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Ultraviolet Photodetection Properties of ZnO/Si Heterojunction Diodes Fabricated by ALD Technique Without Using a Buffer Layer

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Abstract—**The fabrication and characterization of a Si/ZnO thin film heterojunction ultraviolet photodiode has been presented in this paper. ZnO thin film of ~100 nm thick was deposited on <100> Silicon (Si) wafer by atomic layer deposition (ALD) technique. The Photoluminescence spectroscopy confirms that as-deposited ZnO thin film has excellent visible-blind UV response with almost no defects in the visible region. The room temperature current-voltage characteristics of the n-ZnO thin film/p-Si photodiodes are measured under an UV illumination of 650 µW at 365 nm in the applied voltage range of ±2V. The current-voltage characteristics demonstrate an excellent UV photoresponse of the device in its reverse bias operation with a contrast ratio of ~ 1115 and responsivity of ~0.075 A/W at 2 V reverse bias voltage.**

Index Terms—**ZnO, silicon, ALD, heterojunction photodiode, contrast ratio, responsivity**

I. INTRODUCTION

Ultraviolet (UV) photodetectors have wide commercial and military applications including flame detection, water purification, money counting, ozone layer detection, missile warning systems etc [1, 2]. Although, GaN (~3.45 eV) and SiC (~3.26 eV) based UV photodetectors are already in commercial use, their large cost and poor compatibility with other semiconductors including Si are the major drawbacks to achieve low-cost and efficient UV detectors [3, 4]. As an alternative, many researchers are trying to explore the low-cost, environment friendly and wide band gap (~3.34 eV) zinc oxide (ZnO) material with large exciton energy (~60 meV larger than GaN ~25 meV) for the UV detection applications [5, 6]. They have shown their interest to investigate ZnO based UV photodetectors with different configurations such as Schottky diode [5, 6], MSM (metal-semiconductor-metal) [3, 7, 8], MISM (metal-insulator-semiconductor-metal) [2, 8] and p-n heterojunction [9-13] photodiode structures. Since, ZnO is an intrinsically n-type semiconductor, the fabrication of a stable and controllable p-type ZnO thin film is very difficult [11]. Hence, ZnO is employed as the n-type semiconductor layer in most of the ZnO based p-n heterojunction UV photodiode structures [10-12].

Among various substrates used for the ZnO thin film based UV detectors [5-7], Si can be considered to be of special interests because of its compatibility with the modern days CMOS technology [11]. The ZnO thin films can be deposited on large Si wafer by various chemical and physical methods such as vapour transport [9], hydrothermal [10], thermal evaporation [11], pulsed laser deposition (PLD) [14], magnetron sputtering [15], atomic layer deposition (ALD) [16, 17] and sol-gel techniques [12, 13]. Luo *et al.* [9] reported the fabrication of ZnO nanowire/Si heterojunction photodiodes via VLS (vapor liquid solid) growth mechanism with the help of gold as

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a catalyst. The device has exhibited responsivity of 0.07 A/W at 365 nm [9]. Periasamy *et al.* [11] reported the fabrication of ZnO nanowire/Si heterojunction photodiodes by thermal evaporation method with the help of aluminium doped ZnO (AZO) as a seed layer. They [11] measured responsivity of the photodiode as 0.18 A/W under 365 nm UV light. Yakuphanoglu *et al.* [12] reported the fabrication of a ZnO nanostructure/Si heterojunction photodiode grown by sol-gel method without using any seed layer. Although, they [12] measured the I-V characteristics under UV illumination but they did not report the responsivity of their photodiodes. Sahu *et al.* [14] reported the fabrication of ZnO thin film /Si heterojunction photodiodes by pulsed laser deposition (PLD) method without using any seed layer. However, they [14] observed a very poor forward-to-reverse current ratio (~2 at ±4 V) with a very large reverse saturation current (~4.6×10^{-5} A). After critical review of the above works, it is observed that, in general, the n-ZnO thin film grown on a suitable seed layer-covered p-Si substrate can help to improve the performance of n-ZnO thin film/p-Si heterojunction photodetectors [9-11]. Since the growth of a seed layer is an additional step required in the fabrication process, the cost of fabrication is higher than that of the devices without seed layer. As Si and ZnO has a large amount of lattice mismatching and thermal coefficient difference [18], growth of crystalline ZnO directly on Si is not very easy, therefore adequate research is required for achieving low-cost n-ZnO/p-Si heterojunction photodiodes of reasonably good performance for practical applications without using any seed layer. In this work, an attempt has been made to report the fabrication and room temperature UV photodetection properties of a n-ZnO thin film /p-Si heterojunction diode obtained by depositing ZnO thin film directly on Si wafer (i.e. without using any seed layer) by using the ALD technique which is commonly recommended for the conformal deposition of high quality ZnO thin films with precise thickness and composition control at low deposition temperature [16, 17, 19]. Although, the ALD grown n-ZnO film has already been used in the metal/n-ZnO/metal structure (MSM type) based UV detectors with palladium Schottky contacts [8], but, to the best of our available knowledge, the ALD grown ZnO thin film for the fabrication of n-ZnO /p-Si heterojunction photodiode is believed to be considered for the first time in this paper.

II. EXPERIMENTAL DETAILS

In the present work, ZnO thin film was deposited on a p-Si <100> wafers (of thickness ≈380 µm and resistivity 2-7 Ω.cm) by using the ALD technique. Thoroughly cleaned and dried p-Si wafers were placed in ALD chamber (equipment model TFS 200 from BENEQ). Diethyl zinc [Zn $(C_2H_5)_2$, DEZN] and DI water were used as the source of zinc and oxygen respectively in the chamber with the pulse duration of 100 ms each to produce large area ZnO films on the Si substrates. Nitrogen was used as the carrier gas as well as purging gas with purging time of 1 sec. The temperature of the substrate and precursor was maintained at 150ºC and 20ºC respectively during the deposition of ZnO thin films. After 500 cycles of deposition, the thickness of the ZnO film was measured as 100 nm. The samples were then gone through rapid thermal annealing process at 550ºC for 20 minutes in nitrogen gas environment to ensure the continuous film surface with fewer interstitial defects and better passivity of the top surface [20]. The room-temperature photoluminescence (PL) spectroscopic analysis was carried out to study the optical properties of the as-deposited ALD grown ZnO films under consideration.

An ohmic contact of 20 nm/ 80 nm titanium/aluminium (Ti/Al) with 1 mm diameter was then deposited on the top of the ZnO films by thermal evaporation method through shadow mask technique. A layer of Al (100 nm) was deposited on the bottom of the Si wafer to make bottom ohmic contact of the device. The films were again annealed in the RTA (rapid thermal annealing) furnace for 10 min at 450ºC in nitrogen environment to improve the quality of electrodes [21]. The schematic diagram of n-ZnO/p-Si thin film heterojunction photodetector is shown in Fig. 1. The current-voltage characteristics of the device were measured using the semiconductor parameter analyzer (model B1500A, Hewlett-Packard) at room-temperature under dark and UV illumination conditions. A UV lamp of 365 nm wavelength and 650 µW power [Benchmark, India] was used as the UV illumination source to investigate the UV detection properties of the

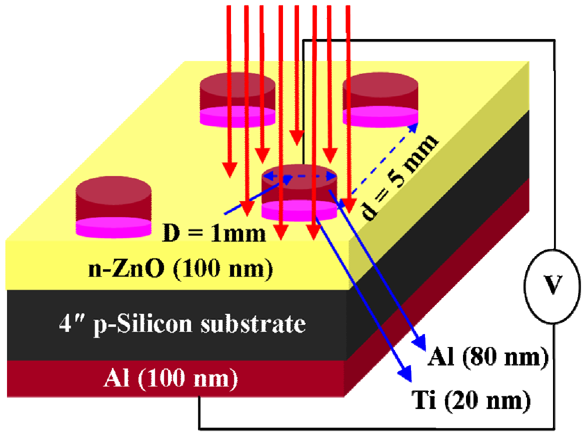

Fig. 1. Schematic diagram of ZnO/Si photodiode.

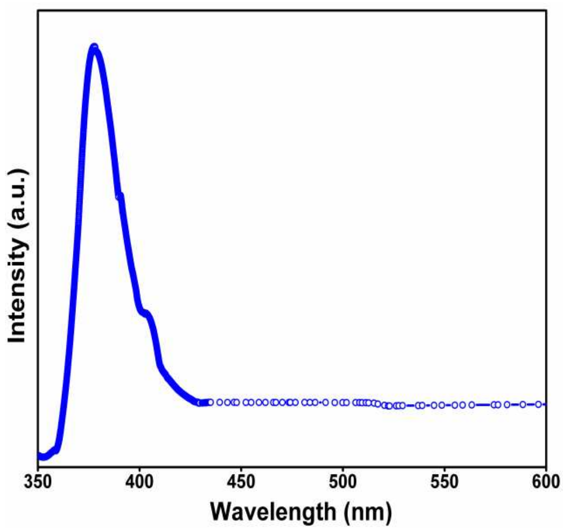

Fig. 2. Photoluminescence spectra of ZnO thin film grown on Si wafer.

heterojunction photodiode under consideration.

III. Results and Discussion

Fig. 2 shows the PL spectroscopy of the ZnO/Si heterostructure at room temperature. Only a strong near-band-edge emission peak at 377 nm due to the donor–acceptor pair transitions is observed in the PL spectra. However, absence of any other emission peaks from various types of defects (e.g. the green band emission due to the oxygen vacancy in ZnO film at ~550 nm [9]) in the PL characteristic indicates that the as-grown ZnO film is almost free from defects with enhanced UV detection property at ~377 nm.

The current(I)-voltage(V) characteristics of the n-ZnO/p-Si thin film planar heterojunction photodiode were measured at room temperature in the dark and under illuminated conditions at 365 nm with a 650 µW incident optical power. The I-V characteristics at dark condition show a typical *p-n* junction behavior with the rectifying junction as shown in Fig. 3. The rectification ratio is 127 at ±2 V in dark condition which is much larger than that reported by Sahu *et al.* [14]. The other parameters such as the ideality factor, reverse saturation current, turn-on voltage and barrier height of the heterojunction can be determined by using the thermionic model to express the I-V characteristics as [12]:

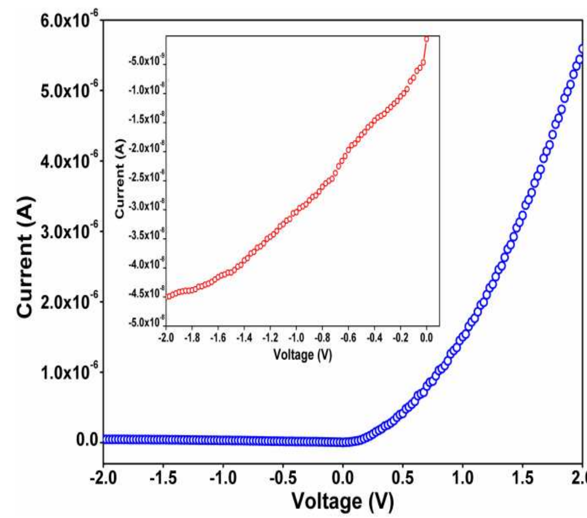

Fig. 3. Dark current characteristics of ZnO/Si heterojunction photodiode; (inset) Enlarged view of the characteristics in reverse bias.

$$I = I_0\left[\exp(qV/nkT)-1\right] \quad (1)$$

where q is the electronic charge, k is the Boltzmann's constant, I_0 is the temperature-dependent reverse saturation current (also known as dark current of the photodiode), n is the ideality factor and T is the absolute temperature.

By using the conventional method [8], the parameters n and I_0 are estimated from the *ln(I)* versus *V* plot at room temperature as ~2.72 and ~4.15×10^{-9} A respectively. The turn-on voltage is calculated from I-V characteristics as ~0.6 V. The effective barrier height (φ_{bh}), one of the important parameter for a photodiode, can be estimated from the I-V characteristics measured at dark condition by using the expression of I_0 as [1]:

$$I_0(T) = AA^*T^2 \exp\left(\frac{-q\Phi_b}{kT}\right) \quad (2)$$

where A and A^* are the contact area and Richardson constant respectively. Using the values of A and A^* (=32 $Acm^{-1}K^{-2}$ for m^*=0.27m_0) in Eq. (2) the effective barrier height of n-ZnO thin film/p-Si heterojunction photodiode under consideration is determined as 0.76 eV. The key parameters of the device clarify that the interface quality of the n-ZnO thin film /p-Si heterojunction is comparatively better than the heterojunction photodiode reported by Yakuphanoglu *et al.* [12] by using sol-gel method without using a buffer layer.

The room temperature current-voltage characteristics of the n-ZnO/p-Si thin film heterojunction diode, measured under dark and illuminated conditions at 365 nm are compared in Fig. 4. The measured values of the dark current (i.e. the reverse saturation current I_0) is ~44.8 nA and current under UV illumination at 365 nm is ~48.5 µA respectively at 2 V reverse bias. The resultant contrast ratio which is defined as the ratio of photocurrent and dark current [8] is measured as ~1115 which appears to be much larger than the reported data [12]. The reason behind this huge enhancement of photocurrent is investigated further.

When the incident light enters the ZnO material through the inter-electrode space and gets absorbed through ZnO thin film, a large quantity of photo-exited electron-hole pairs (EHPs) is generated in the entire region of the ZnO layer [11]. These photo-generated electrons and holes in the depletion region of the Si/ZnO heterojunction are drifted in the opposite directions in the presence of the electric field in the depletion region under reverse bias operation thereby leading to the collection of excess photocurrent through the metallic contacts in addition to the dark current [9, 12]. The large surface-to-volume ratio of the nanocrystals present in ZnO thin film and the deep level surface trap states make the photo carrier lifetime longer [9, 11]. On the other hand, the increase in the photocurrent (see Fig. 4) with the reverse bias voltage is a result of the increase in the average velocity of the photo-generated carriers owing to the increased electric field in the depletion region [9]. Since the width of the depletion region is also increased

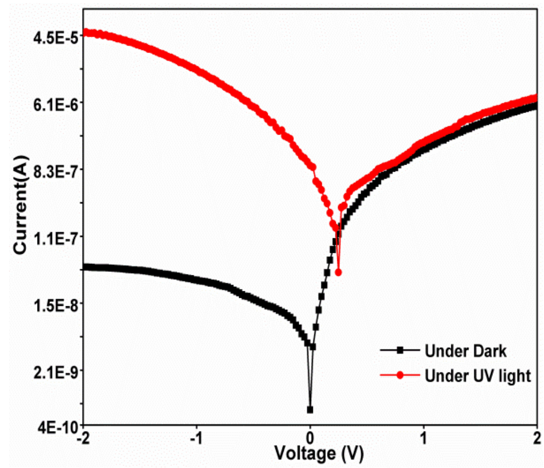

Fig. 4. Response of the Si/ZnO photodiode with and without UV light illumination.

with the reverse bias, the depletion capacitance is decreased thereby reducing the RC time constant of the photodiode [11]. In brief, the long lifetime and short transit time of the excess carriers generated over the large area of the ZnO film under reverse bias operation results in a significant photocurrent in the device.

The responsivity (R) defined as the ratio of the measured photoresponse current to the incident optical power on the UV photodiode can be expressed as [11]:

$$R = I_{ph} / P_{opt} \quad (3)$$

where P_{opt} is the incident optical power, and I_{ph} is the output photocurrent measured from ZnO/Si photodiode. The responsivity of the photodiode at -2 V bias voltage under the UV illumination at 365 nm with incident optical power of 650 µW is estimated to be ~0.075 A/W which is in good agreement with that reported by Luo et al. for their ZnO nanowire/Si heterojunction photodiodes prepared by vapour transport method [9].

The optical to electrical conversion efficiency of the photodiode, termed as the external quantum efficiency (EQE) η is defined by [8]:

$$\eta = \frac{hc}{q\lambda} R = 1240 \frac{R}{\lambda} \quad (4)$$

where, h is the Planck's constant, c is the velocity of light and λ is the wavelength of the light. The value of η of the p-Si/n-ZnO thin film heterojunction photodiode is obtained as ~25% at -2 V bias voltage.

We now estimate the specific detectivity (D) of the heterojunction photodiode considered in this paper. The parameter D can be written as [8]:

$$D = \frac{\lambda\,\eta\,q}{hc}\left(\frac{RA}{4\,kT}\right)^{1/2} \tag{5}$$

Where *RA* is known as the as zero-biased resistance-area product of the device obtained from the current density (*J*) –voltage (*V*) characteristics as follows [8]:

$$RA = \left(\frac{\partial J}{\partial V}\right)^{-1} \tag{6}$$

Converting the measured I-V characteristics into J-V characteristics, the resistance-area product (*RA*) is obtained as RA=30.828 $\Omega.m^2$ and the voltage-dependent detectivity (D) of the proposed device is calculated as 6.44×10^9 $mHz^{1/2}\,W^{-1}$ at -2 V bias voltage.

It may be noted that the proposed device is showing the UV detection characteristics only when it is operated under reverse bias condition. However, the p-Si/n-ZnO thin film device shows the photovoltaic effects [9-10] when it is operated under a low forward bias condition (see Fig. 4). The open circuit voltage of the device is estimated as $V_{oc} = 0.25$ V, the short circuit current and fill factor are derived as $I_{sc} = 9.3\times10^{-7}$ A and $FF = 0.2$ respectively. The photovoltaic effects in the low forward bias and UV photoresponse under reverse bias of the p-Si/n-ZnO thin film heterojunction diode may be attributed to the large exciton energy of the ZnO material [10].

IV. CONCLUSION

In this work, the UV detection properties of the ALD-grown n-ZnO thin film/p-Si heterojunction photodetectors without using a seed layer have been demonstrated possibly for the first time in the literature. The photoluminescence characteristics show the growth of high quality ZnO layer on Si with almost no defects in the visible region. At 650 μW incident UV light of 365 nm wavelength, the photodetectors show a very high contrast ratio (~1115) with responsivity of ~0.075 A/W, external quantum efficiency of ~25% and detectivity of $\sim 6.44\times10^9$ $mHz^{1/2}\,W^{-1}$ at 2V reverse bias voltage. The performance parameters of the device are appeared to be promising for high-performance, low-cost commercial UV detection applications.

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