Fabrication of Si/ZnO Vertical n-n⁺ and p-p⁺ Isotype Junction Devices by Pulsed Laser Deposition

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Abstract—Device development and electrical characterization of high quality zinc oxide (ZnO) thin films grown on silicon (100) substrates are presented in this paper. Thin films of ZnO are grown at an optimized growth temperature of 300° C and two oxygen overpressure regimes on n and p-type Si substrates by pulsed laser deposition technique. Current-voltage characteristics of four devices are investigated by deposition of silver contacts on ZnO films and back gating the substrates. Rectifying properties are observed for two devices: one, for the n-Si substrate device with the film grown at low (6.66×10^{-4} Pa) oxygen overpressure and two, for the p-Si device with ZnO grown at high (3.33×10^{-2} Pa) oxygen. For the other two devices, namely the devices with the films grown on n-Si at high oxygen and p-Si at low oxygen pressure less pronounced rectifications are observed. Forward bias currents follow a quadratic current-voltage (IV) relationship, and this is in agreement with space-charge-limited current transport theory. Our results confirm the effects of the growth conditions including oxygen overpressure and growth substrate on intrinsic carrier concentrations and, hence, electrical properties of ZnO thin films. We conclude that output characteristics of Si/ZnO junction devices can be adjusted by modifications of growth conditions to create p-n equivalent junctions. The results have significant contributions to the development of future ZnO-based devices.

Introduction—Because of its unique properties, ZnO is a technologically important compound semiconductor with a wide range of applications. At room temperature, its direct bandgap of 3.37 eV makes it an ideal material for ultra violet (UV) optoelectronic devices [1]. Moreover, its high exciton binding energy, piezoelectric properties, thermal and chemical stability, non-toxicity [1-5], and abundant availability [4] have made ZnO a material of choice for short wavelength optoelectronic applications [4], various sensors (gas sensors [6], surface acoustic wave sensors, biological sensors [7][8], and micro-electro-mechanical system (MEMS) sensors [9]) as well as UV emitters and detectors [1][2]. Device applications of ZnO, however, are hampered by growth challenges which make it difficult to grow stable and reliable p-type ZnO [4][5]. In fact, the problem of p-type conductivity in ZnO is still an open question. Doping, co-doping, and other growth techniques have failed to produce solid fabrication and explanation of p-type ZnO. Intrinsic native defects including oxygen vacancies and zinc interstitials along with extrinsic growth contaminants such as the ever present hydrogen and its complexes not only make ZnO grow typically n-type, but may also result in compensating p-type doping in ZnO. We, on the other hand, have taken advantage of this native defect interplay and the growth dynamics in pulsed laser deposition (PLD) to grow high quality n and p-type ZnO thin films on Si (100) substrates [3]. Structural, optical, and electrical properties of the grown layers have been presented earlier [2][3]. In the present work, the electrical properties of Si/ZnO junction devices are investigated for n and p-Si/ZnO devices which are grown at an optimized temperature [3] and two different oxygen overpressures. This work emphasizes the significance of growth conditions and their contributions to the electrical properties of PLD grown ZnO thin films on Si substrates.

Experiment—A set of four devices are fabricated. Thin films of ZnO are grown on oxide removed n-type and p-type Si (100) substrates by PLD as described in our previous work [2]. The thicknesses of the films are measured by a Tencor Alpha Step 200 profilometer, and it is confirmed that the films are between 150 and 200 nm thick. All four devices are prepared at a constant optimized temperature of 300° C, while two of the samples are grown in the high (3.33×10^{-2} Pa) and the other two in the low (6.66×10^{-4} Pa) oxygen overpressure regimes. 40 nm thick silver contacts (circular contacts of 1 mm radii) are then deposited on ZnO surface by electron beam evaporation, and the devices have large area contacts over the whole back of the substrate for current-voltage (*IV*) measurements. The boron doped p-Si substrates used here have resistivity of 14-22 $\Omega \cdot \text{cm}$ ($p_0 = 5.9\text{-}9.4 \times 10^{14} \text{ cm}^{-3}$), and the phosphorus doped n-type substrates have resistivity of 2-3 $\Omega \cdot \text{cm}$ ($n_0 = 1.5\text{-}3.2 \times 10^{15} \text{ cm}^{-3}$). *IV* measurements were done at room temperature by applying bias and grounding the substrates through the large area back contacts (figure 1). The integrity and Ohmic behavior of silver contacts are verified by Hall effect (Ecopia HMS-5000) prior to electrical measurements. Thus, the effects of ZnO/Ag and Si/Ag junctions on transport properties and electrical characteristics of Si/ZnO junctions are negligible. Figure 1 shows the structure of our devices with thickness of different areas along with the external applied voltage.

Results & Discussions

n-Si/ZnO Devices

The n-Si/ZnO device which is fabricated at the low oxygen overpressure (6.66×10^{-4} Pa) has high defect concentrations [3], specifically higher levels of oxygen vacancies. Therefore, the grown

film is heavily doped, i.e. n^+ with much higher electron concentration (10^{20} cm^{-3}) than the lightly doped n-Si substrate (10^{14} cm^{-3}). This doping difference creates a p-n equivalent junction between the grown layer and the substrate; more specifically, the substrate appears as the equivalent p-region with respect to the ZnO film, resulting in an isotype junction device with non-linear IV characteristics. Similar to p-n junctions, the diffusion barrier is affected by the biasing condition of the device and rectifying properties are expected. IV characteristics of this device are shown in figure 2. When the input voltage is positive, the junction is reverse biased since the n-region, or ZnO thin layer, is at higher potential. It is forward biased for negative input voltages.

The n-Si/ZnO device grown at high oxygen overpressure, on the other hand, has lower defects due to better growth conditions [3]. In this case, the concentrations of the substrate and the grown film are closer (table 1); thus, a less pronounced rectification is expected, as shown in figure 3 where a “soft” nonlinear asymmetric IV characteristic is observed. Current transport mechanism and output characteristics of this device are consistent with space-charge-limited current (SCLC) transport as discussed below.

p-Si/ZnO Devices

The IV characteristics of p-Si/ZnO devices are shown in figures 4 and 5. Based on our Hall Effect measurements [3] these films show p-type conductivity at room temperature. Moreover, high oxygen overpressure reduces intrinsic donor-like defects and improves p-type behavior which in turn makes the grown films p^+ with respect to the substrate resulting in a p-p+ isotype

junction. Carrier concentrations and Hall coefficients for all of our devices are presented in table 1.

Therefore, rectifying properties for the p-Si/ZnO device grown at high oxygen pressure are expected. Figure 4 shows forward ($V>0$) and reverse bias ($V<0$) properties of this device. Lowering growth oxygen pressure increases intrinsic defects count which in turn increases the electron concentration of the grown ZnO layer; therefore, an increase in the reverse current will be observed. This increase in the reverse current is shown in figure 5 (at -2 V) as compared with figure 4. Similar to the n-Si/ZnO device grown at high pressure, the rectification property is decreased for the p-Si/ZnO device grown at low pressure.

A comparison between figure 3 and figure 5 suggests that structural differences between the films grown on n and p-Si substrates affect the electrical properties of the grown films. On the other hand, rectification is degraded for n-n and p-p compared to n-n⁺ and p-p⁺ junctions, respectively (figures 3 and 5 compared to figures 2 and 4, respectively). This degradation confirms the effects of growth conditions and more specifically defects on electrical properties of the Si/ZnO junction devices. Table 2 summarizes all devices along with the growth conditions and observed behavior.

IV characteristics and the vertical transport mechanism of our Si/ZnO devices are explained by the formation of a space-charge region at the junction between the substrates and the grown ZnO layer [10]. In cases where the grown films have high carrier concentrations, the current is easily injected to the Si substrates and the transport properties are dominated by the substrates. For low-field biasing conditions, the applied electric field is the dominant field throughout the device and

transport is bulk-limited; i.e., no band bending occurs in the valence (conduction) band of ZnO which acts metallic for the p-Si/ZnO (n-Si/ZnO) device [10] [11], respectively. On the other hand, increasing the applied voltage across the device increases the charge transport between the ZnO and Si and affects the space-charge region. The current is limited by the depletion region which dominates the transport properties. For high fields, we observed a quadratic dependence in IV characteristic (shown in figure 6) which is in agreement with SCLC transport theory. In this case, the current density J can be calculated as the following have:

$$J = nev \quad \text{eq. 1}$$

Where

n is the electron concentration

e is the unit charge for an electron

v is the drift velocity of electrons

Substituting for the drift velocity, using the Poisson's equation, and the fact that the electric field vanishes at the Si/ZnO Ohmic contact, from eq.1 we have:

$$J_z = \frac{1}{2} \mu \epsilon (E_z)^2 \quad \text{eq. 2}$$

Where

μ is the electron mobility

E_z is the vertical component of the electric field

This gives us the space-charge-limited current transport mechanism with the quadratic current-voltage relationship. Such quadratic relationship between current and voltage has been observed for ZnO nanowalls [11].

Semi-logarithmic IV characteristic plots of the devices (for forward and reverse bias conditions) show the typical behavior of the junctions. As discussed earlier, oxygen overpressure during the growth process changes the defect concentration. Figure 7 and figure 8 show the IV characteristics for n-Si/ZnO (figure 7) and p-Si/ZnO (figure 8) devices grown at low and high oxygen pressure. It is evident that the rectification properties are observed for n-Si and p-Si devices grown at low and high pressures, respectively, which are in good agreement with our previous theoretical discussions (see table 2). As discussed, these p-n equivalent devices are isotype, so the reverse saturation currents would be significantly larger than a typical p-n junction where both carriers participate.

In contrast, devices grown under high pressure on n-Si and low pressure on p-Si show poor rectification which is explained by the Ohmic metal-semiconductor (MS) junction.

Conclusions—Si/ZnO junction devices are fabricated and their electrical properties are discussed. Low oxygen overpressure increases (decreases) electron (hole) concentration of the films and results in an isotype n-Si/n⁺ZnO (p-Si/p-ZnO) junction. High oxygen growth, on the other hand, decreases (increases) electron (hole) concentration of the grown layer and makes an n-Si/n-ZnO (p-Si/p⁺ZnO) isotype device. Based on our results, rectification behaviors equivalent to p-n junctions are observed for n-Si/n⁺ZnO and p-Si/p⁺ZnO devices while the other two devices show poor rectification. Forward biased quadratic IV behavior of these devices is

consistent with SCLC transport theory. Moreover, high reverse currents are justified by the fact that these junctions are isotypic. Our results show the effects of growth conditions, oxygen overpressure, and growth substrate on the electrical properties of these junctions.

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Figures

Figure 1. The structure of our devices. Thin films of ZnO (150-200 nm) are grown on n and p-type Si substrates ($500\text{ }\mu\text{m} \pm 50\text{ }\mu\text{m}$) by PLD. Silver contacts (40 nm thick circular contacts of radius 1mm) are then deposited by electron beam evaporation. For IV measurements, substrates are grounded through large area back contacts and the external voltage is applied to the thin film.

Figure 2. IV characteristics of n-Si/n⁺ZnO system for the film grown at 300° C and low oxygen overpressure. High electron concentration makes the film heavily doped with respect to the lightly doped substrate. Rectification is observed for this n-n⁺ isotype junction device.

Figure 3. IV characteristics of n-Si/n-ZnO system for the film grown at 300° C and high oxygen overpressure. High oxygen overpressure improves the quality of the grown film and lowers electron concentration (compared to low pressure growth). For this device, electron concentrations are more comparable between the substrate and ZnO thin film. A “soft” non-linear asymmetric IV characteristic is observed.

Figure 4. *IV* characteristics of p-Si/p⁺ZnO system for the film grown at 300° C and high oxygen overpressure. High carrier concentration makes the film heavily doped with respect to the lightly doped substrate. Rectification is observed for this p-p⁺ isotype junction device.

Figure 5. *IV* characteristics of p-Si/p-ZnO system for the film grown at 300° C and low oxygen overpressure. Low oxygen overpressure degrades the quality of the grown film. The reverse current for this p-p isotype junction is significantly larger than the p-p⁺ device (fig. 4).

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270 Figure 6. Quadratic dependence of IV characteristics of the studied devices. Experimental data
 271 points are fitted by quadratic equations for (a) $n-n^+$, (b) $n-n$, (c) $p-p^+$, and (d) $p-p$ isotype
 272 junctions.

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Figure 7. The log IV characteristics for n-Si/ZnO devices grown at low (blue, ▲) and high (red, ■) oxygen overpressure and 300° C.

Figure 8. The log IV characteristics for p-Si/ZnO devices grown at low (red, ■) and high (blue, ▲) oxygen overpressure and 300° C. High reverse saturation currents are due to the isotype character of the junctions.

Table 1. Growth conditions, carrier concentrations, and Hall coefficients for the studied Si/ZnO devices.

Growth Condition	Carrier Concentration [cm^{-3}]	Hall Coefficient [cm^3/C]
	$n = -4.2 \times 10^{19} \sim -4.5 \times 10^{19}$	$R_H = -0.14$

1. n-Si, low oxygen pressure		
2. n-Si, high oxygen pressure	$n = -1.5 \times 10^{18} \sim -2.5 \times 10^{18}$	$R_H = -3.12$
3. p-Si, high oxygen pressure	$p = \sim +2.0 \times 10^{19}$ at Room Temperature	$R_H = +0.31$
4. p-Si, low oxygen pressure	$p = \sim +2.0 \times 10^{18}$ at Room Temperature	$R_H = +3.12$

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Table 2. A summary of the studied devices, growth conditions and IV characteristics results for n and p-Si/ZnO devices grown at 300 °C.

Growth Condition	Device Structure	
5. n-Si, low oxygen pressure		<ul style="list-style-type: none"> No forward bias current Reverse bias current is quadratic
6. n-Si, high oxygen pressure		<ul style="list-style-type: none"> Lower n doping of ZnO results in “soft” non-linear asymmetric IV characteristics
7. p-Si, high oxygen pressure		<ul style="list-style-type: none"> No reverse bias current Forward bias current is quadratic

<p>8. p-Si, low oxygen pressure</p>		<ul style="list-style-type: none"> Lower p doping of ZnO results in “soft” rectification
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