

Si/ZnO NANO STRUCTURED HETEROJUNCTIONS BY APCVD METHOD

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Abstract: In this paper, polycrystalline pure zinc oxide nano structured thin films were deposited on two kinds of single crystal and polycrystalline of p and n type Si in three different substrate temperatures of 300, 400 and 500 °C by low cost APCVD method. Structural, electrical and optical properties of these thin films were characterized by X ray diffraction, two point probe method and UV visible spectrophotometer respectively. IV measurements of these heterojunctions showed that turn on voltage and series resistance will increase with increasing substrate temperature in polycrystalline Si, while in single crystal Si, turn on voltage will decrease. Although they are acceptable diodes, their efficiency as a heterojunction solar cell are so low.

Keywords: Heterojunction, Thin film silicon solar cell, Air pressure CVD, p-type Si, Diodes, ZnO

1. INTRODUCTION

ZnO is a material with a wide range of applications. Although it is used in different composites for corrosion resistant increasing [1] and improvement of mechanical properties [2], due to wide band gap, high transparency and good conductivity [3-11], it is a suitable electrode in solar cell and a proper partner in p-n junctions. Also In 2001, n-ZnO/p-Si heterojunction photodiodes were fabricated by sputter deposition of n-ZnO films on p-Si substrates by Kim et al. [12]. They showed that high levels of photocurrent under reverse bias conditions are achievable when the stoichiometry of n-ZnO films is improved by optimizing the process conditions, such as the substrate temperature and Ar/O₂ ratio. It was concluded that crystalline quality alone is not sufficient condition for the best photodiode performance. In 2002, a similar study was done by Lee et al [13] in which n-ZnO/p-Si heterojunction photodiodes were fabricated by sputter deposition of n-ZnO films on p-Si substrates again. It was concluded that for a photodiode the quality of the diode junction is as important as that of the n-ZnO film deposited on p-Si. In 2006, Sun et al. reported on the fabrication and electroluminescence of an n-ZnO nano rod/p-Si heterojunction [14] in which ZnO

nano rods were grown on p-type Si substrates employing an easy low-temperature aqueous solution method. In the same year, antimony doping was used to realize p-type ZnO films on n-Si (100) substrates by molecular beam epitaxy [15]. IV curves showed rectifying behavior similar to a p-type Schottky diode with a turn on voltage around 2.4 V, which was consistent with the Schottky barrier of about 2.2 V obtained from CV characterization. In 2007, electrical performances of the heterojunction of n-ZnO nano wires with p-Si substrate at the nanometer scale were characterized using an ultrahigh vacuum conducting atomic force microscopy [16]. The abnormally high diode ideality factor 2 was explained by modeling of a ZnO/Si p-n junction as a series of diodes, the actual ZnO/Si junction diode and two Schottky diodes at the metal/ZnO and metal/Si junctions. The tunneling across p-n junction would also play a role in the externally measured high ideality factor. In 2008, heterojunction diodes of n-type ZnO/p-type silicon (100) were fabricated by pulsed laser deposition of ZnO films on p-Si substrates in oxygen ambient at different pressures [17]. The turn on voltage of the heterojunctions was found to depend on the ambient oxygen pressure during the growth of the ZnO films. In 2009, a series of n-ZnO/p-Si thin films heterojunctions were

fabricated by a low cost sol-gel technique for different ZnO film thicknesses and the dark as well as photo current voltage (IV) characteristics were investigated in details by Mridha et al. [18]. In 2010, a series of n-ZnO/n-SiC/p-Si and n-ZnO/p-Si heterojunctions were prepared by DC sputtering [19]. It was found that the photoelectric conversion efficiency of the n-ZnO/n-SiC/p-Si heterojunction is about four times higher than that of the n-ZnO/p-Si heterojunction. In 2011, the temperature dependent heterojunction behavior of n-type zinc oxide (ZnO) nano wires/p-Si diodes grown by thermal evaporation was explored [20]. The turn on and breakdown voltage of the device slightly decreased with an increase of temperature whereas the saturation current of the device increased. The effective potential barrier height was found increasing with the increase in temperature.

Based on review of above articles it is clear that these kinds of junctions have various applications. We decided to investigate effect of deposition temperature and kind of Si wafer on ZnO/Si heterojunctions by low cost APCVD method which has been used rarely in the last decade. First we explored electrical and structural properties of ZnO layers deposited on Si wafers. Then we examined its IV characteristics as a diode and then we investigated these heterojunctions as solar cell.

2. EXPERIMENTAL TECHNIQUES

2. 1. Sample Preparation

The fabrication of these p-n junctions has been described elsewhere [21]. ZnO films were deposited onto silicon substrates in an open tube system by the oxidation of $C_4H_6O_4Zn.2H_2O$ as described in our previous work about tin oxide layers [22]. It comprises of a horizontal tubular furnace which has a diameter of 80 mm and about 100 cm long. Oxygen with a flow rate of 200 sccm (Standard centimeter cubic per minute) was injected through the $C_4H_6O_4Zn.2H_2O$ powder maintained inside the quartz furnace near the substrate.

Before deposition, the silicon substrates were

degreased about 2 minutes in solution of hydro fluoric acid and deionised water then rinsed in deionised water. These silicones are cleaned ultrasonically in acetone and rinsed again in deionised water. The cleaned Si substrates are introduced in a tubular furnace. The thickness of two types of Si were 650 and 750 μm , their resistivity were $3.51 \times 10^2 \Omega.cm$, $4.95 \times 10^2 \Omega.cm$, their mobility were 207, 822 (cm^2/Vs) and their carrier concentration were 2.44×10^{14} , $4.63 \times 10^{12} (cm^{-3})$ for polycrystalline and single crystal Si respectively. Polycrystalline Si is p-type with B doped, while single crystal Si is n type with P doped. Single crystal silicon's orientation is (400). Our samples were grown at oxygen flow rate of 200 sccm in substrate temperature of 300, 400 and 500 $^{\circ}C$ during 1 hour. The mass of $C_4H_6O_4Zn.2H_2O$ powder was kept constant during all experiments. We have deposited half part of Si substrate with zinc oxide layer. Total area of all kinds of Si was 2 cm^2 . So we have deposited 1 cm^2 of Si with zinc oxide layer. To prevent deposition of zinc oxide on the other part we used a mask. In order to obtain efficiency of these heterojunctions as a cell, we deposited Au contacts on both sides of zinc oxide and Si by DC sputtering method and with using a mask, only 1 cm^2 of cells were illuminated under the radiation of 100 mw/cm^2 .

2. 2. Sample Characterization

First we explored electrical and structural properties of ZnO layers deposited on Si wafers by two point probe, Hall measurement (RH 2010-PhysTech system) and X ray diffraction with $Cu-K\alpha$ radiation (Philips-pw-1830). A UV visible spectrophotometer (Cary 100 Scan Varian) was employed for obtaining transmittance spectra for ZnO layers deposited on glass to be sure about ZnO layers' transmittance. Spectrophotometric transmittance graph of the film was used for the thickness calculation by Swanepoel method [23]. We examined its IV characteristics in dark as a diode by IV measurement. Finally we investigated these heterojunctions as solar cell under 100 mw/cm^2 illumination.

3. RESULTS AND DISCUSSION

3. 1. Electrical Properties

Table 1 shows the values of sheet resistance and thickness of the samples for various substrate temperatures and types of the substrate. Results related to glass substrate have been presented for more comparing.

It is clear with increasing temperature, sheet resistance of the samples increases for zinc oxide films grown on single crystal, polycrystalline silicon and glass. We can conclude that with increasing substrate temperature, the number of oxygen atoms adsorbed on thin films increases and as a result, lattice deficiency decreases. In fact with increasing substrate temperature, layers approach to stoichiometry [24]. Also, resistance of thin films deposited on poly crystalline Si is less than samples deposited on single crystal Si and less than glass. If we consider to XRD results, we can conclude that the effect of Si substrate in the sample grown on polycrystalline Si at all temperatures is less than single crystal Si. So the resistivity of samples grown on poly crystalline Si is better than single crystal Si.

Films deposited on Si substrates have less resistance compared to glass substrate which is due to better conductivity of Si compared to glass.

Thickness of the films varies between 480-530 nm.

3. 2. Structural and Optical Properties

Fig. 1 shows typical XRD patterns of the ZnO layers grown on single and polycrystalline Si at three substrate temperatures of 300, 400 and 500 °C. It is worth noticing this fact that samples which have been grown at all substrate temperatures have polycrystalline structure. With increasing the temperature in samples grown on single crystal Si, preferred orientation changes from (100) to (002), while in samples deposited on poly crystalline Si, preferred orientation remains (100).

As expected in both cases, with increasing temperature, the intensity of the preferred peak increases due to improving crystallinity. Effect of Si substrate is clear with its peak at about 70°C for single crystal Si and at 28 °C for polycrystalline Si.

Optical transparency of the above mentioned films is shown in Fig. 2. The transmittance in the visible spectrum is high for different substrate temperature which is acceptable for solar cell applications. As it is clear, transparency doesn't have distinct change due to low carrier concentration of the samples. As a result, absorption of free carrier concentration is low and transparency is high. These results are in accordance with Fay et al. report [25].

3. 3. IV Characteristics of p-n Junctions

Fig. 3 represents the IV characteristics of the poly crystalline Si/ ZnO heterojunction at

Table1. The values of sheet resistance, carrier concentration and thickness of the samples for various substrate temperatures and types of the substrate

Temperature (°C)	Carrier Concentration (cm ⁻³)	Thickness (nm)	Sheet resistance		
			Poly crystalline Si/ZnO	Single crystal Si/ZnO	Glass substrate
300	1.57×10^{16}	508	10.65 kΩ/□	346 kΩ/□	6.1 MΩ/□
400	5.98×10^{15}	526	25.1 kΩ/□	515kΩ/□	39.9 MΩ/□
500	4.74×10^{14}	487	77 kΩ/□	-	27.1 MΩ/□

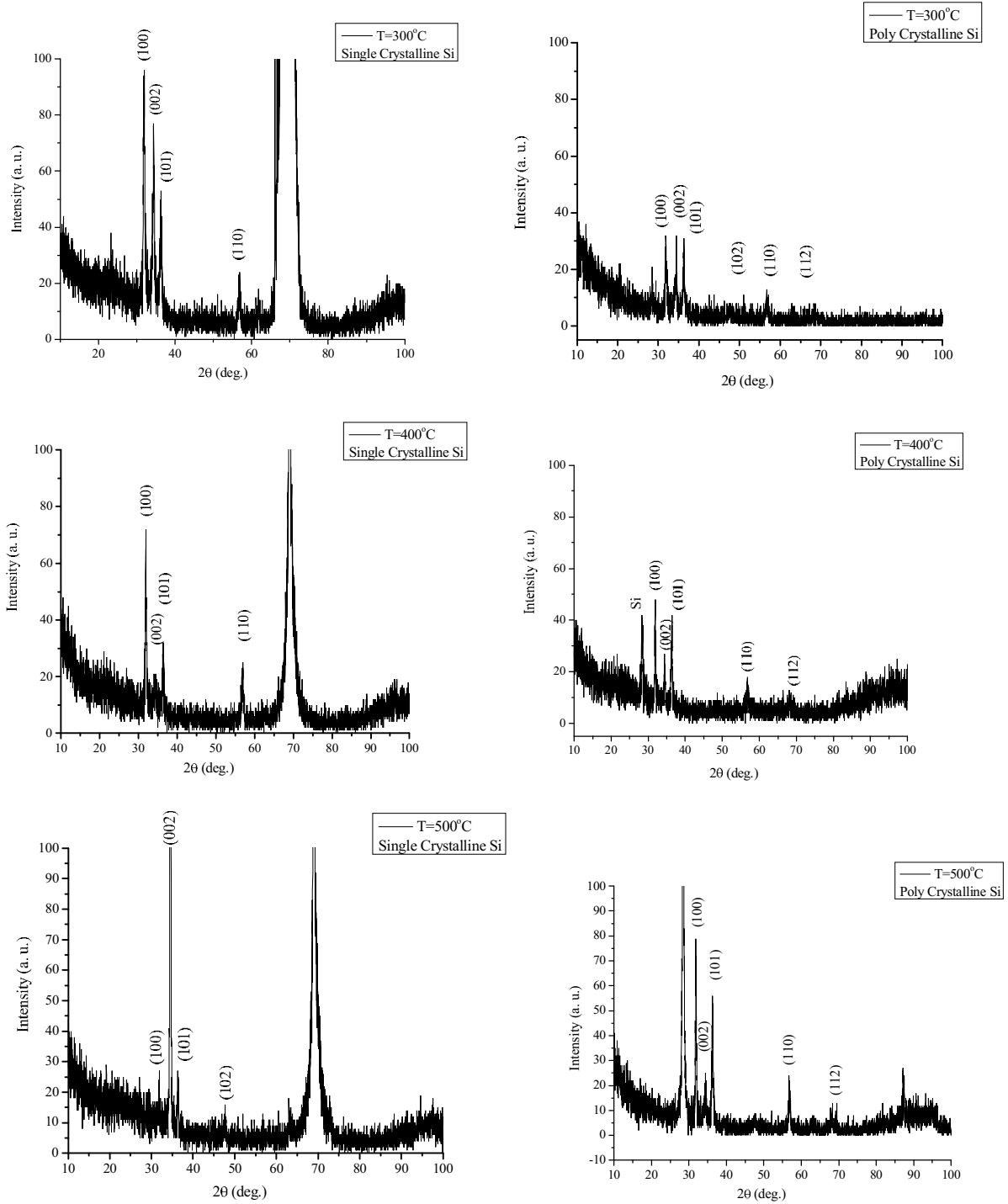


Fig. 1. XRD patterns of the ZnO layers grown on single and polycrystalline Si at three substrate temperatures of 300, 400 and 500 °C

different substrate temperature.

From Fig. 3, weak rectifying curves are observed for the samples grown at substrate temperatures of 400 and 500 °C and a clear

rectifying curve is observed for the sample grown at substrate temperature of 300 °C. But in all samples, the rectification has an inverse trend of a p-n junction. This suggests that the diode is a p-

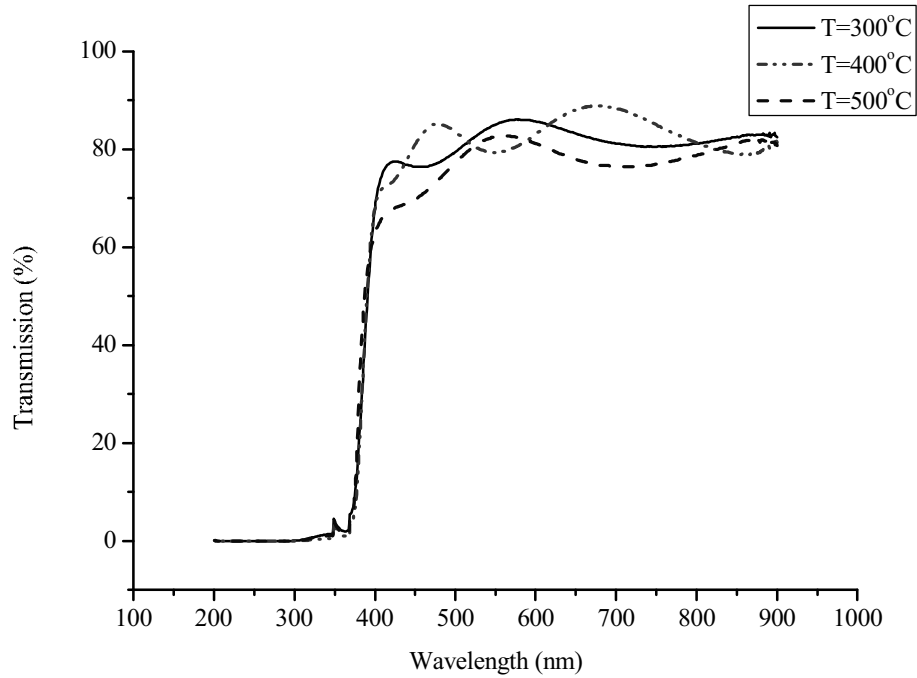


Fig. 2. Optical transparency of ZnO thin films grown on glass substrate at three substrate temperatures of 300, 400 and 500°C

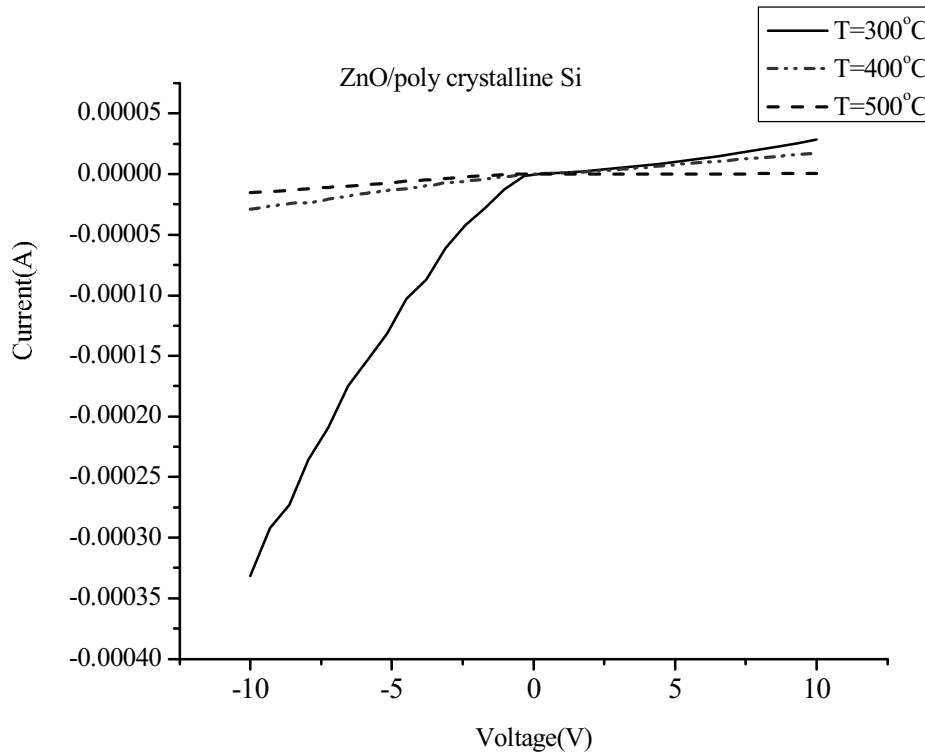


Fig. 3. IV characteristics of the poly crystalline Si/ ZnO heterojunction at different substrate temperature.

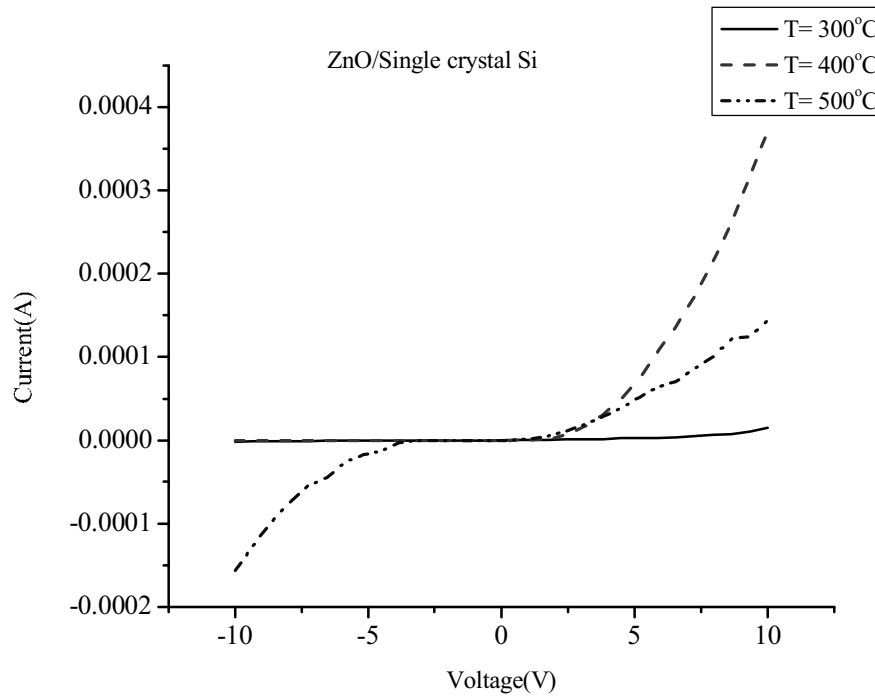


Fig. 4. IV characteristics of the single crystal Si/ ZnO heterojunction at different substrate temperature.

type Schottky diode [15]. The turn on voltage of the diode is around -2.4 V for the diode grown at 500°C which decreases to about -1 V for the diode grown at 300°C as seen from the IV curves. We can conclude based on Ajimsha's report [17], when the substrate temperature during the deposition of ZnO is increased, the carrier concentration decreases due to improving stoichiometry and hence the Fermi level keeps out the bottom of the conduction band. This means that, upon increase of the substrate temperature, the Fermi level may even go far away from the conduction band, resulting in the difficult flow of electrons from the ZnO side to the p-Si side. Hence the voltage required for considerable current increases and thereby the turn on voltage increases. Also from the slope of IV curves, as expected, series resistance of the diodes are increasing with substrate temperature. So due to series resistance a part of the applied voltage is effectively wasted and hence a larger applied voltage is necessary to achieve the same level of current compared to the ideal value. Hence the turn on voltage will increase with the

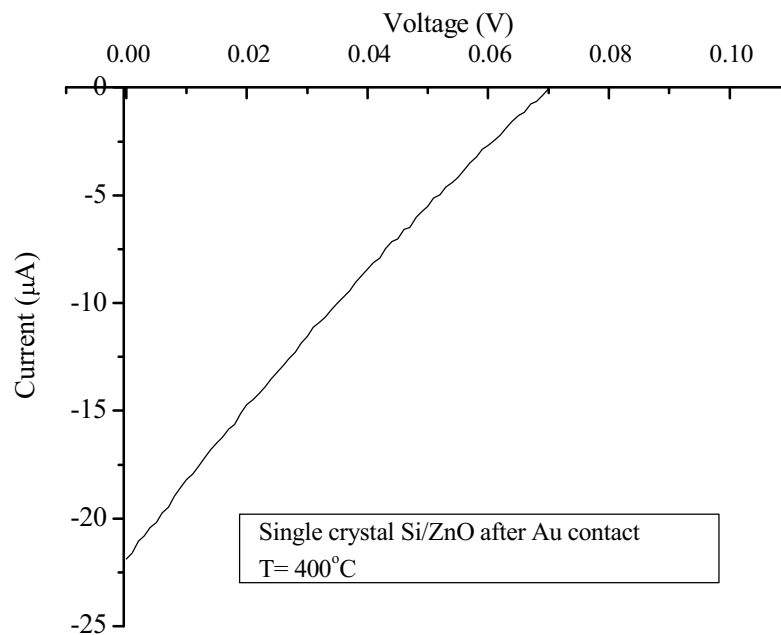
increase of series resistance as a result of substrate temperature increasing.

Fig. 4 represents the IV characteristics of the single crystal Si/ ZnO heterojunction at different substrate temperature.

From the figure, it is clear that the sample grown at substrate temperature of 300°C doesn't show any rectifying behaviour, but two other samples present clear rectifying behaviour. It seems with increasing substrate temperature from 400 to 500°C turn on voltage decreases from 5 V to 0.5 V. From the slope of IV diagram we can conclude that series resistance increases with increasing substrate temperature. Although with increasing substrate temperature forward current decreases, reverse current increases. We can relate this observation with the type of Si substrate. Unlike the samples grown on p-type polycrystalline Si, in this case turn on voltage decreases. If we consider energy diagram of n type Si, we can result in that with decreasing carrier concentration as a result of temperature increasing, the barrier difference is lowered in this case and so turn on voltage decreases.

Table 2. VOC, ISC, efficiency and fill factor of these two solar cells at substrate temperature of 400 °C after depositing Au contacts

V _{OC} (V)	0.071
I _{SC} (μA)	21.87
FF	0.226
Efficiency (%)	3.5×10^{-4}

**Fig. 5.** The room temperature IV under radiation of single crystal Si/ZnO obtained at substrate temperature of 400 °C after depositing Au contacts

In order to investigate these heterojunctions' application as a solar cell, Fig. 5 represents the room temperature IV under 100 mw/cm² illumination of single crystal Si/ZnO obtained at substrate temperature of 400 °C after depositing of Au contacts on both sides of Si and ZnO. Also, table 2 shows VOC, ISC, efficiency and fill factor of this solar cell. As it is clear although they can be used as an acceptable Schottky diodes, these cells have a long way to be

modified as a solar cell but because of the simple manufacturing process it is noteworthy to continue this way.

4. CONCLUSION

According to this paper we have studied effect of type of substrate and growth temperature on the properties of Si/ ZnO diodes. At high temperatures samples grown on single crystal Si

had higher resistance than polycrystalline Si. From XRD patterns can be concluded that samples grown at higher temperatures have better crystallinity. IV measurements showed that in the case of polycrystalline Si/ZnO diodes with increasing substrate temperature series resistance and turn on voltage increase while in single crystal Si turn on voltage will decrease. Although they are acceptable diodes, their efficiency as a heterojunction solar cell are so low.

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REFERENCES

1. Allahkaram, S. R., Faezi Alivand, R. and Bakhsh, M. S., "Corrosion behavior of electroless Ni-P/nano ZnO coatings", *Iranian Journal of Materials Science & Engineering*, 2013, 10, 10-17.
2. Khaleghian, M., Kalantar, M. and Ghasemian, S. S., "Comparision of mechanical and electrical properties of pizelectric composites PZT/ZnO and PZT/Al₂O₃ fabricated by powder metallurgy", *Iranian Journal of Materials Science & Engineering*, 2015, 12, 71-82.
3. Yu, C. F., Chen, S. H., Sun, S. J. and Chou, H., "Influence of the substrate temperature on the electrical and magnetic properties of ZnO:N thin films grown by pulse laser deposition", *J. Phys. D: Appl. Phys.*, 2009, 42, 035001-035004.
4. Haga, K., Katahira, F., Watanabe, H., "Preparation of ZnO films by atmospheric pressure chemical-vapor deposition using zinc acetylacetonate and ozone", *Thin Solid Films*, 1999, 343-344, 145-147.
5. Fu, Z., Lin, B., Zu, J., "Photoluminescence and structure of ZnO films deposited on Si substrates by metal-organic chemical vapor deposition", *Thin Solid Films*, 2002, 402, 302-306.
6. Kopalko, K., Wjick, A., Godlewski, M., Łusakowska, E., Paszkowicz, W., Domagała, J.Z., Godlewski, M.M., Szczerbakow, A., Świątek, K., and Dybko, K., "Growth by atomic layer epitaxy and characterization of thin films of ZnO", *phys. stat. sol. (c)*, 2005, 2, 1125-1130.
7. Romero, R., Leinen, D., Dalchiale, E. A., Ramos-Barrado, J. R., Martin, F., "The effects of zinc acetate and zinc chloride precursors on the preferred crystalline orientation of ZnO and Al-doped ZnO thin films obtained by spray pyrolysis", *Thin Solid Films*, 2006, 515, 1942-1949.
8. Terasako, T., Yagi, M., Ishizaki, M., Senda, Y., Matsuura, H., Shirakata, S., "Optical properties of ZnO films grown by atmospheric-pressure chemical vapor deposition using Zn and H₂O as source materials", *Thin Solid Films*, 2007, 516, 159-164.
9. Bacaksiz, E., Parlak, M., Tomakin, M., Ozcelik, A., Karakiz, M., Altunbas, M., "The effects of zinc nitrate, zinc acetate and zinc chloride precursors on investigation of structural and optical properties of ZnO thin films", *Journal of Alloys and Compounds*, 2008, 466, 447-450.
10. Lare, Y., Godoy, A., Cattin, L., Jondo, K., Abachi, T., Diaz, F. R., Morsli, M., Napo, K., del Valle, M. A., Bernede, J. C., "ZnO thin films fabricated by chemical bath deposition, used as buffer layer in organic solar cells", *Applied Surface Science*, 2009, 255, 6615-6619.
11. Pacio, M., Juarez, H., Escalante, G., Garcia, G., Diaz, T., Rosendo, E., "Study of (1 0 0) orientated ZnO films by APCVD system", *Materials Science and Engineering B*, 2010, 174, 38-41.
12. Kim, H. Y., Kim, J. H., Par, M. O., Im, S., "Photoelectric, stoichiometric and structural properties of n-ZnO film on p-Si", *Thin Solid Films*, 2001, 398-399, 93-98.
13. Lee, J. Y., Choi, Y. S., Kim, J. H., Park, M. O., Im, S., "Optimizing n-ZnO/p-Si heterojunctions for photodiode applications", *Thin Solid Films*, 2002, 403-404, 553-557.
14. Sun, H., Zhang, Q. F. and Wu, J. L., "Electroluminescence from ZnO nanorods with an n-ZnO/p-Si heterojunction structure", *Nanotechnology*, 2006, 17, 2271-2274.
15. Mandalapu, L. J., Xiu, F. X., Yang, Z., Zhao, D. T., and Liu, J. L., "p-type behavior from Sb-doped ZnO heterojunction photodiodes", *Applied Physics Letters*, 2006, 88, 112108-(1-3).
16. He, J. H. and Ho, C. H., "The study of electrical characteristics of heterojunction based on ZnO

- nanowires using ultrahigh-vacuum conducting atomic force microscopy”, *Applied Physics Letters*, 2007, 91, 233105-233108.
17. Ajimsha, R. S., Jayaraj, M. K., and Kukreja, L. M., “Electrical Characteristics of n-ZnO/p-Si Heterojunction Diodes Grown by Pulsed Laser Deposition at Different Oxygen Pressures”, *Journal of Electronic Materials*, 2008, 37(5), 770-775.
 18. Mridha, S., Dutta, M., Durga Basak, “Photoresponse of n-ZnO/p-Si heterojunction towards ultraviolet/visible lights: thickness dependent behavior”, *J Mater Sci: Mater Electron*, 2009, 20, 376-379.
 19. Xiaopeng, W., Xiaoqing, C., Lijie, S., Shun, M. and Zhuxi, F., “Photoelectric conversion characteristics of ZnO/SiC/Si heterojunctions”, *Journal of Semiconductors*, 2010, 31, 103002-(1-3).
 20. Al-Heniti, S., Badran, R. I., Al-Ghamedi, A. A. and Al-Agel, F. A., “Electrical properties of p-Si/n-ZnO nanowires heterojunction devices”, *Advanced Science Letters*, 2011, 4, 24-28.
 21. Nash, T. R. and Anderson, R. L., “Accelerated life tests of SnO₂—Si heterojunction solar cells”, *IEEE Transaction on Electron Devices* ED, 1977, 24, 468-472.
 22. Maleki, M., Rozati, S. M., “Dependence of Si/SnO₂ Heterojunction Properties on Growth Temperature and Type of Silicon”, *Chem. Vap. Deposition*, 2013, 19, 290-294.
 23. Swanepoel, R., “Determination of the thickness and optical constants of amorphous silicon”, *J. Phys. E: Sci. Instrum.*, 1983, 16, 1214-1222.
 24. Kang, S. J., Joung, Y. H., Shin, H. H. and Yoon, Y. S., “Effect of Substrate Temperature on Structural, Optical and Electrical Properties of ZnO Thin Films deposited by Pulsed Laser Deposition”, *J Mater Sci: Mater Electron*, 2008, 19, 1073-1078.
 25. Fay, S., Kroll, U., Bucher, C., Vallat-Sauvain, E., Shah, A., “Low pressure chemical vapour deposition of ZnO layers for thin-film solar cells: temperature-induced morphological”, *Solar Energy Materials & Solar Cells*, 2005, 86, 385-397.