الأمونيا دون استخدامها كعامل SILAR وترسيبها على ركائز زجاجية باستخدام طريقة على التوالي، ودُرِسَت الخصائص البصرية Z4و Z3 محفز. سُمِيت العينات المذكورة سابقاً بـ عن وجود طور بلوري (XRD) والمورفولوجية والبنيوية لها. كما كَشَفَت بيانات حيود الأشعة السينية مع قمم تتوافق مع المستويات (111)، (022)، و(131). كما تم قياس حجم CdS وبنية مكعبة لـ على التوالي. Z4و Z3 البلورات للمستوى (111) وكانت 20.506 و54.661 نانومتر للعينتين) حبيبات نانوية متجانسة للعينات المحضرة. FESEMأظهرت صور المجهر الإلكتروني الماسح (باستخدام مطيافية الأشعة فوق البنفسجية والمرئية CdS تم قياس أطياف الامتصاص وفجوة الطاقة لـ و2.35 Z3) تساوي 2.3 إلكترون فولت للعينةE_gفجوة الطاقة ( )، والتي أظهرت أنUV-Vis(للمستشعرات (I-V) وكلاهما يميل نحو الانزياح الأحمر. أظهرت خصائص Z4 إلكترون فولت للعينة استجابة ضعيفة تحت الضوء المرئي، ولكن استجابة أعلى بكثير للضوء فوق Z4و Z3 الضوئية ميكرو 3.7×10^{-7} إلى 4.09×10^{-8}البنفسجي. عند انحياز 5 فولت، زاد التيار الضوئي من . كما ظهرت Z4 ميكرو أمبير للعينة 1.4×10^{-7} إلى 1.8×10^{-8}، بينما زاد منZ3أمبير للعينة . حيث كان زمن الاستجابة 3.4 و3.21 Z3بأنها ذات استجابة أعلى من Z4 حساسية الضوء للعينة Z4 هو 3.2 ثانية وللعينة Z3 ، على التوالي، بينما كان زمن الانحلال للعينةZ4 وZ3ثانية للعينتين .هو 3.2 ثانية

CdS
SILAR
الهياكل النانوية
الأغشية الرقيقة
المستشعرات الضوئية

1. INTRODUCTION

Photodetectors play a fundamental role in different technological fields. The diverse applications of photodetectors include warning systems, communication, fire alarm, etc. have attracted many of research interests[1]. Recently, photodetectors based on CdS gained a great intention due to their important properties[2]. Cadmium sulfide is considered the most important and promising nanomaterial[3]. Due to its electrical conductivity, high sensitivity, and optical transparency; CdS Nanostructure is mostly preferred to be used in various applications such as solar cells, photodetectors, light emitting diodes, sensors, transistors, and photovoltaic [4]. The CdS is an unique Group II-IV semiconductor that acts like an n-type semiconductor[5] and an inorganic compound with zero-dimensional quantum confinement [6]. At room temperature, the CdS band gap is equal to 2.42 eV and its valence electrons can be easily excited to the conduction band if the incident light has a wavelength less than or equal to 495 nm which is in the visible light region[7].

Cadmium sulfide thin films can be grown in a hexagonal (wurtzite) or a cubic structure[8]. During the past years, cadmium sulfide Nanostructure has gained a significant role in different fields like Material science, Physics, Nanotechnology, Medicine, Biology, and other different scientific fields. Various forms of CdS Nanomaterial can be produced, with the most common forms being core-shell Nanoparticles, Nanowires, Nanorods, and quantum dots[9, 10]. Each form has its unique features that can be synthesized by different techniques including (chemical bath deposition, solvothermal, electrochemical deposition, laser ablation, hydrothermal, and SILAR) [11]. The successive ionic layer adsorption and reaction (SILAR) technique was first used in 1985 by Nicolau [12]. It is well known as a costless, eco-friendly, simple, less time-consuming method, and can prepare thin films at low

temperatures on any substrate [13]. The growth rate of CdS thin film in the SILAR technique can be controlled easily through different parameters such as time, pH, concentration of solution, temperature, and number of immersions and layers [14]. The pH is considered to be an important parameter for most CdS thin film preparation, it can affect the reaction kinetics and material's structure[15, 16]. pH solution of CdS in the SILAR technique should be adjusted to ($pH > 7$) by adding Sodium Hydroxide (NaOH) or Ammonium Hydroxide (NH4OH) as a complexing agent[17]. The principle work of the SILAR method is simply based on immersion of the substrates in separate cationic and anionic precursors, followed by rinsing the substrates between every immersion with water [18].

In the present work, CdS thin films were synthesized by the SILAR method without using ammonia or any catalyst to build photodetectors and compared with photodetectors based on CdS that were prepared with ammonia as a catalyst. The samples in this article were labeled as Z3 (without using ammonia) and Z4 (with the presence of ammonia), respectively.

2. Experimental details

2.1 Glass Substrates Cleaning

The glass substrates were cleaned to remove the undesirable materials to obtain accurate results. Firstly, the substrates were rinsed with deionized water. Secondly, the substrates were immersed in an acetone for 3 minutes and then in a beaker contains ethanol for 3 minutes. Lastly, they were rinsed with deionized water for 3 minutes and dried in the oven for 10 minutes under 80 °C.

2.2 Preparation of CdS Samples by SILAR Method

Firstly, to deposit CdS on a sample without using ammonia, a glass substrate was immersed in a beaker contains 0.05M of cadmium acetate with purity ~97% for 30 s so the surface of the glass substrate absorbs (Cd^{+2}) ions and then rinsed with deionized water for 5 s to remove any homogenous precipitation. After that, the glass substrate was immersed in 0.05 M of thiourea with purity ~99% as a source of (S^{-2}) ions for 30 s and also rinsed with deionized water for 5 s. This cycle of CdS deposition was repeated for 130 cycles under fixed temperature at 50 °C. Secondly, for deposing CdS on a sample with the presence of ammonia the exact same process, conditions, and cycles were used but with adding ammonia and adjusting the pH of Cd solution to ~10. At the end, a homogenous CdS thin films deposited on glass substrates were obtained (see **Table 1**).

Table 1. Parameters of CdS thin films prepared by SILAR method.

Parameters	Solution without ammonia (Z3)		Solution with ammonia (Z4)	
	Cadmium acetate	Thiourea	Cadmium acetate	Thiourea
Concentration (M)	0.05	0.05	0.05	0.05
Temperature (°C)	50	50	50	50
Time of immersion (S)	30	30	30	30
Number of cycles	130	130	130	130

2.3 Preparation of photodetectors

Samples Z3 and Z4 were fabricated as photodetectors by clinging electrodes on the edges of the substrates with silver paste. A UV source and a visible light source are used to illuminate the samples (Z3 and Z4) for electrical measurements. The deposited CdS thin films of samples (Z3 and Z4) were characterized using X-ray diffraction (Analytical X'Pert pro), UV-visible spectroscopy (SCINCO Mega-2100), FESEM (Zeiss Supra 55VP), and electrometer (Keithly 2400 device) for electrical properties (I-V).

3. Results and discussion

3.1 Structural Properties

Figure 1(a, b) shows the XRD results of CdS thin films for samples Z3 (prepared without using ammonia) and Z4 (prepared with

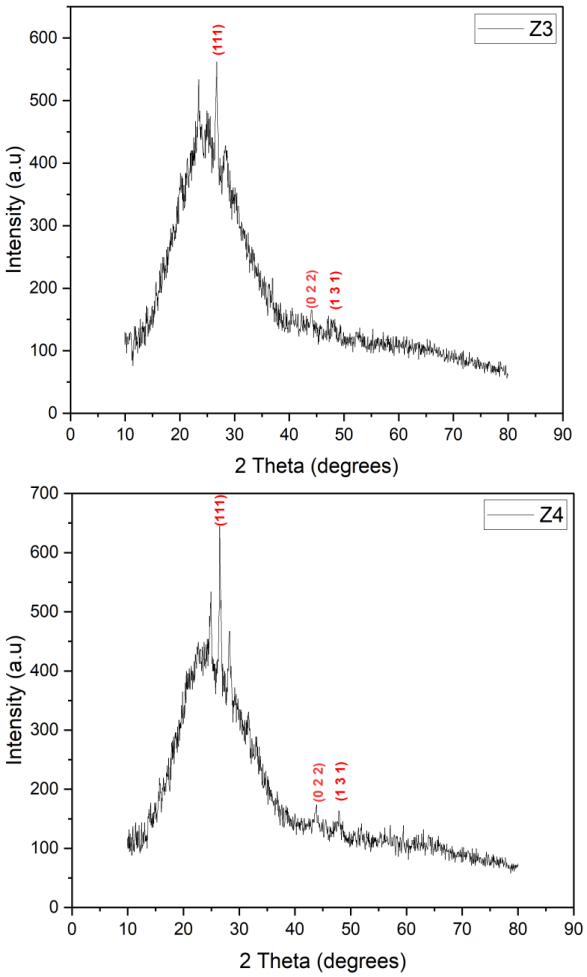

Fig. 1. Shows the XRD profile of CdS thin films for Z3 and Z4 samples.

using ammonia) respectively. The XRD pattern for sample Z3 was observed to be intense peaks located at 26.552°, 44.048°, and 52.173° and for sample Z4, the observed peaks located at 26.514°, 43.985°, and 52.095°. sample Z3 and Z4 are corresponding to planes (111), (022), and (131) respectively. These results confirmed a cubic CdS crystalline phase with small crystal size. The crystal size was measured using Debye-Scherrer equation [19]:

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (1)$$

Where, k is Scherrer constant (0.98), λ is the XRD wavelength ($\lambda = 1.5406$ Å), β is the full width at half maxima (FWHM), and θ is Bragg's angle. The measured crystal size for the main plane (111) was 20.506 nm for sample Z3 and 54.661 nm for sample Z4.

3.2 Morphological properties

The surface morphology of grown CdS thin films was investigated using FESEM at magnification 200 kx. **Figure 2(a, b)** shows that CdS thin films for both samples were homogenous and small nanosized grains with average diameters 61.83 and 62.45 nm of samples Z3 and Z4 samples respectively.

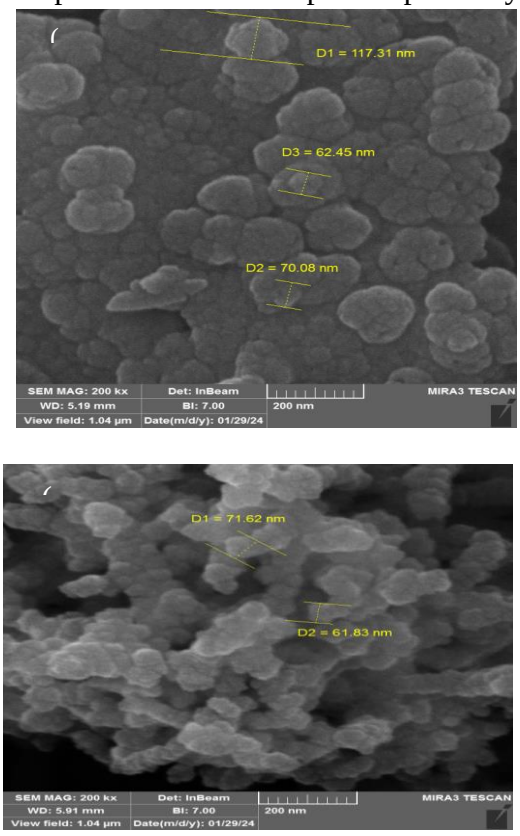

Fig. 2. The morphological properties of CdS investigated by FESEM for (a) Z3 and (b) Z4 respectively.

Fig. 2. The morphological properties of CdS investigated by FESEM for (a) Z3 and (b) Z4 respectively.

3.2 Optical Properties

The absorption spectra of deposited CdS samples were measured at room temperature with wavelengths ranging from 380-800 nm using the UV-visible spectroscopy (see **Fig. 3a**). The energy band gap was calculated using Tauc's formula[20]:

$$\alpha = \frac{A\,(Eg - h\nu)^n}{h\nu} \qquad (2)$$

Figure 3b shows the energy band gap of Z3 sample (CdS prepared without using ammonia) that equals to 2.3eV, and **Fig 3c** shows that sample Z4 (CdS prepared with using ammonia) had an energy band gap equals to 2.35 eV. Both samples have slightly less value than the energy band gap of bulk CdS = 2.4 eV, this means they were tended toward a longer wavelength (redshift) due to changing in size or a difference in the shape of crystal structure.

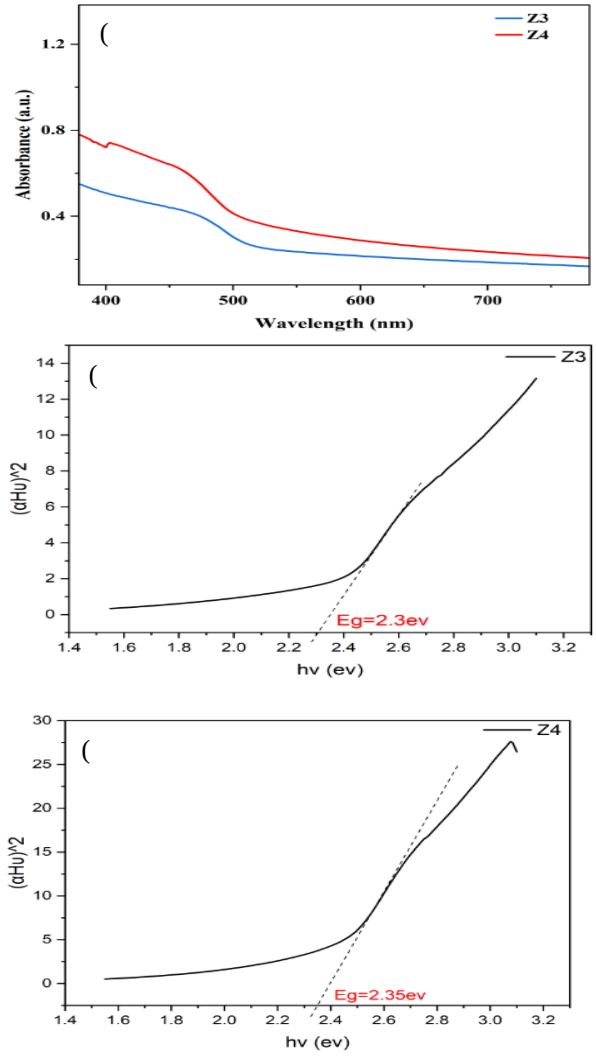

Fig. 3. Illustrate (a) the absorption spectra of CdS samples, (b) and (c) Energy band gap of samples Z3 and Z4, respectively.

Electrical Properties

3.4.1 Current-Voltage (I-V) Characterization

The electrical properties, namely photosensitivity, responsivity, and quantum efficiency of photodetectors for samples Z3 and Z4 were calculated. The CdS photodetectors were studied with voltages (-10, +10) V under dark, visible light, and UV light. **Figure 4a** of sample Z3 showed a weak current when the photodetector under darkness and visible light, while a higher response under UV light with wavelength of 395 nm. **Figure 4b** of sample Z4 showed a weak current response under darkness, a small response under visible light, and a higher response under UV light. The increasing in current under UV light could be resulted due to the photoconductive effect (electron-hole pairs generation) [21]. Because of the current increment, the responsively[22], photosensitivity[23], and quantum efficiency[24] that were calculated by equations (3), (4), and (5) respectively, were also seen to be increased (see **Table 2**).

$$R_\lambda = \frac{I_p}{P_{opt}} \tag{3}$$

$$S = \left(\frac{I_p - I_{dark}}{I_{dark}}\right) \times 100\% \tag{4}$$

$$\eta = R_\lambda \left(\frac{h\upsilon}{e}\right) \tag{5}$$

where, R_λ, I_p, P_{opt}, S, I_{dark}, η, h, υ, and e are the responsivity, output current, optical incident power, photosensitivity, dark current, quantum efficiency, plank's constant, frequency, and electron charge, respectively.

3.4.1 Current – Time (I-T) Characterization

To detect light efficiently, the photo-switching measurements were investigated at room temperature by applying UV light of wavelength 395 nm and intensity of 200 $\mu W/cm^2$ on photodetectors. The ON/OFF condition was measured at 5 V voltage bias and time 10 s/10 s. The photocurrent of Z3 was increased from 4.09×10^{-8} to 3.7×10^{-7} µA (see **Fig. 5a**), while increased from 1.8×10^{-8} to 1.4×10^{-7} µA for Z4 (see **Fig. 5b**) then both are suddenly decreased when UV source is off. The curves pattern shows a repeatable and excellent photoresponse of photodetectors Z3 and Z4 under UV light. Also, the photosensivity through time was measured. In

Figure 5c, the photosensitivity of Z4 is much higher than Z due to the effect of the energy gap calculated in **Fig. 3(b, c)** that may be very close to the wavelength used, which may affects the response further[25]. The rise time and decay time properties of the photodetectors were also measured. The rise time and the decay time of sample Z3 was 3.4 s and 3.2 s respectively. While for sample Z4, the rise time was 3.1 s and the decay time was 3.2 s as shown in **Fig. 6(a, b)**

Parameters	Voltage	Visible Light		UV Light	
		Z3	Z4	Z3	Z4
Responsivity	1	0.012	0.019	0.016	0.090
	2	0.021	0.031	0.217	0.090
	3	0.023	0.033	0.315	0.097
	4	0.027	0.038	0.400	0.102
	5	0.031	0.040	0.426	0.174
	6	0.031	0.042	0.531	0.185
	7	0.036	0.044	0.964	0.246
	8	0.036	0.047	1.120	0.291
	9	0.038	0.095	1.750	0.311
Photosensitivity	1	1.210	4.123	13.729	13.729
	2	1.330	3.568	12.456	12.456
	3	1.589	3.349	10.783	10.783
	4	1.509	2.333	13.548	13.548
	5	1.188	2.404	14.042	14.042
	6	1.068	2.321	17.416	17.416
	7	0.944	1.689	15.737	15.737
	8	0.952	3.602	14.004	14.004
	9	0.952	3.602	88.450	14.004
Quantum efficiency	1	0.027	0.045	0.045	0.246
	2	0.049	0.074	0.596	0.248
	3	0.053	0.077	0.863	0.266
	4	0.064	0.089	1.100	0.280
	5	0.072	0.094	1.170	0.477
	6	0.074	0.098	1.460	0.506
	7	0.084	0.104	2.640	0.674
	8	0.085	0.110	3.080	0.798
	9	0.090	0.224	4.800	0.853

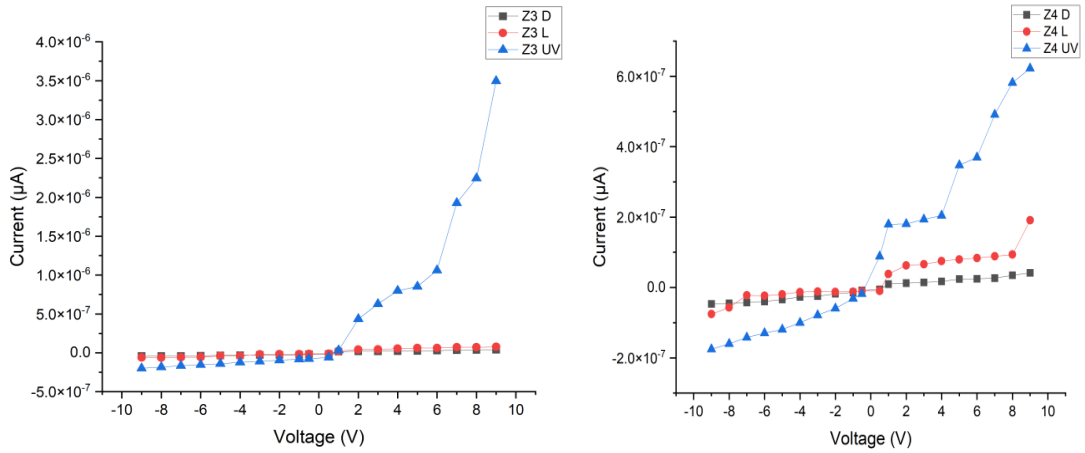

Fig. 4. Shows the currant-voltage properties of sample (a) Z3 and (b) Z4, respectively, under dark, visible light, and UV.

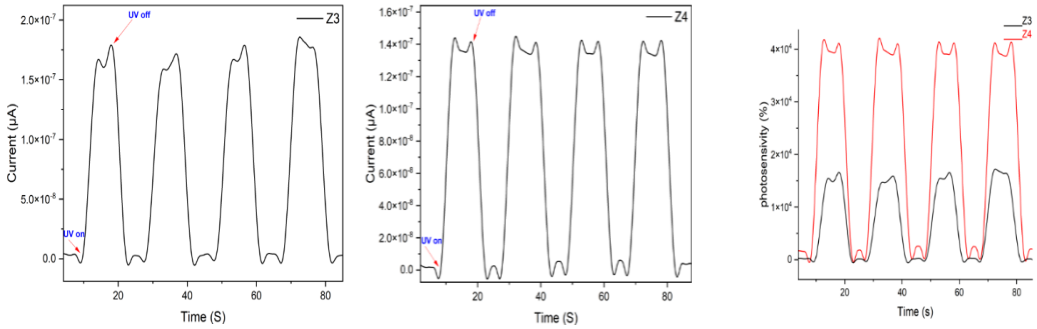

Fig. 5. Presents the currant-time properties of sample (a) Z3 and (b) Z4, respectively. While (c) shows the photosensivity of both samples.

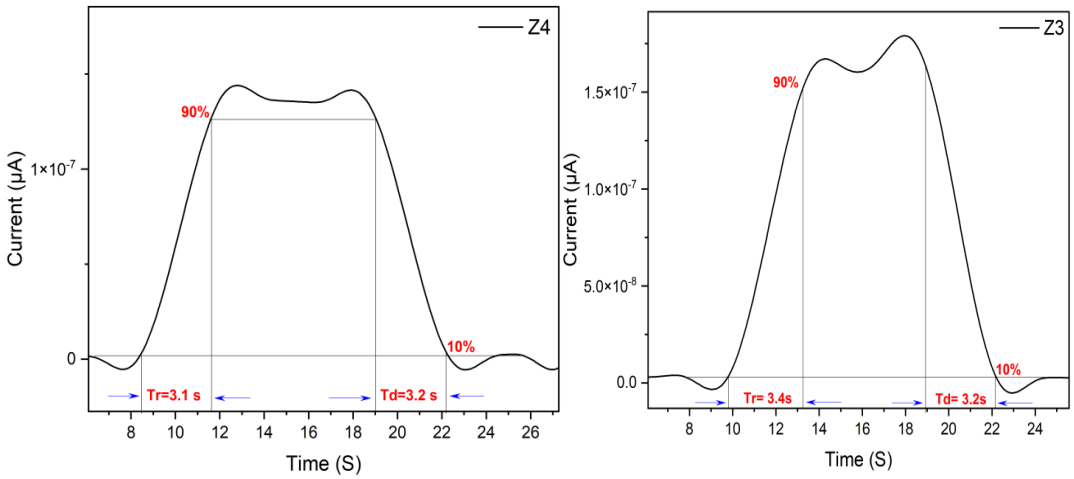

Fig. 6. Presents (a) the rise time and decay time of sample Z3, and (b) the rise time and decay time of sample Z4.

4. CONCLUSION

Cadmium sulfide can be synthesized and deposited on glass substrates using the SILAR method without ammonia and with the presence of ammonia as a complex agent. The structural properties analyzed by XRD

showed a cubic structure of CdS films with a high intensity of the peak at the preferred orientation (111), while the morphological properties investigated by FESEM showed homogenous nanosized grains for both samples Z3 and Z4. The optical properties and the energy band gap were characterized by UV-Vis spectroscopy, the results revealed a redshift for Z3 and Z4. The energy gap values showed that the samples are smaller than typical energy gap of CdS, which may be due to a change in size and the shape of the crystal structure. The electrical properties (I-V) of photodetectors showed a higher responsivity to UV light for both samples, so in this case, responsivity, photosensitivity, and quantum efficiency increased too. The photosensivity of Z4 showed a higher response than Z3. The rise time of Z4 is a bit faster than sample Z3, but both have the same decay time. Also, they showed a good, fast, and repeatable response for both samples. The resulting data showed a very slight difference in synthesizing CdS without ammonia (sample Z3) compared to CdS synthesized with ammonia (Z4), which means CdS can be prepared with good results without using ammonia, and that will lead to less toxicity in the experiment.

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