Lateral Heterogeneities in ZnO electrodeposits and their Impact on Electrical and Optical Properties

Tiju Thomas, a Shawn Chatman, b Jake Wells, Lisa Emberley, Muhammad Asim Rasheed, c and Kristin M. Poduska a,z

Department of Physics and Physical Oceanography, Memorial University of Newfoundland, St. John’s, NL A1B 3X7, Canada

We demonstrate that ZnO/metal junctions, produced by a commonly used electrochemical oxidation procedure, are prone to lateral (two-dimensional) heterogeneities. These heterogeneities are not apparent in bulk structural measurements (such as X-ray diffraction data), but are evident in the electrodeposits’ electrical (current–voltage) and optical (luminescence) properties. The spatial variations in the ZnO films are related to incomplete oxidation during the final stage of their multi-step electrochemical formation process. Support for this explanation comes from a surprisingly simple circuit that accurately models the current-voltage response as a combination of resistive (Ohmic) and rectifying (Schottky) junction contacts at the ZnO/substrate interface.

Electrochemical synthesis of metal oxide materials is an expedient way to produce thin films of many functional semiconductors for potential device applications, and it has received increasing attention during the last two decades. In the case of ZnO formation, the most widely used method of electrochemical synthesis involves using an applied potential to produce an interfacial pH change in the immediate vicinity of the working electrode surface that triggers ZnO formation. This complex process has been studied and utilized extensively, and is seemingly well understood. Control over ZnO electrodeposition (Princeton Applied Research 273A). Since rectification behavior is a key part of this work, for each sample we confirmed that the rectification occurs only at the growth interface between the substrate and the ZnO electrodeposits, and that the contact electrodes (stainless steel A286, McMaster-Carr) used for the measurements do not introduce any rectification on their own. Representative data is shown in Fig. 1a,b. Fluorescence microscopy images (Leica DM 2500) were obtained under Hg lamp illumination and analyzed with ImageJ software.

Results and Discussion

In principle, metal-semiconductor junctions can yield either purely resistive (Ohmic) or purely rectifying (Schottky) current-voltage (I–V) relations. Based on representative I–V responses and bulk structural information from XRD data from earlier studies, it would appear that electrodeposited ZnO junctions can be of similar quality to Schottky rectifiers prepared by other synthesis methods. In this study, we probed the I–V responses of rectifying ZnO electrodeposits with a finer spatial resolution (~1 mm²) to come to a rather different conclusion. We find that there is a disconcerting amount of variability in the rectification responses, and that rectification values among different (~1 mm²) regions of the same (8 mm diameter) sample can show as much variation as occurs among different samples that were prepared under identical conditions. These findings suggest that there are lateral heterogeneities in the electrodeposits on sub-millimeter length scales.

We find that, unlike analyses presented in many previous studies of ZnO rectifying junctions (prepared by a variety of methods, including electrodeposition), the samples described here have electrical responses that are best described with an equivalent circuit that includes both resistive and rectifying components:

\[ I = \frac{V}{R_s} + aA T^2 \exp \left( -\frac{\Phi_B}{k_B T} \right) \exp \left( \frac{V}{nk_B T} \right). \]

Two-component model, shown schematically in the inset for Fig. 1b, assumes that current flows in parallel through both a shunt resistance (R_s) and a Schottky rectifier (characterized by an exponential current increase for larger values of forward applied voltage V). The magnitude of the current I through the junction also depends on the junction area a, Richardson’s constant (A = 32 A cm⁻² K⁻²), the Schottky barrier voltage Φ_B, Boltzmann’s constant k_B, and a Schottky ideality factor n. An example of this model applied to experimental data is shown in Fig. 1b.

The two-component equivalent circuit given in Eq. 1, although simple, is not obvious and has not been applied to electrodeposited thin films in the past. Other models proposed for heterogeneous

References

1. Electrochemical Society Active Member.
2. Present address: Materials Research Centre, Indian Institute of Science, Bangalore 560012, India.
3. Present address: Pacific Northwest National Laboratory, Geochemistry Group, P.O. Box 999, Richland, Washington 99352, USA.
4. Present address: Department of Metallurgy and Materials Engineering, Pakistan Institute of Engineering and Applied Sciences, Islamabad 45650, Pakistan.
5. E-mail: kris@mun.ca

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metal-semiconductor interfaces have introduced multiple components for accurate fits to experimental data. For our electrodeposited junctions, shunt resistances are relatively large (≥ 0.5 kΩ) which suggests that $R_s$ corresponds to a semiconducting – rather than a metallic – conduction pathway. In other words, each electrodeposited film contains a mixture of both Ohmic and Schottky ZnO/substrate junctions. High Schottky ideality factors ($n > 10$) and relatively large reverse currents are also consistent with the dual conduction pathway proposed with this equivalent circuit.

Fig. 1(c,d) shows the range of extracted values for the shunt resistance ($R_s$) and Schottky barrier voltage ($\phi_B$) as a function of deposition potential. Despite the fact that Eq. 1 describes the experimental I–V data very well, $R_s$ and $\phi_B$ vary significantly in different areas of a given sample, and among samples that are identically prepared. Thus, there are significant lateral heterogeneities in the electrical responses of ZnO electrodeposited junctions.

An interesting correlation exists between the electrical rectification and optical luminescence properties since both show evidence of lateral heterogeneity. ZnO is known to support a range of intrinsic and extrinsic defects that can lead to luminescence peaks in the blue, green, and yellow wavelength regions. Fig. 2a is a representative fluorescence microscopy image of a ZnO electrodeposited in full color (red-green-blue, RGB), showing a predominant yellow luminescence with isolated regions of blue intensity. The scattered distribution of the blue intensity in these electrodeposits is much different than the more uniform luminescence displayed by ZnO that has a purely Ohmic contact with the same kind of stainless steel substrate (Fig. 2b). Using the distribution profile of the blue luminescence intensity as a indicator of lateral heterogeneity within the ZnO film, we applied standard thresholding and masking techniques to images such as Fig. 2c (which is a gray-scale representation of a single channel from an RGB image (shown here for the blue channel of the RGB image in (a))). When the experimental data (thick red line) are fit (thin black line) to the equivalent circuit shown in the inset, a shunt resistance ($R_s$) is fit (thin black line between 0.01 and 1.4 V) to the equivalent circuit. For our electrodeposited junctions, shunt resistances are relatively large ($≥ 0.5 kΩ$). High Schottky ideality factors ($n > 10$) and relatively large reverse currents are also consistent with the dual conduction pathway proposed with this equivalent circuit.

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Figure 1. (Color online) Representative I–V data for (a) a purely resistive (Ohmic) contact between electrodeposited ZnO and its steel substrate and (b) a rectifying (Schottky) response at a ZnO/steel interface. The stainless steel contact electrodes for each measurement were the same; the difference was in the ZnO deposition conditions (-0.9 V and pH 5.5 for (a) and -1.1 V and pH 5.5 for (b)). When the experimental data (thick red line) are fit (thin black line between 0.01 and 1.4 V) to the equivalent circuit shown in the inset, a shunt resistance ($R_s$) is fit (thin black line between 0.01 and 1.4 V) to the equivalent circuit. For our electrodeposited junctions, shunt resistances are relatively large ($≥ 0.5 kΩ$). High Schottky ideality factors ($n > 10$) and relatively large reverse currents are also consistent with the dual conduction pathway proposed with this equivalent circuit.

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varying electrical rectification and the spatial inhomogeneity of the visible-range luminescence characteristics.

A connection between rectification properties and luminescence variations in electrodeposits has not been reported in the literature, and it is not necessarily to be expected. This is because the electronic structure at the ZnO/substrate (two-dimensional) interface determines the quality of the Schottky junction, while luminescence can be due to a wide variety of intrinsic or extrinsic defects (including dopants) at crystal surfaces or in the bulk.\textsuperscript{14,16,17} We note that energy-resolved photoluminescence measurements on our electrodeposits are inconclusive due to low overall luminescence intensities.

The electrical and optical signatures of heterogeneities shown in Figs. 1 and 2 are likely related to lateral variations in the ZnO nucleation and growth that occur during this commonly used electrodeposition process. The ZnO electrodeposition from acidic electrolytes has been widely understood as a multi-step process that involves metal deposition and subsequent oxidation.\textsuperscript{3,4,18} For the deposition potentials (-0.85 to -1.5 V) and starting electrolyte pH values (3.0-7.5) used in this study, it is thermodynamically favorable to deposit elemental Zn.\textsuperscript{19} However, concurrent nitrate reduction in the aqueous electrolyte increases the pH in the vicinity of the working electrode to oxidize the Zn and promote formation of ZnO.\textsuperscript{3}

In support of this mechanism, the Schottky barrier heights (φ\textsubscript{B}) extracted from fits of our I–V data (summarized in Fig. 1d) are consistent with values expected for junctions between ZnO and metallic Zn.\textsuperscript{5} Furthermore, our earlier studies on similar rectifying samples show that lateral variations in Zn content at the ZnO/substrate interface.\textsuperscript{6} These experimental findings, in conjunction with success of two-component equivalent circuit (Eq. 1), suggests that the Zn-rich material at the ZnO/substrate interface is the result of incomplete oxidation during the early stages of ZnO electrodeposition. We also note that lateral variations in Zn content at the ZnO/substrate junction are a unique characteristic of rectifying samples, and these inhomogeneities are not present in electrodeposited Ohmic samples.\textsuperscript{5,6,20} Thus, if one wishes to minimize heterogeneities in rectifying ZnO electrodeposited junctions, more careful control of the oxidation stage of the ZnO formation process would be necessary.

**Conclusion**

Lateral heterogeneities can be an inherent characteristic of an electrochemical oxidation process that is widely used\textsuperscript{4,18,20} to produce ZnO electrodeposits in aqueous electrolytes. These variations do not appear in bulk structural data, such as lattice constants derived from XRD data, but they are very easy to detect in simple current-voltage measurements and in fluorescence microscopy images. Since many semiconductors are prone to defects at concentrations that are too low to detect by bulk methods, the findings of this study could have important implications for other semiconductors\textsuperscript{1,2} prepared by similar electrochemical oxidation methods.

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**References**