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Photoresponse of *n*-ZnO/*p*-SiC heterojunction diodes grown by plasma-assisted molecular-beam epitaxy

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High quality n-ZnO films on commercial p-type 6H-SiC substrates have been grown by plasma-assisted molecular-beam epitaxy, and n-ZnO/p-SiC heterojunction mesa structures have been fabricated. Current-voltage characteristics of the structures had a very good rectifying diode-like behavior with a leakage current less than 2×10^{-4} A/cm² at -10 V, a breakdown voltage greater than 20 V, a forward turn on voltage of \sim 5 V, and a forward current of \sim 2 A/cm² at 8 V. Photosensitivity of the diodes was studied at room temperature and a photoresponsivity of as high as 0.045 A/W at -7.5 V reverse bias was observed for photon energies higher than 3.0 eV. © 2005 American Institute of Physics. [DOI: 10.1063/1.1949730]

The semiconductor ZnO has a direct wide band gap $(E_g \sim 3.3 \text{ eV})$ and is attractive for optoelectronics applications due to advantages over GaN such as the availability of ZnO bulk single crystals and a large exciton binding energy $(\sim 60 \text{ meV})$.¹ Because growth of reproducible high quality *p*-type ZnO films has not yet been achieved,² fabrication of ZnO *p*-*n* homojunctions based light-emitting diodes remains to be accomplished. For this reason, growth of *n*-type ZnO on other *p*-type materials could provide an alternative way for realizing ZnO based p-n heterojunctions. This approach has received considerable attention, and many hetero-p-n junctions have been realized using various *p*-type materials with *n*-ZnO: Si, GaN, AlGaN, SrCu₂O₂, NiO, ZnTe, Cu₂O, CdTe, diamond, ZnRh₂O₄, and GaAs.² ZnO-based heterostructures have been considered as a candidate not only for light-emitting devices but also for photodetectors.^{3–6} Among the available transparent conductive oxide materials, ZnO films have promising properties for photodetectors due to their good electrical and optical properties, relatively low deposition temperatures, simplicity of fabrication processes, and, therefore, low cost. Moreover, ZnO-based photodetectors have superior resistance to ionizing radiation and highenergy particles, and does not require an antireflection layer.¹ The main factor influencing the properties of heterostructures is the close lattice match of the components. In this respect, 6H–SiC $[E_g \sim 2.9 \text{ eV} \text{ (see Ref. 7)}]$ is a good candidate since it has wurtzite crystal structure and relatively good lattice matching to ZnO with lattice mismatch of $\sim 4\%$, and p -6H-SiC substrates are commercially available. Previously, 6H-SiC substrates have been used for heteroepitaxial growth of ZnO and high quality of the grown ZnO films has been demonstrated.^{8,9} So far, there has been only one report on the growth of *n*-type ZnO on *p*-type 6H-SiC,¹⁰ which relies on the chemical vapor deposition (CVD) method for ZnO deposition. However, CVD method uses high oxygen pressure (1-0.1 Torr) during growth that leads to oxidation of the SiC substrate before ZnO growth commences. As a result, the grown n-ZnO/p-SiC heterostructures exhibited very poor current-voltage characteristics.¹⁰ For this reason, the molecular-beam epitaxy (MBE) method would be more convenient for fabricating n-ZnO/p-SiC-type heterostructure devices. In this vein and for the present work, n-ZnO films were grown on p-6H-SiC substrates by plasma-assisted MBE and n-ZnO/p-6H–SiC heterojunction diodes were fabricated, and their photoresponse properties were studied.

MBE growth of 0.5-µm-thick ZnO layers was performed on 1×1 cm² *p*-type 6H–SiC substrates at 600 °C with a growth rate of 1.1 Å/s. This growth was preceded by low-temperature deposition of a thin ZnO buffer layer at 300 °C for 3 min. The grown ZnO films showed unintentionally doped *n*-type conductivity with an electron concentration of $\sim 8 \times 10^{17}$ cm⁻³. Commercially grown *p*-6H–SiC substrates were 400 μ m thick and had a hole concentration of 4×10^{17} cm⁻³. The surface morphology and crystalline structure of the grown ZnO films were characterized by reflection high-energy electron diffraction (RHEED) and atomic force microscopy techniques. A streaky RHEED pattern, indicating two-dimensional growth, and smooth film surface morphology with an rms roughness as low as 1.45 nm were observed. Photoluminescense (PL) from the films was measured at both 10 K and 300 K using the 325 nm line of a He-Cd laser. Mesa diode structures with a diameter of 250 μ m were fabricated by conventional photolithography. Ohmic contacts to n-ZnO layer and p-SiC substrate were achieved by vacuum evaporation of 300/1000 Å thick Au/Al and Au/Ni metal layers, respectively. The photo response of the n-ZnO/p-6H–SiC heterostructure diodes were studied as a function of the incident photon energy, excitation intensity, and reverse bias voltage. The diodes were illuminated both from ZnO and SiC sides.

The 10 K PL spectrum for a MBE-grown ZnO film is shown in Fig. 1. The spectrum consists of very intense UV near band edge emission peaks, and a very weak broad defect-related emission with a maximum at 2.7 eV (inset of Fig. 1). The latter, broad, emission originates mainly from the 6H-SiC substrate as a result of secondary excitation by UV emission from ZnO and also to a lesser extent from the defect related transitions in ZnO (green band). The near band edge emission consisted of four peaks at 3.375, 3.366, 3.363, and 3.358 which are denoted in the figure as FX_A , $D_1^0X_A$,

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FIG. 1. PL spectrum of the ZnO film grown on *p*-type 6H–SiC substrates by MBE (T=10 K).

 $D_2^0 X_A$, and $D_3^0 X_A$, respectively. The peak at 3.375 eV is known to be the free *A*-exciton line, and the peaks at 3.366, 3.363, and 3.358 eV are located in the energy region which is usually attributed to donor-bound excitons.¹¹ There is also an additional feature at 3.337 eV which may correspond to two-electron satellites of donor-bound exciton peaks or to the excitons bound to structural defects.¹¹

Studies of the current-voltage (*I-V*) characteristics of the fabricated *n*-ZnO/*p*-SiC mesa structures revealed the presence of good *p*-*n* heterojunction between *n*-ZnO and *p*-SiC. Figure 2 shows the room-temperature *I-V* characteristics of a typical ZnO/*p*-SiC heterostructure diode. A very good rectifying diode-like behavior is observed with a leakage current less than 10^{-7} A (2×10^{-4} A/cm²), and a forward current of $\sim 10^{-3}$ A (~ 2 A/cm²) at 8 V bias. Breakdown voltage changed from sample to sample in the 20–23 V range, probably due to nonuniformity of the grown ZnO films. The ideality factor was estimated from the *I-V* plot using the following diode equation:¹²

$$J = J_s \left[\exp\left(\frac{qV}{nkT}\right) - 1 \right],\tag{1}$$

where J_s is the saturation current density, *n* the ideality factor, *k* the Boltzmann constant, and *T* the absolute temperature. The ideality factor obtained is >2, indicating that conduction is dominated by nonthermionic processes. The results show that the *I-V* characteristics of our *n*-ZnO/*p* -SiC heterostructures are comparable to that of the best wide band gap material-based heterostructure diodes reported previously.^{13,14}

Electroluminescense (EL) measurements under forward bias showed no light emission from the n-ZnO/p-SiC heterojunction. The absence of the EL emission can be explained by noting that electron injection takes place mainly from the direct band gap n-ZnO into the indirect band gap p-SiC. It should be noted that no EL was observed either under forward bias in Ref. 10 from n-ZnO/p-SiC heterostructures grown by CVD. However, emission was reported under reverse bias conditions, and was attributed to impact ionization of crystal lattice at high electric fields.¹⁰ Such a behavior may be typical to n-ZnO/p-SiC heterojunctions due to particular band alignment. The salient features of the band alignment in n-ZnO/p-SiC heterojunction can be determined to a first extent from the Anderson model using the



FIG. 2. Room-temperature *I-V* characteristics of n-ZnO/p-SiC heterojunctions in both logarithmic and linear (inset on the right) scales. The inset on the left depicts the schematic of the energy band diagram of the n-ZnO/p-6H–SiC heterostructure.

known electron affinities of ZnO (χ_{ZnO}) and 6H–SiC (χ_{SiC}). It should be pointed out, of course, that this model describes the band diagram of the ideal case when there is no lattice mismatch between contacting materials, and there are no imperfections at the interface; however, it allows us to sketch the most probable heterojunction band alignment. However, there is a good deal of dispersion in the literature in that different electron affinity values have been used by different for 6H-SiC $(3.3-4.2 \text{ eV})^{15-17}$ and ZnO authors (4.2-4.52 eV).¹⁸⁻²⁰ Nevertheless, the energy band diagrams of n-ZnO/p-6H-SiC heterojunction constructed for any pairs of χ has the same configuration, type II band alignment, as shown in the inset of Fig. 2. The conduction band offset ΔE_C is calculated as the difference between electron affinities of ZnO and 6H–SiC: $\Delta E_C = \chi_{ZnO} - \chi_{SiC}$. The valence band offset ΔE_V is obtained from $\Delta E_V = \Delta E_C + \Delta E_g$, where ΔE_g is the energy band gap difference between ZnO and 6H-SiC: 0.4 eV. As seen from this diagram, the conduction band offset is much less than that of the valence band, which means that electron injection from n-ZnO to p-SiC is more likely than hole injection from *p*-SiC to *n*-ZnO. Since SiC is an indirect semiconductor, electron hole recombination in SiC does not result in discernable visible emission. Again, these arguments are for the ideal case, and direct measurements are required to determine the exact band structure of the heterojunction.

Photoresponse properties of the n-ZnO/p-6H-SiC heterojunctions were also measured at RT, and in contrast to EL, high photosensitivity to UV radiation was observed. The photocurrent was observed to change almost linearly with the incident light intensity. The responsivity was measured for different reverse bias voltages with illumination from both ZnO and SiC sides, and the results are shown in Fig. 3. In the case of illumination from the ZnO side, substantial increase in the photoinduced current commences at a photon energy of 3.0 eV, reaching its peak at 3.280 eV, which corresponds to the band gap of ZnO at RT. The peak position did not shift with applied reverse bias. With increasing photon energy, the photocurrent increases as a result of larger absorption coefficient at higher photon energies. The responsivity at 3.280 eV was 0.011 A/W for zero bias, and it increased linearly with increasing reverse bias, reaching



FIG. 3. Room-temperature spectral photoresponsivity of the n-ZnO/p-SiC photodiode illuminated both from the ZnO and 6H–SiC (inset) sides for various reverse biases.

0.045 A/W at -7.5 V. These results show that the photoresponse of our *n*-ZnO/*p*-SiC diodes is comparable to that of the best ZnO-based photodetectors reported previously.²¹⁻²³ In those reports, *p*-NiO (see Ref. 21) and *p*-Si (see Refs. 22 and 23) were used as the *p*-type layer. However, since the aforementioned materials have a larger lattice mismatch with ZnO (~9% and ~16%, respectively) and different crystal structures (cubic), the *n*-ZnO/*p*-SiC combination structures have better prospects for photodetector applications. As a result of such a large lattice mismatch, reported *n*-ZnO/ *p*-NiO and *n*-ZnO/*p*-Si heterostructure-based photodiodes had very large leakage dark current densities: ~2 A/cm² at -6 V, 5×10⁻³ A/cm² at -4 V,²² and 9×10⁻⁴ A/cm² at -5 V,²³ while this value in our case was as low as 2 ×10⁻⁴ A/cm² at -10 V.

The inset in Fig. 3 presents the spectral response of the photodiode when illuminated from the SiC side. The spectrum consists of a narrow band with a maximum at 3.058 eV and a full width at half-maximum of 0.1 eV, which did not change with reverse bias. The responsivity at 3.058 eV for zero bias was 0.002 A/W and it increased with applied reverse voltage, reaching 0.005 A/W at 7.5 V. The responsivity in this case is 6-10 times smaller than that in the case of illumination from the ZnO side due to absorption of highenergy photons in the thick SiC substrate and the smaller absorption coefficient of the indirect 6H-SiC semiconductor compared to that of direct band gap ZnO. The spectral behavior of the *n*-ZnO/*p*-SiC heterojunction photodiode when the ZnO side is illuminated can be explained as follows. Since the band gap of ZnO is wider than that of 6H–SiC (3.3 and 3.05 eV, respectively) it serves as a "window," and the photons with energies less than the band gap of ZnO penetrate into the SiC side of the heterostructure, generating excess carriers in SiC. As the photon energy is increased, carriers are generated closer and closer to the heterointerface, and when it becomes equal to $\sim 3.3 \text{ eV}$, photogeneration of carriers occurs in ZnO. Further increase in the photon energy leads to the formation of excess carriers only in ZnO. In the case of illumination from the SiC side (Fig. 3, inset), photons with energies less than or near the band gap energy of SiC penetrate the entire thickness of the SiC substrate (400 μ m) and generation of charge carriers takes place in the SiC increases, the penetration depth of the photons decreases rapidly, and the light absorption takes place primarily in the regions far from the depletion region. Consequently, the excess carriers that are generated cannot reach the depletion region in the time scale of their lifetime, and cannot represent photocurrent contributions due to recombination in SiC.

In summary, n-ZnO/p-6H-SiC-type heterojunction diodes were fabricated using unintentionally n-type doped ZnO films grown on p-type 6H-SiC substrates by plasma-assisted MBE. The *I-V* measurements showed good rectifying diodelike behavior with low leakage current ($<10^{-7}$ A at 20 V), high breakdown voltage (<-20 V), and forward current of $\sim 1 \times 10^{-3}$ A at 8 V. The ideality factor was greater than 2, indicating interface defect-mediated conduction. When the diodes were illuminated from the ZnO side of the heterojunction with UV radiation of energy >3.28 eV, a photoresponsivity as high as 0.045 A/W at -7.5 V reverse bias was observed. These results show that n-ZnO/p-6H-SiCheterojunction diodes are promising candidates for UV photodetector applications. Further optimization of ZnO growth conditions on 6H--SiC and the thickness of ZnO layer can lead to improved results.

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