Journal of Nano- and Electronic Physics
Vol. **16** No 1, 01025(5pp) (2024)

Журнал нано- та електронної фізики
Том **16** № 1, 01025(5cc) (2024)

REGULAR ARTICLE

Effect of Aluminum (Al: 0, 1, 2 and 3 wt.%) Doping on Electrical Properties of ZnO:Al/*p*-Si Heterojunction for Optoelectronic Applications

M.A. Bouacheria[1,*], A. Djelloul[2,†], L. Benharrat[2], M. Adnane[1]

[1] *LMESM, Département de Technologie des Matériaux, Faculté de Physique, Université des Sciences et de la Technologie d'Oran Mohamed Boudiaf USTO-MB, BP 1505, El M'naouer, 31000 Oran Algérie*
[2] *Centre de Recherche en Technologie des Semi-Conducteurs pour l'Energétique 'CRTSE', 02 Bd Frantz Fanon, BP 140, 7 Merveilles, Alger, Algérie*

(Received 05 December 2023; revised manuscript received 18 February 2024; published online 28 February 2024)

In this paper, the electrical properties different diodes were reported. Pure and Al-doped ZnO thin films of different concentrations (Al: 1, 2 and 3 wt.%) were deposited by sol-gel dip-coating onto *p*-Si substrate to form heterojunctions. Zinc acetate dehydrate, Hexahydrate aluminum chloride, ethanol and ethanolamine were used as a starting material, doping, solvent and stabilizer, respectively. The dip-coating process with drying was repeated 6 times to obtain multilayer films. The morphological and electrical properties of the thin films as a function of Al concentration have been investigated using atomic force microscopy (AFM) and current-voltage (*I-V*) measurements at room temperature. AFM images revealed that grain sizes and surface roughness increase with increasing Al concentration. *I-V* characteristics of the diodes exhibited high and low currents under forward and reverse bias, respectively. The ideality factors (n), rectification ratio (RR) and barrier heights (BH) were found to range from 1.97 to 8.34, 0.84 to 5958 and 0.80 to 0.86 eV for different Al doping concentrations, respectively. These findings showed no monotonic behaviour of the calculated parameters with varying Al doping concentrations. The best electrical characteristic was obtained for the sample *n*-ZnO: 2 % Al/p-Si, with an ideality factor of 1.97 eV, reverse-saturation current of $1.69 \cdot 10^{-8}$ A, rectification ratio of 5958 at ± 2 V, and barrier height of 0.85 eV.

Keywords: Al-doped zinc oxide, Silicon, Heterojunction, Sol-gel, Dip-coating, Electrical properties, Optoelectronic applications.

DOI: 10.21272/jnep.16(1).01025

PACS numbers: 61.72.uf, 61.72.uf, 73.40.Kp, 81.15._z, 85.30.De, 85.60._q

1. INTRODUCTION

Zinc oxide (ZnO) is one of the most important oxide transparent conductors (TCO) materials, because of their direct large band gap (E_g = 3.37 eV), exciton band energy (60 meV) at room temperature [1, 2], with a natural conductivity of type (n), besides its electrical conductibility along with its high transmittance in the visible region which make it a suitable material for optoelectronics [3, 4] and solar cells [5, 6]. ZnO thin films have been deposited using many techniques including chemical vapour deposition [7], chemical bath deposition [8], doctor Blade [9], electrochemical deposition [10], pulsed laser deposition [11], magnetron sputtering [12], spray pyrolysis [13-15] and sol-gel process [16-18]. This last is advantageous since it is simple technique, inexpensive and secure, that is also suitable for large area thin films preparation with homogenous doping level [19]. ZnO/*p*-Si heterojunctions are of particular interest, due to large binding energy of ZnO thin films and the fact that silicon has an important place in the microelectronic industry, with advantages such as high quality and the inexpensiveness. Despite such drawbacks, researchers have focused on improving the performance of *n*-ZnO/p-Si heterojunction devices by studying the effect of doping such as (Ag, Al, In, Ni, Cd, Cu, Co, Fe, Sn and Pb etc.) [20-24] due to the vital importance of ZnO for use in photovoltaic (PV) devices with improved performance [25]. In the present work, we have experimentally studied the effects of the Al doping on the *n*-AZO/*p*-Si hetero-junctions using current-voltage (*I-V*) measurements at room temperature.

2. EXPERIMENTAL DETAILS

2.1 Synthesis of the AZO/*p*-Si Heterojunction

Pure and Al-ZnO thin films were successfully deposited on *p*-type Si (100) substrates (resistivity in the range 1–20 Ω·cm and thickness of 350 μm) using the sol-gel technique by Dip-coating method under atmospheric conditions. For the pure ZnO sample, the starting solution is a mixture of zinc acetate dehydrate

* Correspondence e-mail: mohammedamine.bouacheria@univ-usto.dz
† djelloulcrtse@gmail.com

(ZAD) $Zn(CH_3COO)_2{\cdot}2H_2O$, dissolved in ethanol ($C_2H_6O$). Besides, we have used aluminum chloride hexahydrate ($AlCl_3.6H_2O$) as aluminum precursor material to prepare three other 25 mL solutions of 1 %, 2% and 3 % aluminum to zinc molar ratio. The dip-coating process with drying was repeated 6 times to obtain multilayer films. Before performing the deposition process, p-type Si (Boron doped) substrates were initially cleaned with RCA (cleaning procedure) to remove the organic residues and metal ions. For current-voltage (*I-V*) measurements, silver (Ag) eutectic was used to make electrical contacts (ohmic contact) on the top of AZO films and the back side of the *p*-Si substrates. The active area of the devices is about 1×1 cm^2. The ZnO: *x* Al ($x = 0$, 1, 2 and 3 at. %)/*p*-Si thin films deposition process is schematically summarized in Fig. 1.

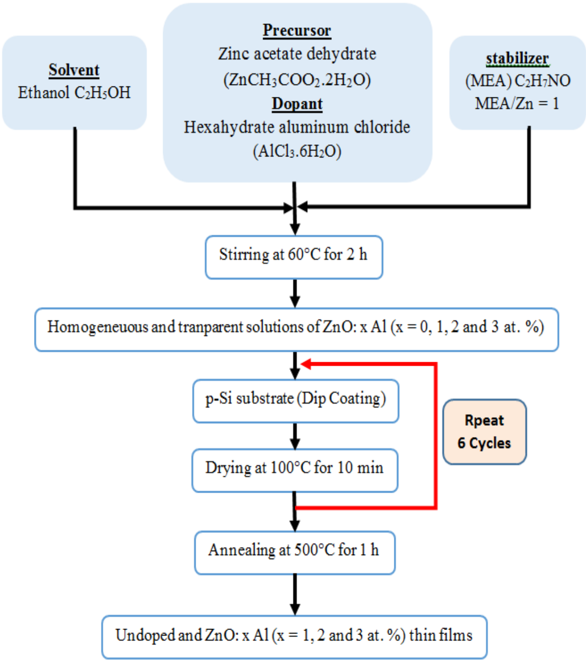

Fig. 1 – A schematic view of sol-gel dip coating process of Undoped and ZnO: *x* Al ($x = 1$, 2 and 3 at. %) thin films

2.2 Characterizations of the AZO/p-Si Heterojunction

The film surface morphology was analyzed by Atomic Force Microscope (AFM). The current-voltage (*I-V*) characteristics were analyzed to examine the heterojunction properties with Keithley 2400 source meter under dark and illumination conditions. All measurements and spectra were taken at room temperature.

3. RESULTS AND DISCUSSION

3.1 AFM Analysis

Atomic force microscopy (AFM) is an effective technique used to determine the topography, surface morphology and roughness of films.

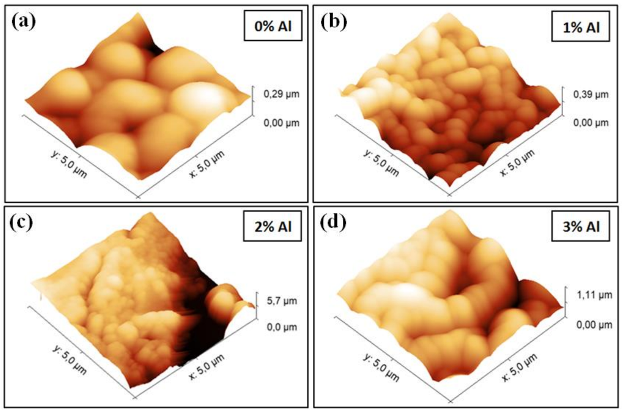

Fig. 2 – The 3D AFM images of: a) undoped ZnO, b) ZnO: 1% Al, c) ZnO: 2% Al and d) ZnO: 3% Al thin films

Fig. 2 shows the three-dimensional (3D) surface morphology of ZnO: *x* Al ($x = 0$, 1, 2 and 3 at. %) thin films deposited by sol-gel dip-coating onto *p*-Si substrate. The films are dense and continuous; the surface is well covered with a relatively large grains and pinholes free. The average height of the roughness profile (R_a) and the mean square deviation of the roughness profile (R_{RMS}) of the surface were determined using Gwyddion-SPM (scanning probe microscopy) data visualization and analysis on a surface of (5×5) µm^2. The morphological parameters (R_{RMS} and R_a) of the films are gathered in Table 1.

Table 1 – Morphological parameters of Undoped and ZnO: *x* Al ($x = 1$, 2 and 3 at. %) thin films

Samples	R_a (nm)	R_{RMS} (nm)
Undopped ZnO	1.07	1.38
ZnO-Al 1 % at.	2.66	3.45
ZnO-Al 2 % at.	34.57	44.86
ZnO-Al 3 % at.	5.17	6.92

R_{RMS} mean deviation of roughness profile, R_a Average height of the roughness profile.

Table 1 represent the values of AFM parameters. For all the films, the 3D images show the presence of well-developed grains. The R_{RMS} values are 1.38 nm (Undoped ZnO), 3.45 nm (film doped at 1 %), 44.86 nm (film doped at 2 %) and 6.92 nm (film doped at 3 %), which confirms the enhancement of the roughness of the films. As the doping concentration increases, the R_a of the films also increases from 1.07 nm (Undoped ZnO) to 34.57 nm (film doped at 2 %) and decreases to 5.17 nm (film doped at 3 %) with Al-doping.

3.2 Electrical Properties

Fig. 3a and b show the linear and semilog *I-V* characteristics under dark conditions of *n*-ZnO:Al/*p*-Si heterojunctions at different Al concentrations, respectively. All these heterojunctions show a recovery of the characteristics with the increase in the doping rate. An increase in direct current with doping is also observed from these curves. It is clearly seen that the current increases nonlinearly for the applied voltages. This nonlinear behavior might be due to nonuniform distribution of doping atoms and the existence of defects or series resistance (R_s)

interface states [26, 27]. The results suggest that the film doped with 2 % Al proved to be better, allowing to obtain a diode with a rectifying character of better quality and a low reverse current. Low threshold potential value diodes are very important for different applications including photodiodes and light emitting diodes (LEDs) due to their low power consumptions.

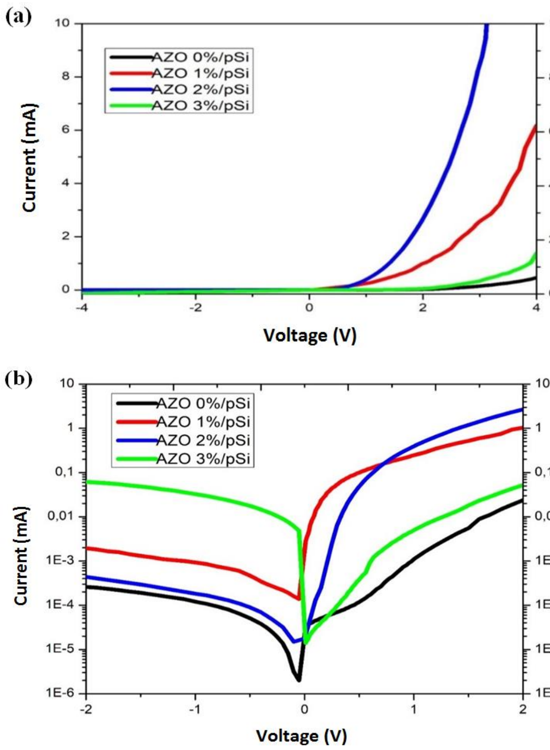

Fig. 3 – The measured current-voltage characteristics of *n*-ZnO:Al/*p*-Si heterojunctions at different Al concentrations, in the dark: a) linear *I-V*, and b) semilog *I-V*

The electrical parameters of *n*-ZnO:Al/*p*-Si heterojunctions at different Al concentrations such as: the rectification factor (*RR*), the ideality factor (*n*), the saturation current (I_S) and the potential barrier (Φ_b) are given by following equations [28]:

$$I = I_S \exp\left(\frac{qV}{nk_BT} - 1\right) \qquad (1)$$

where *q, V, k, T* and *n* denote charge of electron, applied bias voltage, Boltzmann's constant, temperature (300 K) and ideality factor, respectively. I_S is the reverse saturation current expressed as [29],

$$I_s = AA^*T^2 exp\left(-\frac{q\phi_b}{k_BT}\right) \qquad (2)$$

where *A* is the contact area of a diode, *A** is the theoretical Richardson's constant (32 A·cm^2/K^2). By using Eq. 2, the ideality factor n can be can be written as [30]

$$n = \frac{q}{kT} ln\left(\frac{I_s}{AA^*T^2}\right) \qquad (3)$$

Also, if Eq. (3) is reorganized according to the barrier height, it can be written by [31]

$$\Phi_b = \frac{kT}{q}\left(\frac{dV}{d(\ln I)}\right) \qquad (4)$$

Table 2 – Electrical parameters of *n*-ZnO:Al/*p*-Si heterojunctions at different Al concentrations

Al-doping (%)	*RR* = *I*(+ 2*v*)/ *I*(– 2*v*)	*n*	I_S (A)	Φ_b (eV)
0	91.92	8.34	$1.05 \cdot 10^{-8}$	0.86
1	527.17	3.82	$1.01 \cdot 10^{-7}$	0.80
2	5958	1.97	$1.69 \cdot 10^{-8}$	0.85
2	0.84	6.27	$1.57 \cdot 10^{-8}$	0.85

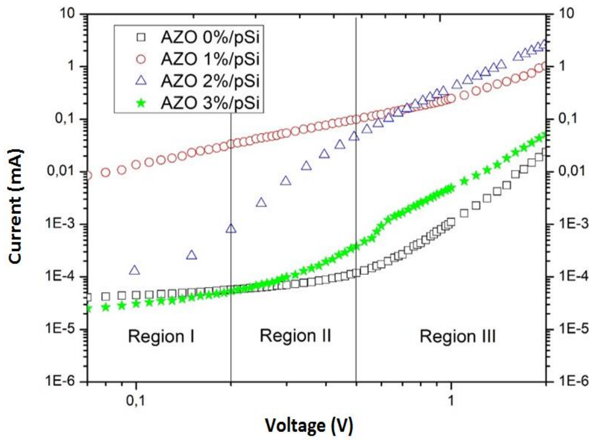

Fig. 4 – The log *I-V* characteristics of ZnO:Al/*p*-Si heterojunction diode at different Al concentrations, in the dark

Table 2 shows the calculated values of electrical parameters of *n*-ZnO:Al/*p*-Si heterojunctions. *I-V* characteristics of the diodes exhibited high and low currents under forward and reverse bias, respectively. The ideality factors (*n*), rectification ratio (*RR*) and barrier heights (*BH*) were found to range from 1.97 to 8.34, 0.84 to 5958 and 0.80 to 0.86 eV for different Al doping concentrations, respectively. These findings showed no monotonic behaviour of the calculated parameters with varying Al doping concentrations. The best electrical characteristic was obtained for the sample *n*-ZnO: 2 % Al/*p*-Si, with an ideality factor of 1.97 eV, reverse-saturation current of $1.69 \cdot 10^{-8}$ A, rectification ratio of 5958 at. ± 2 V, and barrier height of 0.85 eV.

Fig. 4 shows the logarithmic *I-V* characteristics of ZnO:Al/*p*-Si heterojunctions at different Al concentrations, in the dark. We note that there are three different regions depending on the junction voltage value:

– The first region ($0 < V < 0.2$): This is the low current region controlled by the space charge limited current (SCLC) mechanism [32].

– The second region ($0.2 < V < 0.5$): has an exponential shape for $V > 3\,kT/q$, the logarithmic plot allows us to deduce the ideality coefficient *n* and the saturation current I_S.

- The third region ($0.5 < V < 2$): highlights the effect of high bias voltages; the characteristics follow a power law ($I \sim V^L$).

4. CONCLUSIONS

In this study, the electrical properties of different diodes were reported. Pure and Al-doped ZnO thin films of different concentrations (Al: 1, 2 and 3 wt. %) were deposited by sol-gel dip-coating onto p-Si substrate to form heterojunctions. The morphological and electrical properties of the thin films as a function of Al concentration have been investigated using AFM and

I-V measurements at room temperature. AFM images revealed that grain sizes and surface roughness increase with increasing Al concentration. The RMS roughness of the films are found to be 1.38 nm, 3.45 nm, 44.86 nm and 6.92 nm for undoped ZnO, films doped at 1 %, 2 % and 3 %, respectively. This implies that the films have a smooth surface. *I-V* characteristics of the diodes exhibited high and low currents under forward and reverse bias, respectively. The best electrical characteristic was obtained for the sample *n*-ZnO: 2% Al/*p*-Si, with an ideality factor of 1.97 eV, reverse-saturation current of $1.69 \cdot 10^{-8}$ A, rectification ratio of 5958 at. ± 2 V, and barrier height of 0.85 eV.

AKNOWLEDGEMENTS

The authors would like to thank the General Directorate for Scientific Research and Technological Development (DGRST).

REFERENCES

1. P. Sreedev, V. Rakhesh, N.S. Roshima, *IOP Conf. Series: Mater. Sci. Eng.* **377**, 012086 (2018).
2. D. Pellegrino, G. Franzò, V. Strano, S. Mirabella, E. Bruno, *Chemosensors* **7**, 18 (2019).
3. A. Zaier, F. Oum El az, F. Lakfif, A. Kabir, S. Boudjadar, M.S. Aida, *Mater. Sci. Semicond. Proc.* **12**, 207 (2009).
4. R. Koutavarapu, R.K.N.R. Manepalli, B.T.P. Madhav, M.C. Rao, J. Shim, *J. Mater. Sci.: Mater. Electron.* **32**, 11264 (2021).
5. C. Tong, J.H. Yun, Y.J. Chen, et al., *ACS Appl. Mater. Interfaces* **8** No 6, 3985 (2016).
6. M. Melouki, H.F. Mehnane, A. Djelloul, Y. Larbah, M. Adnane, *J. Nano- Electron. Phys.* **13** No 4, 04004 (2021).
7. M. Purica, E. Budianu, E. Rusu, M. Danila, R. Gavrila, *Thin Solid Films* **485**, 403 (2002).
8. D. Pellegrino, G. Franzò, V. Strano, S. Mirabella, E. Bruno, *Chemosensors* **7**, 18 (2019).
9. N. Houri, A. Djelloul, M. Adnane, *J. Nano- Electron. Phys.* **12** No 6, 06004 (2020).
10. M. Harati, D. Love, W.M. Lau, Z. Ding, *Mater. Lett.* **89**, 339 (2012).
11. R.K. Jamal, M.A. Hameed, K.A. Adem, *Mater. Lett.* **132**, 31 (2014).
12. B. Sarma, D. Barman, B.K. Sarma, *Appl. Surf. Sci.* **479**, 786 (2019).
13. V.G. Nair, R. Jayakrishnan, J. John, J.A. Salam, A.M. Anand, A. Raj, *Mater. Chem. Phys.* **247** No 1, 122849 (2020).
14. A. Djelloul, Y. Larbah, M. Adnane, B. Labdelli, M.I. Ziane, A. Manseri, A. Messaoud, *J. Nano- Electron. Phys.* **10** No 2, 02036 (2018).
15. S.K. Swami, N. Chaturvedi, A. Kumar, V. Kumar, A. Garg, V. Dutta, *Sol. Energy* **231**, 458 (2022).
16. M. Ayachi, F. Ayad, A. Djelloul, L. Benharrat, S. Anas, *Semiconductors* **55** No 5, 566 (2021).
17. C. Zegadi, A. Abderrahmane, A. Djelloul, S. Hamzaoui, M. Adnane, D. Chaumont, K. Abdelkebir, *Int. Rev. Phys.* **9** (2015).
18. M.A. Bouacheria, A. Djelloul, M. Adnane, Y. Larbah, L. Benharrat, *J. Inorg. Organometal. Polym. Mater.* **32**, 2737 (2022).
19. S. Sali, M. Boumaour, S. Kermadi, A. Keffous, M. Kechouane, *Superlattice. Microst.* **52**, 438 (2012).
20. F. Yang, J. Song, X. Chen, X. Lu, J. Li, Q. Xue, B. Han, X. Meng, J. Li, Y. Wang, *Sol. Energy* **228**, 168 (2021).
21. J. Mayandi, R.K. Madathil, C. Abinaya, K. Bethke, V. Venkatachalapathy, K. Rademann, T. Norby, T.G. Finstad, *Mater. Lett.* **288**, 129352 (2021).
22. M. Nie, H. Sun, H.L. Cai, Z.H. Xue, C. Yang, Q. Li, L.Z. Qin, M.Y. Wu, *Mater. Lett.* **271**, 127785 (2020).
23. P. Dhamodharan, C. Manoharan, M. Bououdina, R. Venkadachalapathy, S. Ramalingam, *Sol Energy* **141**, 127 (2017).
24. J.N. Ma, W. Zhang, J.Y. Lin, Y. Sun, J.G. Ma, H.Y. Xu, Y.C. Liu, G.C. Yang, *J. Alloy. Compd.* **819**, 153012 (2020).
25. Z.L. Wang, *J. Phys. Condens. Matter* **16**, R829 (2004).
26. S.K. Singh, P. Hazra, *Superlattice. Microst.* **128**, 48 (2019).
27. L. Agarwal, S. Tripathi, *Semicond. Sci. Technol.* **35** No 6, 065001 (2020).
28. S.M. Sze, K.K. Ng, *Physics of Semiconductor Devices* (Wiley, New York, 2006).
29. S. Singh, P. Chakrabarti, *Superlattice. Microst.* **64**, 283 (2013).
30. I. Ay, H. Tolunay, *Solid State Electron.* **51**, 381 (2007).
31. K. Ozel, A. Atilgan, N.E. Koksal, A. Yildiz, *J. Alloy. Compds.* **849**, 156628 (2020).
32. M. Dutta, D. Basak, *Appl. Phys. Lett.* **92**, 212112 (2008).

Вплив домішок алюмінія (Al: 0, 1, 2 і 3 мас.%) на електричні властивості гетеропереходу ZnO:Al/*p*-Si для застосувань в оптоелектроніці

M.A. Bouacheria[1], A. Djelloul[2], L. Benharrat[2], M. Adnane[1]

[1] *LMESM, Département de Technologie des Matériaux, Faculté de Physique, Université des Sciences et de la Technologie d'Oran Mohamed Boudiaf USTO-MB, BP 1505, El M'naouer, 31000 Oran Algérie*

[2] *Centre de Recherche en Technologie des Semi-Conducteurs pour l'Energétique 'CRTSE', 02 Bd Frantz Fanon, BP 140, 7 Merveilles, Alger, Algérie*

У цій статті розглядаються електричні властивості різних типів діодів. Тонкі плівки ZnO чистого та легованого Al різної концентрації (Al: 1, 2 та 3 мас. %) були нанесені золь-гелевим методом на підкладку *p*-Si для формування гетеропереходів. Цинк ацетат дегідрат, гексагідрат алюмінію хлорид, етанол і етаноламін використовували як вихідний матеріал, домішка, розчинник і стабілізатор відповідно. Процес нанесення покриття зануренням із сушінням повторювали 6 разів для отримання багатошарових плівок. Морфологічні та електричні властивості тонких плівок як функцію концентрації Al були досліджені за допомогою атомно-силової мікроскопії (АСМ) і вимірювань струму-напруги (*I-V*) при кімнатній температурі. АСМ-зображення показали, що розміри зерен і шорсткість поверхні збільшуються зі збільшенням концентрації Al. ВАХ діодів показали високі та низькі струми при прямому та зворотному зміщенні відповідно. Коефіцієнт ідеальності (*n*), коефіцієнт випрямлення (RR) і висота бар'єру (BH) коливаються в діапазоні від 1,97 до 8,34, 0,84 до 5958 і 0,80 до 0,86 еВ для різних концентрацій легування Al відповідно. Ці дослідження показали відсутність монотонної поведінки розрахованих параметрів при зміні концентрацій домішок Al. Найкращі електричні характеристики отримано для зразка *n*-ZnO: 2 % Al/*p*-Si, з коефіцієнтом ідеальності 1,97 еВ, зворотним струмом насичення $1{,}69 \cdot 10^{-8}$ A, коефіцієнтом випрямлення 5958 при ± 2 Вт, а висота бар'єру становила 0,85 еВ.

Ключові слова: Al-легований оксид цинком, Кремній, Гетероперехід, Золь-гель, Покриття зануренням, Електричні властивості, Оптоелектронні застосування.