



## Lateral Heterogeneities in ZnO Electrodeposits and Their Impact on Electrical and Optical Properties

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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 electrodeposit's 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 equivalent circuit that accurately models the current-voltage response as a combination of resistive (Ohmic) and rectifying (Schottky) junction contacts at the ZnO/substrate interface.  
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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.<sup>1,2</sup> 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.<sup>3,4</sup> Control over ZnO electrodeposit epitaxy, texture, morphology, carrier concentration, and orientation has been demonstrated,<sup>2,4</sup> as has selectivity between purely resistive (Ohmic) or rectifying (Schottky) electrical responses.<sup>5,6</sup> Here, we show that electrodeposited rectifying ZnO junctions, fabricated using a well-characterized nitrate reduction route,<sup>3</sup> have spatial (lateral) inhomogeneities that are not apparent using common characterization techniques such as X-ray diffraction or scanning electron microscopy. The origin of this effect is related to incomplete conversion of Zn<sup>2+</sup> to ZnO on some parts of the working electrode during the multi-step electrochemical synthesis process. These findings have two important implications. First, for the specific case of ZnO electrosynthesis, it means that the lateral heterogeneities inherently coincide with the presence of the rectifying electrical responses, thereby limiting the usefulness of this film production method unless the oxidation process can be controlled more completely. Second, for the general case of oxide formation by electrochemical methods, it shows the importance of using spatially resolved measurements in conjunction with bulk measurements to assess film quality for potential device applications.

### Experimental

For this study, more than 60 ZnO electrodeposits (thicknesses ~1 μm) were analyzed to span a range of deposition potentials and pH conditions that yield rectifying junctions. All samples were prepared at a constant deposition potential (selected in the range between -0.85 and -1.5 V<sub>Ag/AgCl</sub>) from pH-adjusted electrolytes (pH=3–7.5 achieved by adding either NaOH or H<sub>2</sub>SO<sub>4</sub>) that contained 0.01 M Zn(NO<sub>3</sub>)<sub>2</sub> in ultrapure water (18.2 MΩ·cm, Barnstead Nanopure), as described elsewhere.<sup>6,7</sup> Stainless steel working electrodes (A286, McMaster-Carr) were cleaned in acetone and ethanol prior to use. Electrodeposits were crystalline wurtzite-type ZnO with no evidence of crystalline secondary phases, as confirmed by X-ray diffraction

(XRD) data (Rigaku D/MAX 2200 PC, Cu Kα source). I–V measurements were completed with the same potentiostat used for the 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 electrodeposit, 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.<sup>8</sup>

### Results and Discussion

In principle, metal-semiconductor junctions can yield either purely resistive (Ohmic) or purely rectifying (Schottky) current-voltage (I–V) relations.<sup>9–11</sup> 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.<sup>9,5</sup> In this study, we probed the I–V responses of rectifying ZnO electrodeposits with a finer spatial resolution (~1 mm<sup>2</sup>) to come to a rather different conclusion. We find that there a disconcerting amount of variability in the rectification responses, and that rectification values among different (~1 mm<sup>2</sup>) 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<sup>5,9–11</sup> 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:

$$I = \frac{V}{R_s} + aAT^2 \exp\left(\frac{-\phi_B}{k_B T}\right) \exp\left(\frac{V}{nk_B T}\right). \quad [1]$$

This 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 ( $A = 32 \text{ A cm}^{-2} \text{ K}^{-2}$ ), the Schottky barrier voltage  $\phi_B$ , 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

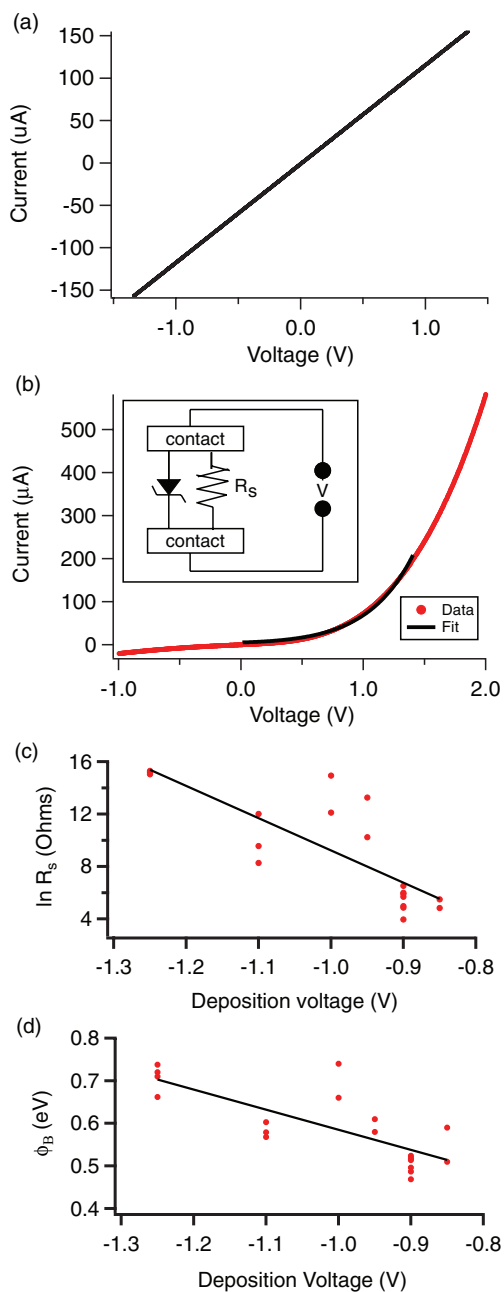
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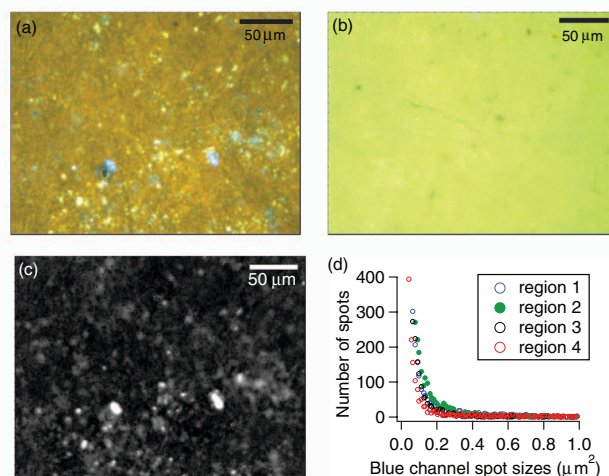
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**Figure 1.** (Color online) Representative I–V data for (a) a purely resistive (Ohmic) contact between electrodeposited ZnO and its steel substrate and (b) a rectifying (Schottky) response at a ZnO/steel interface. The stainless steel contact electrodes 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  $R_s = 200 \pm 100$  k $\Omega$  and Schottky barrier voltage  $\phi_B = 0.590 \pm 0.003$  eV are extracted. Fitted values for (c) shunt resistance and (d) barrier voltage as a function of deposition potential show considerable variation. Uncertainties in  $R_s$  and  $\phi_B$ , based on the fit to experimental I–V data, are contained within the size of the markers. The solid trend lines serve as guides to the eye.

metal-semiconductor interfaces have introduced multiple components for accurate fits to experimental data.<sup>12</sup> For our electrodeposited junctions, shunt resistances are relatively large ( $\geq 0.5$  k $\Omega$ ) 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



**Figure 2.** (Color online) (a) Representative fluorescence micrograph (in red-green-blue (RGB) color) of a rectifying ZnO electrodeposit. In comparison, (b) shows the more uniform luminescence that is characteristic of thin films with Ohmic ZnO/metal contacts. (c) A gray-scale representation of a single channel from an RGB image (shown here for the blue channel of the RGB image in (a)) can be used to quantify the lateral heterogeneities in the luminescence of the rectifying electrodeposits. (d) shows representative frequency distributions for the size ranges of the discrete blue spots that appear in fluorescence micrographs from four different regions (each 300  $\mu\text{m} \times 200 \mu\text{m}$ ) of the same rectifying ZnO electrodeposit shown in (a). These blue spots have a non-Gaussian size distribution that is heavily skewed toward smaller areas, and comprise  $4 \pm 2\%$  of the total sample area. A comparable analysis applied to the image for the Ohmic sample shown in (b) yields no detectable discrete blue spots.

are also consistent with the dual conduction pathway proposed with this equivalent circuit.<sup>9</sup>

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.<sup>13–16</sup> Fig. 2a is a representative fluorescence microscopy image of a ZnO electrodeposit 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 an indicator of lateral heterogeneity within the ZnO film, we applied standard thresholding and masking techniques<sup>8</sup> to images such as Fig. 2c (which is a gray-scale representation of the blue channel from Fig. 2a) to provide statistical information. Fig. 2d shows representative distributions of the size of the blue intensity regions, revealing non-Gaussian profiles that are heavily skewed toward smaller spots ( $< 1 \mu\text{m}^2$ ). The area fraction of the blue luminescence regions in rectifying deposits, based on 60 images from 4 samples, is  $4 \pm 2\%$ . Similar lateral variations in the blue luminescence intensity were observed from each and every rectifying ZnO electrodeposit, while ohmic ZnO electrodeposits never showed this kind of spatially distinct mixture of blue and yellow luminescence. Thus, there is a strong correlation between the laterally

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.<sup>14,16,17</sup> 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. ZnO electrodeposition from acidic electrolytes has been widely understood as a multi-step process that involves metal deposition and subsequent oxidation.<sup>3,4,18</sup> 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.<sup>19</sup> 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.<sup>3</sup>

In support of this mechanism, the Schottky barrier heights ( $\phi_B$ ) extracted from fits of our I–V data (summarized in Fig. 1d) are consistent with values expected for junctions between ZnO and metallic Zn.<sup>5</sup> Furthermore, our earlier studies on similar rectifying samples show that there exists a lateral variation in Zn content at the ZnO/substrate interface.<sup>6</sup> 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.<sup>5,6,20</sup> 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<sup>4,18,20</sup> 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<sup>1,2</sup> prepared by similar electrochemical oxidation methods.

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### References

1. A. R. Boccaccini and I. Zhitomirsky, *Curr. Opin. Solid State Mater. Sci.*, **6**, 251 (2002).
2. K.-S. Choi, H. S. Jang, C. M. McShane, C. G. Read, and J. A. Seabold, *MRS Bull.*, **35**, 753 (2010).
3. T. Yoshida, D. Komatsu, N. Shimokawa, and H. Minoura, *Thin Solid Films*, **451-452**, 166 (2004).
4. D. Lincot, *MRS Bull.*, **35**, 778 (2010).
5. S. Chatman, B. J. Ryan, and K. M. Poduska, *Appl. Phys. Lett.*, **92**, 012103 (2008).
6. S. Chatman and K. M. Poduska, *ACS Appl. Mater. Interfaces*, **1**, 552 (2009).
7. T. Ren, H. R. Baker, and K. M. Poduska, *Thin Solid Films*, **515**, 7976 (2007).
8. M. D. Abramoff, P. J. Magelhaes, and S. J. Ram, *Biophotonics Int.*, **11**, 36–42 (2004).
9. J. S. Wright, R. Khanna, L. F. Voss, L. Stafford, B. P. Gila, D. P. Norton, S. J. Pearton, H.-T. Wang, S. Jang, T. Anderson, J. J. Chen, B. S. Kang, F. Ren, H. Shen, J. R. LaRoche, and K. Ip, *Appl. Surf. Sci.*, **253**, 3766 (2007).
10. J. Wager, *Thin Solid Films*, **516**, 1755 (2008).
11. Y. Takada, M. Muraguchi, T. Endoh, S. Nomura, and K. Shiraishi, *Physica E*, **42**, 2837 (2010).
12. P. O. Grabitz, U. Rau, and J. H. Werner, *Thin Solid Films*, **487**, 14 (2005).
13. L. J. Brillson, H. L. Mosbacker, M. J. Hetzer, Y. Strezhemechny, D. C. Look, G. Cantwell, J. Zhang, and J. J. Song, *Appl. Surf. Sci.*, **254**, 8000 (2008).
14. Y. Kim, Y. Kim, and S. Kang, *J. Phys. Chem. C*, **114**, 17894 (2010).
15. C. H. Lan, J. D. Hwang, S. J. Chang, J. S. Liao, Y. C. Cheng, W. J. Lin, and J. C. Lin, *Electrochem. and Solid-State Lett.*, **13**, H363 (2010).
16. S. P. Watkins, Z. W. Deng, D. C. Li, and H. Huang, *J. Appl. Phys.*, **110**, 083506 (2011).
17. J. Cui, *J. Phys. Chem. C*, **112**, 10385 (2008).
18. M. Izaki and T. Omi, *J. Electrochem. Soc.*, **143**, L53 (1996).
19. M. Pourbaix, *Atlas of electrochemical equilibria in aqueous solutions*, Pergamon Press: New York, 1966.
20. B. N. Illy, A. C. Cruickshank, S. Schumann, R. Da Campo, T. S. Jones, S. Heutz, M. A. McLachlan, D. W. McComb, D. J. Riley, and M. P. Ryan, *J. Mater. Chem.*, **21**, 12949 (2011).