Effect of Annealing on Electrical Properties of Radio-Frequency–Sputtered ZnO Films

Y.I. ALIVOV,[1,2] X. BO,[1] S. AKARCA-BIYIKLI,[1] Q. FAN,[1] J. XIE,[1]
N. BIYIKLI,[1] K. ZHU,[1] D. JOHNSTONE,[1] and H. MORKOÇ[1]

1.—Department of Electrical Engineering, Virginia Commonwealth University, Richmond, VA, 23284. 2.—E-mail: yialivov@vcu.edu

We report on the electrical properties of ZnO films and devices grown on different substrates by radio-frequency magnetron sputtering. The films grown on c-plane sapphire were annealed in the range 800–1,000°C. The electron concentration increased with annealing temperature reaching 1.4×10^{19} cm^{-3} for 1,000°C. Mobility also increased, however, reaching its maximum value 64.4 cm^2/V · sec for 950°C anneal. High-performance Schottky diodes were fabricated on ZnO films grown on n-type 6H-SiC by depositing Au/Ni(300/300 Å). After annealing at 900°C, the leakage current (at –5 V reverse bias) decreased from 2.2×10^{-7} A to $\sim 5.0 \times 10^{-8}$ A after annealing at 900°C, the forward current increased by a factor of 2, and the ideality factor decreased from 1.5 to 1.03. The ZnO films were also grown on p-type 6H-SiC, and n-ZnO/p-SiC heterostructure diodes were fabricated. The p-n diode performance increased dramatically after annealing at 950°C. The leakage current decreased from 2.0×10^{-4} A to 3.0×10^{-7} A at –10 V reverse bias, and the forward current increased slightly from 2.7 mA to 3.9 mA at 7 V forward bias; the ideality factor of the annealed diode was estimated as 2.2, while that for the as-grown sample was considerably higher.

Key words: ZnO, radio-frequency (RF) sputtering, Schottky diode, heterojunction

INTRODUCTION

The semiconductor ZnO has a direct wide bandgap ($E_g \sim 3.3$ eV) and is attractive for optoelectronics applications due to the availability of ZnO bulk single crystals and a large exciton binding energy (~60 meV).[1] Because the growth methods and pathways for reproducible high-quality p-type ZnO films have not been developed yet, fabrication of n-p heterostructure devices by growing n-ZnO on other p-type materials, as well Schottky diodes on n-ZnO, could provide an alternative way for exploring and harnessing its advantages. This approach has received considerable attention lately, and there have been a number of reports on such devices.[1,2] The main factor influencing the properties of heterostructures is the close lattice match of the components. In this respect, 6H-SiC ($E_g \sim 2.9$ eV[3]) is a good candidate, since it has the same crystal structure (wurtzite) and relatively good lattice matching to ZnO with lattice mismatch of ~4%, and p-6H-SiC substrates are commercially available. Despite this, there are only a few reports on the growth on ZnO on p-SiC substrates.[4–7] Alivov et al.[4,5] reported on the growth of high-quality n-ZnO on p-6H-SiC heterostructures by plasma-assisted molecular beam epitaxy (MBE), and on their electrical and optical properties. Yuen et al.[7] used p-type 4H-SiC substrates for heteroepitaxial growth and fabricated n-ZnO/p-4H-SiC heterostructures by the cathodic vacuum arc technique. One of the widely used growth methods for ZnO is radio-frequency (RF) magnetron sputtering. Due to its low cost and simplicity, the RF sputtering method sometimes is preferable to other methods, and even though the crystal quality of such ZnO films is low compared to other methods, such as MBE, chemical vapor deposition, and pulsed laser deposition, the quality of RF sputtering films is acceptable for many applications. In this vein, growth and investigation of the properties of ZnO films grown by this method on different substrates is of considerable interest. In this work, the RF sputtering method was employed to grow n-ZnO on 6H-SiC substrates (both on n-type and p-type) and to fabricate

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Schottky and p-n heterojunction diodes, and the dependence of the properties of the fabricated devices on annealing of ZnO films was studied.

Naturally, the quality of the as-deposited RF-sputtered ZnO films is low and some form of post-growth annealing is imperative in order to improve the ZnO film quality. Because Hall measurements on layers grown on conductive layers are inaccurate and extraction of transport properties is convoluted, direct measurements of electrical properties of ZnO films grown on SiC substrates were attempted. For the purpose of transport measurements, ZnO samples were also grown on insulating (0001) sapphire substrates using the same conditions used for growth on SiC. The electrical properties were then studied as a function of annealing temperature. Previously, Özgür et al.[8] studied the dependence of optical properties of RF-sputtered ZnO films and their dependence on annealing temperature with the conclusion that such a treatment led to significant improvement of crystal and optical properties of the ZnO films. However, there were only a few reports on the electrical properties of the ZnO films grown by RF sputtering,[9,10] which constitutes the main topic of the present paper.

EXPERIMENTAL

Approximately 300-nm-thick ZnO layers were deposited directly on c-plane sapphire α-Al_2O_3 and 6H-SiC substrates at 750°C by RF magnetron sputtering in an Ar + O_2 ambient atmosphere. The chamber process pressure and plasma power were 4.20 mTorr and 100 W, respectively. Two different types of 6H-SiC substrate were used: (1) n-6H-SiC substrates with an electron concentration of 2.6×10^{17} cm^{-3}; (2) ~0.2-μm-thick p-type 6H-SiC layers with apparent hole concentration 1×10^{18} cm^{-3} grown on n-type n-SiC substrates. To study the effect of annealing on electrical properties of the layers, different pieces cut from the same ZnO/α-Al_2O_3 sample were annealed at 850°C, 900°C, 950°C, and 1,000°C for 1 h in air.

Mesa diode structures with a diameter of 250 μm were fabricated by conventional photolithography on ZnO layers grown on n-SiC and p-SiC substrates to fabricate Schottky and n-p heterojunction diodes. Schottky contacts to n-ZnO were made by vacuum evaporation of Au/Ni (300/300 Å). Ohmic contacts to n-ZnO, n-SiC, and p-SiC were formed by depositing Au/Al (300/300 Å), Au/Ti/Ni (300/300/300 Å), and Au/Al (300/500 Å) metal layers, respectively. Electrical properties of the diodes with as-grown and annealed ZnO layers were studied by employing room temperature (I-V), temperature-dependent current-voltage (I-V-T) characteristics and capacitance-voltage (C-V) measurements. The sample that was annealed at the optimum temperature was studied by temperature-dependent Hall measurements in the temperature range of 10–300 K. Optical properties of ZnO films were studied by photoluminescence (PL) at 10 K using the 325-nm line of a He-Cd laser.

RESULTS AND DISCUSSION

ZnO/α-Al_2O_3 Samples

The results of Hall measurements on ZnO/α-Al_2O_3 samples are summarized in Table I. The carrier density of the as-grown sample is 6×10^{16} cm^{-3} and increases with annealing temperature reaching 1.3×10^{19} cm^{-3} 950°C, where it almost saturates. Further increase in the annealing temperature to 1,000°C increases the carrier density only slightly. The mobility also increases from 4.6 cm^2/V · sec for the as-grown sample to 64.4 cm^2/V · sec after annealing at 950°C. However, at 1,000°C, the mobility decreases to 24 cm^2/V · sec. From these data, it is seen that the optimum annealing temperature for ZnO/α-Al_2O_3 samples is 950°C, at which temperature the mobility has the highest value, 64.4 cm^2/V · sec. These results are consistent with the results reported by Özgür et al. previously,[8] who found that samples annealed at 950°C had the highest near band edge photoluminescence emission intensity and smallest full-width at half-maximum. Therefore, it was concluded that 950°C is the optimum temperature for ZnO/α-Al_2O_3 grown by RF sputtering, which through the current study turned out to be the optimum annealing temperature for transport properties as well.

Similar results were found by Kim et al.,[9,10] who studied the effect of rapid-thermal annealing on the electrical, optical, and crystal properties of Al-doped ZnO layers grown by RF sputtering. However, the optimum annealing temperature was found to be 900°C in these reports. This may be explained by the fact the annealing temperature in these reports was changed by 100°C step, not by 50°C, as in the present work. Besides, different annealing times (3 min. and 1 h, respectively) may also be responsible for this difference.

Hall measurements were performed as a function of sample temperature for the sample annealed at 950°C. The temperature was scanned from 10 K to 300 K. The results of measurements are presented in Fig. 1. The carrier concentration changed slightly from 1.05×10^{19} cm^{-3} to 8.6×10^{18} cm^{-3} with temperature, or changed very slightly. The carrier mobility decreases with a decrease of temperature

Table I. Room-Temperature Carrier Concentration and Mobility of ZnO Films on Sapphire Substrate Annealed at Different Temperatures

Anneal Temperature (°C)	As Grown	850	900	950	1000
n (cm^{-3})	6×10^{16}	1.6×10^{17}	5.2×10^{18}	1.3×10^{19}	1.4×10^{19}
μ (cm^2/V · sec)	4.6	6.6	23.0	64.4	34.0

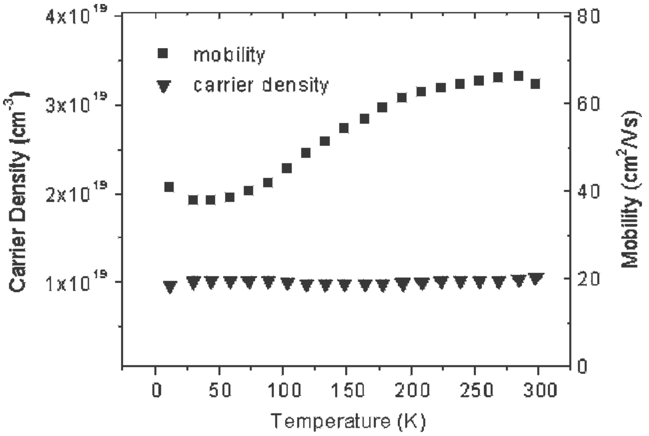

Fig. 1. Temperature-dependent Hall mobility and carrier concentration of the ZnO sample annealed at 950°C.

and, at 44 K, reaches the lowest value of 37.8 cm^2/V · sec. At 10 K, the mobility is 40.6 cm^2/V · sec. Such dependence of the mobility on temperature is indicative of carrier scattering at low temperatures being dominated by the charged centers. An activation energy was derived from Hall measurements considering single donor level and was found to be ~27 meV. A donor activation energy of ~30 meV was reported previously and attributed to interstitial Zn atoms or hydrogen impurities.[1]

Au/Ni/n-ZnO Shottky Diodes

Two different Schottky diodes were fabricated on ZnO layers grown on n-SiC substrates: one type using the as-grown ZnO layers and the other on ZnO annealed at 900°C for 1-h layers. For annealing temperatures higher than 900°C, the surface of the ZnO film became rough. In Fig. 2, I-V characteristics of the as-grown and annealed Schottky diodes are presented. A very strong rectifying diodelike behavior of the I-V characteristics was observed. The I-V curves so presented are representative of about 15 diodes measured for each sample. As seen from this figure, the diodes have very low leakage current equal to ~2.2 × 10^{-7} A for the as-grown sample and ~5.0 × 10^{-8} A for the sample annealed at 900°C at –5 V reverse bias. The forward currents at 5 V were 27 mA and 39 mA for the as-grown and annealed samples, respectively. The rectification factors were thus 1.2 × 10^5 for the as-grown sample and 8 × 10^5 for the annealed sample. The breakdown voltage, determined as the voltage at which an abrupt increase of reverse current occurred, was ~–20 V for the annealed sample and ~–12 V for the as-grown sample. The ideality factors were estimated as ~1.5 and ~1.03 for the as-grown and annealed samples, respectively, from the I-V plot using the diode equation:[11]

$$J = J_S\left[\exp\left(\frac{qV}{nKT}\right) - 1\right] \tag{1}$$

where J_s is the saturation current density, n the ideality factor, k the Boltzmann constant, and T the absolute temperature.

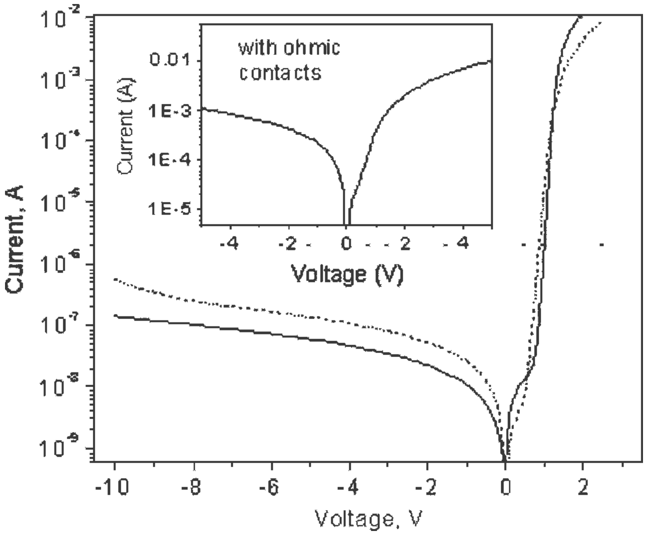

Fig. 2. Room-temperature I-V characteristics of Au/Ni/ZnO Schottky diodes fabricated on as-grown (dashed line) and annealed (solid line) ZnO layers. Inset: room-temperature I-V characteristics of n-ZnO/n-SiC heterostructures with ohmic contacts.

For comparison, an n-ZnO/n-SiC mesa structure with ohmic contacts on both ZnO and SiC was also fabricated using a piece of the sample from which the Schottky diode was fabricated. An I-V characteristic of the fabricated isotype heterostructure is shown in the inset of Fig. 2. The forward current at 5 V was 9.8 mA, and the reverse current at –5 was 1.06 mA, that is, the rectification factor was around ~10. From this, we conclude that the rectifying behavior in our structures with Schottky contacts comes mostly from the Schottky barrier, not from the n-ZnO/n-SiC heterostructure.

The C-V profiling of the diodes was performed in both as-grown and annealed samples, and the carrier concentration in ZnO was found to be 9.0 × 10^{17} cm^{-3} for the as-grown sample and 1.02 × 10^{18} cm^{-3} for the annealed sample. The carrier density profile was very uniform in both cases. The carrier concentrations in the as-grown ZnO layers grown on SiC substrates and on α-Al_2O_3 are substantially different. The possibility that the differences in carrier density in both cases result from different lattice matching conditions (lattice mismatches of ZnO with 6H-SiC and α-Al_2O_3 are ~4% and ~16%, respectively) should be established from further research.

The Schottky barrier height was derived from temperature-dependent I-V measurements spanning 80–600 K. The I-V-T plot for the annealed sample is shown in Fig. 3. The saturation current in Eq. 1 is determined by

$$J_S = A^*ST^2\exp\left(-\frac{\phi_B}{kT}\right) \tag{2}$$

where A* is the effective Richardson constant, S the Schottky contact area, and Φ_B the barrier height. The slope of the plot $\ln(J_S/A^*ST^2)$ versus 1/kT gives the Schottky barrier height Φ_B. The plot for both

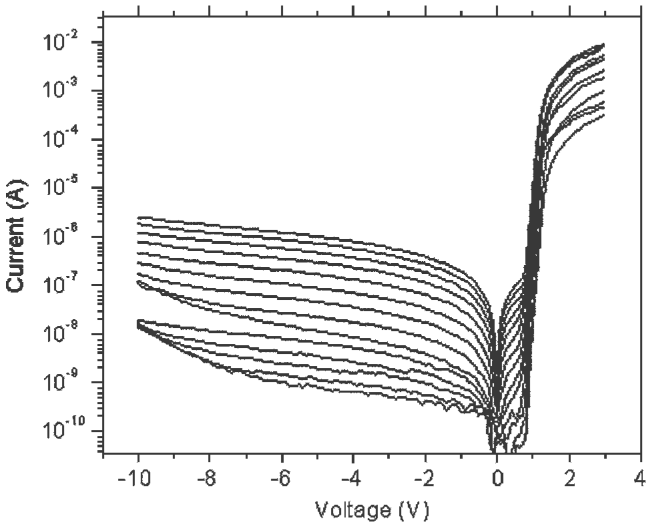

Fig. 3. Temperature-dependent I-V characteristics of Schottky diodes obtained on an annealed n-ZnO/n-SiC sample. The temperature ranged from 130 K to 600 K.

samples is presented in Fig. 4. The slopes for both as-grown and annealed samples were found to be almost the same and equal to 0.25 eV.

A comparison of I-V characteristics of Schottky diodes on the as-grown and annealed ZnO layers indicates that the properties of diodes after annealing are greatly improved; the leakage current is reduced by a factor of 4, and the forward current is increased by a factor of 2. The improvement is also seen from the ideality factors of ~1.5 and ~1.03 for the as-grown and annealed samples, respectively. This improvement most likely comes from an increase of the crystal quality of ZnO films after annealing. In the as-grown sample, there may be higher density of surface states acting as generation centers or assisting in tunneling leakage compared to that of the annealed sample. As we have seen in the case of sapphire, the ZnO film crystalline properties improved significantly after annealing.

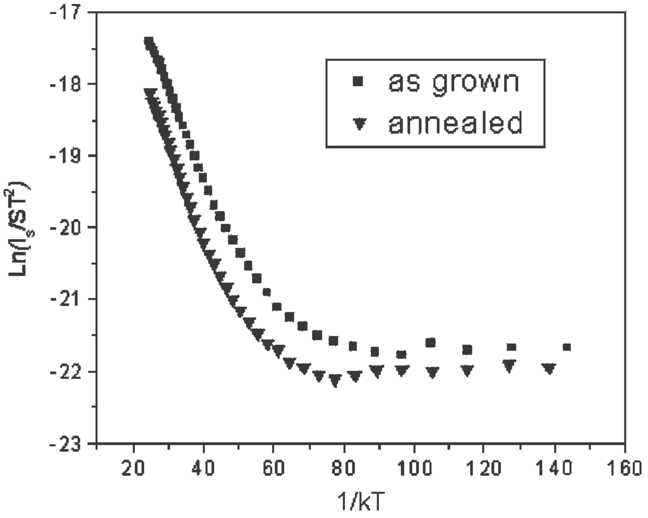

Fig. 4. Arrhenius plot of the saturation current versus inverse temperature. The slope is used to obtain a barrier height of 0.25 eV for both the as-grown and annealed diodes.

n-ZnO/p-SiC Heterostructure Diodes

ZnO films were also deposited on p-SiC substrates by RF sputtering to attain n-ZnO/p-SiC heterostructures. The influence of annealing at 950°C on electrical properties of n-ZnO/p-SiC heterostructures was studied. Unlike n-SiC substrates, ZnO films on p-type SiC substrates were stable to 950°C, and the film surface morphology even improved after annealing. It is possible that this dependence on the substrate polarity is due to different doping and different defect structures, since the formation energies of defects is exponentially dependent on the Fermi level position.

Room-temperature I-V characteristics of the as-grown and annealed n-ZnO/p-SiC heterostructures are shown in Fig. 5. As seen from the figure, the heterojunction properties improved dramatically after annealing. The leakage current decreased from 2.0×10^{-4} A to 3.0×10^{-7} A at –10 V reverse bias, and forward current also increased, albeit slightly, from 2.7 mA to 3.9 mA at 7 V forward bias. The breakdown voltage determined as the voltage at which an abrupt increase of reverse current occurred was more than –50 V for the annealed sample, while the one of the as-grown sample was ~–20 V. The threshold voltage was 2 V for annealed and 4.1 V for the as-grown samples. The ideality factor of the annealed diode was estimated as 2.2 while that for the as-grown sample was more than 5.0. Ideality factors greater than 1 indicate conduction due to point defect mediated processes.[12] This significant improvement of the diode properties following annealing definitely results from an increased crystal quality of ZnO, such as reduction of interface state density between ZnO and SiC.

The temperature-dependent I-V characteristics were also measured on the annealed sample in the temperature range 130–600 K, and the results are presented in Fig. 6. As seen from the figure, the

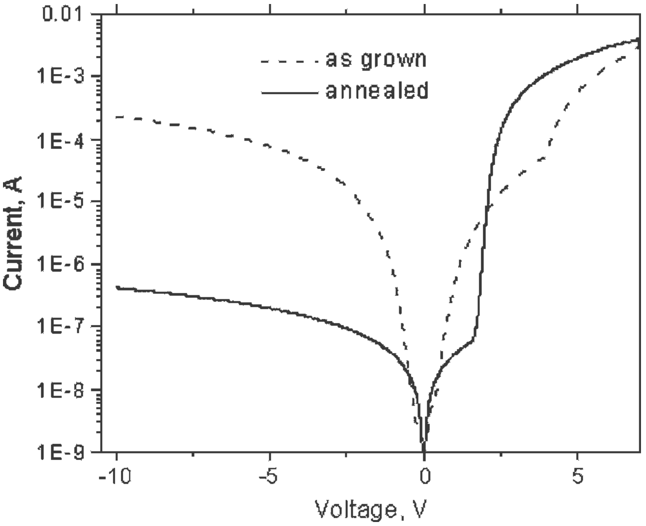

Fig. 5. Room-temperature I-V characteristics of the as-grown and annealed n-ZnO/p-SiC heterostructures. Annealing improves the n-ZnO/p-SiC heterojunction significantly.

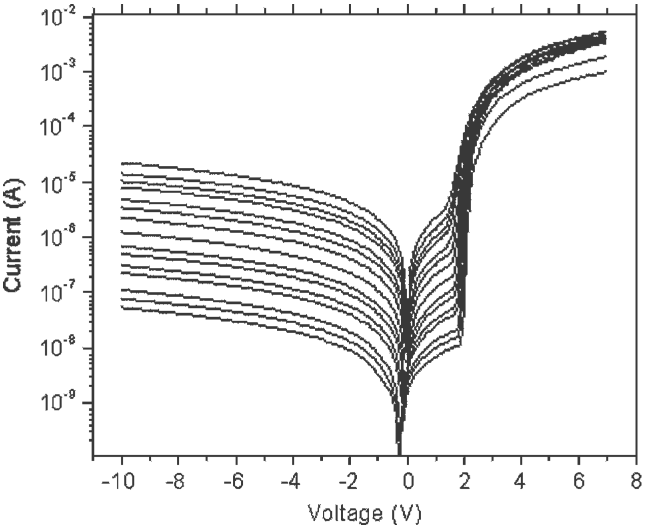

Fig. 6. Temperature-dependent I-V characteristics of n-ZnO/p-SiC heterostructure with the as-grown and annealed ZnO layers. The temperature ranged from 130 K to 600 K.

leakage current decreased by more than three orders when the temperature is reduced from 600 K to 130 K while maintaining the overall shape of the I-V characteristics. An activation energy was estimated from the Arrhenius plot (not shown) and it was found to be ~0.165 eV at 2.5 V forward voltage. This value is very close to the activation energy found in n-GaN/p-SiC heterojunctions, 0.156 eV,[13] where the activation energy was attributed to the Al acceptor level in 6H-SiC.

In summary, ZnO films were grown on c-plane sapphire and n-type and p-type 6H-SiC substrates by RF sputtering, and Schottky and n-ZnO/p-SiC heterojunction diodes were fabricated. The electrical properties of the films and the devices have been studied as a function of annealing temperature. A significant improvement in the electrical parameters of the films and device performance has been observed after annealing. This work demonstrates that useful rectifying properties can be obtained from RF-sputtered ZnO.

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