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Citation: Journal of Applied Physics 117, 155703 (2015); doi: 10.1063/1.4918721
View online: http://dx.doi.org/10.1063/1.4918721
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Hot probe measurements of n-type conduction in Sb-doped ZnO microwires

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(Received 9 December 2014; accepted 10 April 2015; published online 20 April 2015)

The charge carriers type in antimony-doped ZnO (ZnO:Sb) microwires was studied using the hot probe technique. The wires were grown by a simple thermal evaporation method. Contrary to the expected p-type behavior reported for Sb doped ZnO thin films and nanowires, our hot probe measurements of representative single Sb-doped ZnO wires show a stable n-type behavior. The hot probe technique is a simple and efficient way to determine the charge carrier type from thermoelectric measurements on a single semiconductor wire and could offer an alternative to Hall effect measurements. The technique relies on creating a temperature gradient across the wire (i.e., heating one side of the wire relative to the other) and monitoring the resulting open-circuit voltage between the two ends. We also performed Energy Dispersive X-ray Spectroscopy measurements to identify and monitor the elemental composition in these ZnO:Sb wires. © 2015 AIP Publishing LLC.

[http://dx.doi.org/10.1063/1.4918721]

I. INTRODUCTION

ZnO is an extensively studied semiconductor due to its versatile properties.1,2 It has a wide band gap of 3.37 eV, a large exciton binding energy of 60 meV, high electron mobility and thermal conductivity, and a large piezoelectric constant. The main obstacle in the development of ZnO-based devices is the difficulty in achieving a reliable, stable, and low-resistivity p-type doping. This has been attributed to the self-compensating effect introduced by the unintentional native donor defects, unintentional incorporation of hydrogen donors, low solubility of acceptor dopant, and deep acceptor levels.3,4 In order to establish reliable p-type doping of ZnO, special attention has been focused on the group-V elements, including N, P, As, and Sb, due to the possibility of creating p-type conduction. Although p-type behavior has been reported by different research groups for these doped elements, especially Sb-doped ZnO (ZnO:Sb),5-11 stability and reproducibility of the Sb doped p-type conductivity are still under question. Moreover, the electrical properties change from p-type to n-type, as the Sb content decreases in the ZnO:Sb thin films.12 The main point here is that the ionic radii of these elements are much larger than that of oxygen and hence it is very difficult to dope these elements on O sites to produce stable p-type behavior in ZnO.13 In the Sb doped ZnO, the (Sb\textsubscript{Zn}-2V\textsubscript{Zn}) complexes create shallow acceptor levels and are postulated to be responsible for p-type conductivity. Although this model could explain the observed p-type behavior in many ZnO:Sb thin films and nanowires (NWs), the formation of these complexes came under question.14 Recently, Sb was found to also act as a donor (n-type) in ZnO films allowing control of the electron concentration in a wide range from 10\textsuperscript{16} to 10\textsuperscript{19} cm\textsuperscript{-3}.15 Optical evidence for an n-type behavior was also recently reported for ZnO:Sb (NWs).16 It is well known that the conductivity type and stability of ZnO are influenced by the material structure and its deposition method.

The growth of one dimensional ZnO structures is important in developing ZnO based dye-sensitized solar cells,17,18 ZnO nanorods and NWs,19 nanoflowers,20 nanoribbons and nanobelts,21 etc., which are promising for nanoscale electronic and optoelectronic devices. For these applications, predictable, stable, and reproducible electronic properties in 1D nanostructures are critical factors.22 So far, several studies demonstrating p-type ZnO NWs have been reported19,22-27 using different, and in some cases, advanced fabrication methods. Yet these techniques were not widely used and did not give stable, commercially viable optoelectronic devices. In the case of phosphorus-doped ZnO NWs, the p-type conduction was unstable and changed to n-type after 2 months of storage in air.24 For the nitrogen-doped ZnO NWs, the surface adsorption was found to have a significant effect on the transport properties of these NWs.22 ZnO:Sb NWs, on the other hand, showed some success making them a promising candidate for future electronic and optoelectronic devices. The chemical and electrical stability and reproducibility of both the ZnO:Sb thin films and NWs are still under question and require more investigation.

In this paper, we report on the chemical and electrical stability of ZnO:Sb single wires, grown by a simple and low cost, non-vacuum thermal evaporation method that was previously developed by our group.18 The electrical properties of the individual ZnO:Sb wires were monitored using the hot (or thermoelectric) probe technique. The chemical stability was monitored using Energy Dispersive X-ray Spectroscopy (EDX) measurements. The overall results show a stable n-type semiconductor behavior, consistent with recent reports on...
ZnO:Sb NWs. The results were discussed in terms of the Sb dopant mechanism and its lattice position in the ZnO host.

II. EXPERIMENTAL PROCEDURES

ZnO:Sb wires were grown in an alumina crucible by a simple, catalyst-free, and low cost thermal evaporation process. Zn powder (99.995% purity, Aldrich) was used as Zn source and antimony trioxide (99.999% purity, Aldrich) was used as antimony source. Zn and Sb2O3 powders were mixed in various weight ratios and uniformly mixed in a shaker for 30 min at 200 rpm. The well-mixed powder was poured into the crucible with a lid and loaded in an oven for heating at 900 °C for 2 h. Upon natural cooling of the crucible to room temperature, the ZnO:Sb NWs were obtained.

Scanning Electron Microscopy (SEM) was used to characterize the surface morphology of the wires and EDX was used to determine the elemental composition. For the electrical measurements, we used the hot or thermoelectric probe method since it was quite difficult to attach contacts to the sides of a wire and perform Hall effect measurements on individual ZnO:Sb wires. In this method, it is quite easy to determine whether a semiconductor sample (in our case, the sample is a single ZnO:Sb wire) is n-type or p-type by using a heated probe and an ammeter. The conductivity type is determined by the sign of the thermal electromotive force or Seebeck voltage generated by the temperature gradient. It also offers an approximate probe to estimate the concentrations of majority charge carriers and their dynamics parameters. The strength of the hot probe method is that it is a direct and simple way to probe the electrical properties of individual wires.

For these measurements, we designed a simple four-point-probe setup. As shown in Fig. 1(a), a selected individual Sb-doped ZnO wire is connected between the hot probe and the cold probe and the electric circuit is closed by connecting the hot probe through an external resistor to the positive terminal of a sensitive digital voltmeter, while the cold probe is connected to the negative terminal. The heat causes charge carriers in the sample to move away from the hot side as the heat creates an increased number of higher energy carriers, which then thermally diffuse away from the heat contact point as illustrated in Fig. 1(b). So, thermal gradients generate currents in the semiconductor sample and cause a voltage difference across the sample.

For a p-type semiconductor, a positive voltage (an increase in the voltage) readout is obtained when the heat source is placed on the positive terminal while a negative voltage (a decrease in the voltage) readout is obtained for a n-type semiconductor. An alternative view and a simple explanation for this experiment is that for n-type semiconductors, electrons diffuse from the hot to the cold region setting up an electric field that opposes the diffusion. The electric field produces a positive potential that is detected by the voltmeter with the hot probe. Analogous reasoning leads to the opposite potential for p-type semiconductors.

Information on the thermoelectric power or Seebeck coefficient can be also extracted from knowing the temperature gradient between the hot probe and the cold probe. Our measurements were done both in zero applied voltage and in non-zero voltages, as well as using standard DC and AC techniques.

III. RESULTS AND DISCUSSION

Figure 2 shows SEM images of as-grown ZnO:Sb wires. Three different shapes of wires were formed during the growth. Wires of length exceeding 2 cm and a diameter of 5–8 μm are formed on the top (cover) of the crucible (Fig. 2(a)) at a ratio of 1:1. No wires are formed at Zn:Sb2O3 ratio of 1:0, because the pure Sb2O3 is used as both oxygen source and dopant. Because of the space limitation, wires with a length of about 5 mm and a diameter of 3–5 μm are formed around the inside walls of the crucible (Fig. 2(b)), and about 2 mm long wires with diameters of 0.5–1 μm are formed at the bottom of the crucible (Fig. 2(c)). It is remarkable that our extremely simple process reproducibly generates high-quality, about 1-in.-long ZnO:Sb micro-wires that are comparable to the ones produced by the more expensive and elaborate advanced high vaccum growth techniques. Higher magnification SEM images are shown in Fig. 2(d).

To check the chemical stability of the as-grown wires, we focused on a few representative wires and performed EDX measurements to determine their element compositions. These individual wires were chosen to represent the different shapes of wire that are formed during the growth. In the absence of EDX reference standards, wires with comparable dimensions are chosen and aligned close to each other, so one of them is taken as a reference standard during the EDX measurements. Figure 3(b) shows the EDX spectrum for the same ZnO:Sb wire, taken one day after the wire growth. The SEM image for this specific wire is presented in Fig. 3(a). The peaks around 3.6 keV in the EDX spectra clearly show the existence of the antimony. This specific wire was found to contain between 5 and 7 at. % Sb relative to ZnO. The EDX measurements were repeated at different times and the spectra were taken twice a week over a period of two months (data are not shown). In fact, this ratio was found to be almost the same over a period of two months. The same measurements were done on other representative ZnO:Sb wires and the results showed similar behavior, where each of the individual wires was found to contain between 5 and 7 at. % Sb relative to ZnO, indicating chemically stable ZnO:Sb wires. This finding is in good agreement with other recent reports on the ZnO:Sb NWs, which reported about 5 at. % Sb relative to ZnO.
developed a reproducible method to grow Sb doped ZnO (ZnO:Sb) wires with Sb doping to 5 at. %\textsuperscript{18,32} In our previous work,\textsuperscript{18,32} we studied the composition of the fibers using Electron Backscattered Diffraction (EBSD), SEM, EDX, and XRD. We found that the fibers were composed of two parts: the Sb-rich part and Zn-rich part. The Zn-rich part with about 4–5 at. % of Sb is Sb doped ZnO and it exists as the main stem of the wires. The EDX in this work was also measured at the main stem of the wires because the main stem provides the path for the electron flow during all the resistance measurements carried in this study. The Sb-rich part exists as small crystals at the surface of the Zn-rich stem and consists of two compounds: ordonezite (ZnSb$_2$O$_6$) and zinc antimony oxide (Zn$_7$Sb$_2$O$_{12}$).\textsuperscript{18,32}

Although the doping mechanism of Sb remains controversial, our EDX data taken at the main stem of the wires suggest that Sb mainly occupies Zn sublattice positions as we can see from the Sb atomic percentage ratio relative to Zn and O. Zn atoms were found to have about 41–43 at. % while O atoms were found to have about 51–53 at. % of the total composition. Other research groups reported the same conclusion, which indicates that Sb atoms have likely doped into the Zn sites in ZnO:Sb NWs.\textsuperscript{16,34} In this case, Sb is expected to act as a donor in the ZnO host. However, we cannot decisively conclude that the Sb atoms act as donors in these as-grown ZnO:Sb wires, since these wires have mixed phases.

We used the hot-probe method to determine the conductivity and the charge carriers type. In our hot-probe measurements, a standard p-type (Ga,Mn)As semiconductor thin film sample is used as a reference to prevent ambiguity in the results. The left column in Fig. 4 shows both the measured voltage difference across the (Ga,Mn)As sample and the current through the sample, which is created due to the free charge-carrier diffusion because of the heat flow. The measurements were taken at different common temperatures of the hot and the cold probes as a function of the heating time. A copper block was heated up to the required temperature and then placed in contact with either the positive or negative probes (terminals). Measurements were taken for about 300 s. Data recording starts with both terminals at room temperature for about 10 s, then a hot copper block is placed in direct thermal contact with one of the terminals for about 170 s, and then removed and the same probe is cooled down...
FIG. 4. Left column: Hot probe characteristic curves for the p-type (Ga,Mn)As at different temperatures. (a) Measured voltage difference across the (Ga,Mn)As sample when the heat is applied at the positive probe (terminal), (b) measured current through the sample when the heat is applied at the positive probe, (c) measured voltage difference across the (Ga,Mn)As sample when the heat is applied at the negative probe, and (d) measured current through the sample when the heat is applied at the negative probe. Right column: Hot probe characteristic curves for the ZnO:Sb wires at different temperatures. (e) Measured voltage difference across the sample when the heat is applied at the positive probe (terminal), (f) measured current through the sample when the heat is applied at the positive probe, (g) measured voltage difference across the sample when the heat is applied at the negative probe, and (h) the measured current through the sample when the heat is applied at the negative probe. The hot probe measurements for ZnO:Sb wires showed exactly an opposite behavior compared to the p-type (Ga,Mn)As semiconductor.

to room temperature, by attaching a cold copper block to it. When the heat is applied at the positive probe (terminal), these curves show a positive voltage measured between the two probes (across the sample) and a positive current through the sample (in the closed loop circuit) as shown in Figs. 4(a) and 4(b). When the heat is applied at the negative probe (terminal), a negative voltage is measured across the sample and a negative current in the closed loop circuit is observed (see Figs. 4(c) and 4(d)). These curves represent the typical hot probe characteristics of the p-type (Ga,Mn)As semiconductor. By increasing the hot probe temperature, the measured voltage between the two probes also increased.

A three-step process can be observed in the hot probe measurements, related to three different regions observed in the hot probe characteristic curves as shown and labeled in Fig. 4(a). First, the heated probe excites free charge carriers and creates an increased number of carriers with higher kinetic energy and then these energetic carriers will thermally diffuse away from the heat contact point and result in current increase, as seen in the initial part of hot probe curves (region I). As a result, an electric field is created between the two probes. At the same time, the cold probe starts warming up. Both the created electric field and the increased temperature of the cold probe start to prevent the diffusion process and a steady state is reached as seen in the middle part of hot probe curves (region II). Once the heated source is removed, a recombination process of the excited charge carriers happens and results in the reduction of measured current, as seen in the final part of hot probe curves (region III). We determined the hot side temperature by placing a relatively large copper block of known temperature on the terminal. The temperature of the copper block is that of the hot plate that is used to heat it. We just “felt” the temperature of the cold plate by hand as it heated up. For the qualitative analysis of identifying the conduction type and obtaining an approximate estimation of the carriers concentration in ZnO:Sb wires, our very basic measurement technique is found to be sufficient. The smoothness of these hot probe characteristic curves indicates a uniform impurity concentration in the as grown Sb-doped ZnO wires.

Hot probe characteristic curves for a representative ZnO:Sb wire are presented in the left column of Fig. 4. The hot probe measurements showed exactly an opposite behavior compared to the p-type (Ga,Mn)As semiconductor, which indicates that the as-grown ZnO:Sb wires are n-type. This observed behavior is consistent with recent reports, which showed n-type behavior for both Sb-doped ZnO films grown by plasma-enhanced molecular beam epitaxy and Sb-doped ZnO NWs grown using MOVPE with a wide range of dopant concentration. In Figs. 4(f) and 4(g), a negative voltage difference across the Sb-doped ZnO wire and a negative current through the wire were measured when the heat is applied at the positive probe, while a positive current and voltage were measured when the heat is applied at the negative probe as seen in Figs. 4(h) and 4(e). These measurements were done at various temperatures. By increasing the hot probe temperature, both the measured voltage across the wire and the measured current through the wire also increased. This is expected as by increasing temperatures, greater thermal gradients generate more currents. Similar hot probe measurements were done on other Sb-doped ZnO wires with different lengths and similar results were obtained. In fact, these measurements were repeated over a period of two months and almost the exact behavior with n-type conduction was found, indicating electrically stable ZnO:Sb wires.

Although our electrical hot probe measurements showed n-type behavior for these ZnO:Sb wires, we are not able to completely rule out the existence of some compensating defects (possibly Sb on oxygen sites and/or point-defect complexes involving SbO, and SbZn2VZn). The formation of these complexes is less likely in the as-grown ZnO:Sb wires. In addition, the formation of these complexes is highly
dependent on annealing conditions, which is why growing stable p-type ZnO:Sb wires seems to be a difficult task, as one must control the annealing conditions precisely. Since Sb has low acceptor-ionization energies, Oxygen-rich growth or different annealing conditions are required to obtain p-type in ZnO:Sb.\textsuperscript{35} Post-growth oxygen annealing has been reported to enhance hole concentration and even switch the n-type to p-type behavior in ZnO:Sb thin films.\textsuperscript{15,35} With other dopant elements in ZnO, for example, K, the conductivity type was also found to switch from n-type to p-type by varying the annealing conditions.\textsuperscript{36} In our study, the as-grown ZnO:Sb wires were obtained upon natural cooling of the well-mixed powder from 900 °C to room temperature, with no further annealing.

On a fundamental level as we discussed above, thermal gradients generate currents in a semiconductor as the hot excited charge carriers begin diffusing away from the hot probe. The majority carrier currents for n and p-type materials are given by Eq. (1) (Ref. 29)

\[
J_n = -q\mu_n P_n \frac{dT}{dx}; \quad J_p = -q\mu_p P_p \frac{dT}{dx},
\]

where \(P_n < 0\) and \(P_p > 0\) are the differential thermoelectric powers, and \(x\) is the distance between the hot probe and the cold probe. The thermoelectric power (also known as Seebeck coefficient) can be thought of as a current generator, and can be obtained from the measured voltage differences between the hot and cold probes at different temperatures. The slope of the relation between the measured steady state voltages versus temperature is a direct measure of the Seebeck coefficient. The temperature influence on the obtained curves showed in Fig. 4(a) is used to calculate the Seebeck coefficient for the (Ga,Mn)As sample, and it was found to be about \(-0.01\) mV/K.

For the ZnO:Sb wires, the Seebeck coefficient is calculated from the data shown in Fig. 4(f), and it is found to be about \(-0.2\) mV/K. Different Seebeck coefficient values ranging from \(-0.2\) to \(-0.45\) mV/K were reported for ZnO depending on the doping elements.\textsuperscript{37,38} Similar measurements were done on other representative ZnO:Sb wires, with different lengths and the results showed similar values for the Seebeck coefficient.

In Fig. 5(a), the initial part of the hot probe characteristic curves for the same ZnO:Sb wire is shown at different times measured at 100 °C of the hot probe. The data taken one day after the wire growth are shown in blue circles, and the measurements taken after thirty days are shown in red squares. Almost the exact behavior was observed on both days. At 100 °C, the time interval between the initial state and the steady state is about 24 s and the measured voltage at the steady state is about 16.9 mV. In fact, we repeated these measurements over a period of two months (the data are not shown) and got almost the exact behavior. This indicates that the as grown ZnO:Sb wires are electrically stable with n-type behavior.

For completeness, the temperature dependence of the electrical resistivity of a ZnO:Sb single wire is measured using Quantum Design Physical Property Measurement System (PPMS). The electrical resistivity measurements were done with the standard four-point AC method. The \((\rho-T)\) data are presented in Fig. 5(b), which shows a typical behavior of a semiconductor material, where an enhancement in the resistivity is observed with decreasing temperature. At room temperature, the resistivity of the as-grown ZnO:Sb wires is found to range from 20 to 40 Ω cm. The resistivity measurements were repeated for different representative wires with different sizes and lengths. Almost all these representative wires showed similar resistivity values with a similar order of magnitude. In addition, the resistivity measured by PPMS is comparable to the resistivity measured by the hot-probe method. The data presented in Fig. 4 are taken in zero applied voltage, but extra hot probe measurements (data are not shown) are taken also in different applied voltages to compare the resistivity.

For the representative wire shown in Figure 5(b), the resistivity is found to be about 30 Ω cm at room temperature. The estimated majority charge carriers concentration based on this value ranges from \(1 \times 10^{15}\) cm\(^{-3}\) to \(4 \times 10^{16}\) cm\(^{-3}\), depending on the value of the electron mobility in the ZnO:Sb wire and assuming negligible acceptor compensation. Different values, ranging from 5 to 110 cm\(^2\)V s, were reported for the electron mobility in ZnO and in ZnO:Sb.\textsuperscript{9,15,39} The calculated majority charge carriers concentration in the above range is too low for Sb doping to 5 at. % if all Sb atoms are acting as donors. Here, we conclude that not all Sb atoms are acting as donors. Although a part of the Sb atoms seems to occupy Zn sublattice positions and act as donors, some of these Sb atoms might form Sb\textsubscript{Zn}-2V\textsubscript{Zn} acceptor complexes and produce p-type conductivity. The dual effect of the Sb doping in ZnO seems to be responsible for producing high resistivity wires and low charge carrier concentrations. Other

![FIG. 5. (a) Initial part of the hot probe characteristic voltage difference curves for the ZnO:Sb wires at different times and (b) temperature dependent of the electrical resistivity measurements of a single Sb doped ZnO wire.](image-url)
effects, such as Sb on oxygen sites and/or point-defect complexes involving $\text{Sb}_0$ and $\text{Sb}_{2\text{Zn}}-2\text{V}_{\text{Zn}}$, could be responsible for the compensation of the donors as well. These resistivity measurements and calculations were repeated on different individual wires over a period of two months and similar results were found. This is an evidence that the ZnO:Sb wires are stable. In addition, we extended our measurements to investigate any possible Schottky barriers behavior at the metal–semiconductor interface. The DC I–V measurements (data are not shown) on a single ZnO:Sb wire at room temperature showed a pure Ohmic (linear I-V) behavior and confirm the n-type behavior nature of the majority carriers in the as grown ZnO:Sb wires.

IV. CONCLUSION

In conclusion, the hot probe technique is successfully used to estimate the conductivity and to identify and monitor the conduction type in Sb-doped ZnO wires. These wires were grown by a novel thermal evaporation method. The hot probe characteristic curves never changed behavior over a period of two months. The overall results on single Sb-doped ZnO wires show a stable n-type behavior. In addition, the elemental composition of these ZnO:Sb wires was studied using EDX measurements. The high resistivity of the wires suggests the presence of mixed phases rather than a homogeneous single phase of Sb-doped ZnO.

ACKNOWLEDGMENTS

We would like to thank the Jordanian-American commission for educational exchange (Fulbright) for arranging Dr. A. M. Alsmadi research visit to Miami University. The authors are grateful for funding supports from agencies of Colgate-Palmolive Grant for Alternative research (Society of Toxicology), U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contracts No. DE-FG02-07ER46389 and DE-SC0010800, Miami University Committee Faculty Research Grant and Miami University Research Incentive Grant.