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Constant-potential electrochemical synthesis of ZnO on metal substrates enables selective formation of either Ohmic or Schottky-barrier contacts. Using a mildly acidic nitrate-based aqueous electrolyte, there is a substrate-dependent deposition potential below which electrodeposited ZnO heterojunctions display Schottky response with high contact resistances ($\sim 10^5\ \Omega$) and above which Ohmic behavior and low contact resistances ($\sim 1\ \Omega$) occur. Voltammetric evidence for Zn metal deposition, in conjunction with Schottky-barrier heights that are consistent with values expected for a ZnO–Zn junction, suggests that more negative deposition potentials create a Zn-based interface between the substrate and ZnO that leads to rectifying behavior. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2828702]

Zinc oxide (ZnO) is a wide-band, direct-gap semiconductor that is *n* type in its native form due to unintentional hydrogen doping, regardless of synthesis method.[1–4] As such, its ability to form rectifying (Schottky) junctions with metals is one characteristic that promotes its use in diodes, varistors, UV detectors, gas sensors, and piezoelectric transducers.[5] There is also a demonstrated need for low-resistance Ohmic contacts to ZnO for optical and piezoelectric applications.[6] While many performance improvements have been realized, it remains a challenge to apply predictive power to determine what conditions will yield optimal Schottky or Ohmic responses in ZnO/metal heterojunctions.[5,7] Here, we show that electrochemical deposition methods can be used to selectively form either Ohmic or Schottky contacts between polycrystalline ZnO and metals—without compromising the optical response of the ZnO—simply by tuning the applied potential during deposition. We show that this potential selectivity is intimately related to a Zn-based interfacial layer that forms at more negative deposition potentials. Because the resulting barrier heights of these one-step, electrochemically synthesized Schottky junctions are competitive with those prepared by more expensive and resource-intensive methods, our method offers promise for greater economy and control over ZnO heterojunctions for device applications.

Recent reviews highlight substantial efforts to improve the quality of Schottky contacts between ZnO, single crystalline or polycrystalline, and high purity precious metals with high work functions (Au, Pd, Pt).[5,7] Conversely, lower work function metals and alloys (often based on Al and Ag) have been targeted for Ohmic contacts on ZnO.[5–8] Many approaches for controlled current-voltage response of surface contacts focus on modification of the ZnO/metal interface through acid, plasma, laser, or thermal treatments.[7,9–11] The mechanisms behind such improvements are not always investigated, in part because the surface chemistry of ZnO is extremely complex due to the existence of polar and nonpolar faces.[5]

Electrochemical methods have been widely applied to metal deposition, but their use for preparation of functional oxide materials is still a growing area of research.[12–14] Our thin films were prepared using a method described elsewhere[4] based on a nitrate-reduction reaction using $0.01 M$ $Zn(NO_3)_2$ in ultrapure water ($p H = 5$). Substrates were polycrystalline Pt, Au/Cr/glass, or stainless steel (316 series) and were cleaned in HCl and H_2SO_4 prior to use. Cyclic voltammetry data for these different substrates in contact with the working electrolyte were collected with a Hokuto Denko HA 501 potentiostat. Constant applied potentials between -0.70 and -1.50 V (vs Ag/AgCl reference) at 70 °C yielded ZnO films with thicknesses $\sim 1\ \mu$m, as determined with contact-mode atomic force microscopy (Asylum Research MFP-3D). Structural confirmation was enabled by x-ray diffraction (XRD) data obtained with a Rigaku D/MAX 2200PC (Cu $K\alpha$ radiation) and analyzed with the LATCON software package.[15] Optical absorption edges were calculated from diffuse reflectance data (Ocean Optics SD2000, 45° incident angle, collinear reflectance collector). Current-voltage (*I-V*) characteristics of deposited samples were assessed with a Keithley 2400 source meter, employing stainless steel compression contacts (0.06 cm^2).

Electrochemical ZnO deposition produces either Ohmic or rectifying contacts, as shown in Fig. 1. The electrical response of these ZnO heterojunctions is strongly correlated with the potential applied during deposition. For example, ZnO deposits on stainless steel prepared at -0.9 V exhibit Ohmic behavior [Fig. 1(a)] with through-layer resistances of $1-10\ \Omega$. However, more negative deposition potentials ($\leqslant$ -1.1 V) show much higher perpendicular-to-layer resistances ($10^3 - 10^6\ \Omega$) even though the ZnO films have similar thicknesses. In addition, asymmetric rectifying behavior was observed for deposits prepared at these more negative deposition potentials [Fig. 1(b)], indicative of a Schottky barrier at the ZnO/substrate junction. This Ohmic-Schottky deposition potential threshold is also evident on Au (-0.8 V vs Ag/AgCl) and Pt (-1.2 V vs Ag/AgCl) substrates. In contrast, semiconducting substrates with band gaps similar to that of ZnO, such as polycrystalline indium tin oxide (E_g

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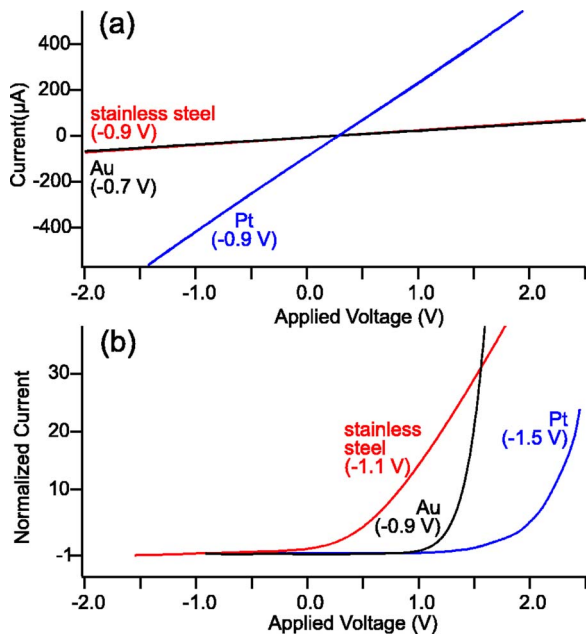b)URL: http://www.physics.mun.ca/~kris/

FIG. 1. (Color online) Electrodeposited ZnO exhibits an Ohmic current-voltage response when prepared at more positive deposition potentials (a), in contrast with asymmetric Schottky behavior for more negative deposition potentials (b). Current values in (b) are scaled relative to reverse-bias leakage currents (~10 nA for Au and Pt and ~100 nA for stainless steel). Positive voltage indicates forward bias.

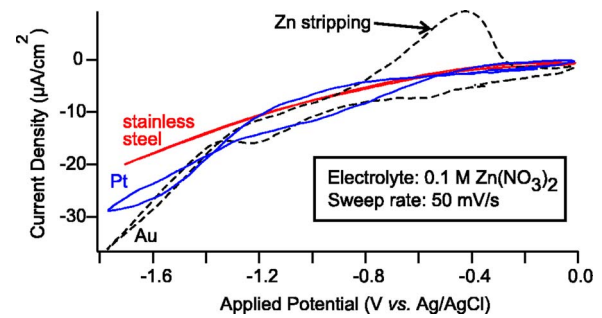FIG. 2. (Color online) Cyclic voltammograms for Au (dashed curve) in $0.1M$ $Zn(NO_3)_2$ show an anodic peak near −0.5 V that is characteristic of Zn metal stripping. The suppression of stripping peaks on stainless steel and Pt substrates (solid curves) during cyclic voltammetry studies in the same electrolyte is consistent with the formation of an electrochemically irreversible Zn alloy, as described in Ref. [21].

≈ 3.7), always yielded Ohmic contacts with electrodeposited ZnO, regardless of deposition potential.

A broad range of complementary experiments confirms that our results are consistent with interfacial effects, rather than deposition-potential-related changes in the ZnO film itself. XRD analyses for samples deposited at a potential between −0.9 and −1.5 V showed diffraction peaks consistent with those of hexagonal wurtzite ZnO's space group ($P6_3mc$) and lattice constants $a=3.255\pm0.001$ Å and $c=5.217\pm0.002$ Å, which are in good agreement with accepted values (3.250 and 5.207 Å, JCPDS No. 36-1451).[16] Relative peak intensity data show that our films are truly polycrystalline but with a preference for (001) orientation, as is typical for electrodeposited ZnO.[4,14,20] Optical absorption edge values for these same ZnO films, calculated from diffuse reflectance measurements, lie in the accepted range for native ZnO (3.3±0.1 eV).[9,11]

The rectifying behavior of our electrodeposited junctions compare favorably with ZnO-based Schottky junctions prepared by other methods, with forward-current to leakage-current ratios of ~50:1 and no breakdown at reverse-bias voltages up to 2 V. It is customary to compare the rectifying behavior with an ideal Schottky response as outlined below:

$$J = A^* T^2 \exp\left(\frac{-q\Phi_B}{kT}\right)\exp\left(\frac{q(V-IR)}{nkT}\right), \tag{1}$$

where J is current density, A^* is Richardson's constant ($A^*=32$ A/cm^2 K^2), T is temperature, q is the fundamental unit of charge, Φ_B is the Schottky-barrier height, k is Boltzmann's constant, V is the applied voltage, I is the resulting current, R is the series resistance, and n is the ideality factor. Schottky-barrier heights for our electrodeposited junctions, calculated by fitting I-V data [Fig. 1(b)] to Eq. (1) showed slight variations with substrate: 0.73±0.05 eV for steel, 0.85±0.05 eV for Au, and 0.90±0.05 eV for Pt. All values

fall comfortably within the range of ZnO Schottky-barrier heights reported by others (0.6–1.0 eV).[7–11,17,18] Another measure of the rectifying quality is the ideality factor (n), with a value of 1 corresponding to a perfect exponential transition from leakage-current to forward-current flow. High values of the ideality factor (>2) are attributed to the existence of multiple current pathways.[7] Our electrodeposited ZnO junctions have high ideality factors ($n\sim10$, determined over 0.5 V), commensurate with ZnO Schottky diodes formed using chemical-vapor deposition,[19] while more ideal Schottky junctions have been prepared by other methods ($n=1.0-2.0$, determined over ~0.1 V).[7,9,10,17]

To a first approximation, the best Schottky barriers occur when the metal's work function (Φ_m) is very different from the electron affinity (χ_{sc}) of the semiconductor,

$$\Phi_B = \Phi_m - \chi_{sc}. \tag{2}$$

For electrodeposited junctions, evidence suggests that a composition-related change in the interfacial electronic states also affects Schottky-barrier formation, height, and ideality. Applied deposition potentials more negative than −1.5 V generally favor Zn metal formation over ZnO.[20] At more positive deposition potentials, electrochemical ZnO formation can be preceded by a Zn metal prelayer, as reported by others.[14] Figure 2 shows that reversible deposition and stripping of Zn metal is possible using our electrolyte. In contrast, ZnO formation is not reversible and has no current associated with it due to the fact that Zn does not change its oxidation state.[20] Substrates such as Pt can support an electrochemically produced Zn surface alloy, although the details of its composition and structure remain elusive.[21]

To confirm that the earliest stages of deposition are critical for controlling the Ohmic/rectifying responses of our ZnO electrodeposits, we compared constant-potential deposition to a pulsed deposition sequence. Rectifying responses were observed for pulse-prepared junctions (−1.5 V for 10 s to deposit Zn metal, followed by subsequent deposition at −0.9 V to deposit ZnO), whereas a constant deposition potential of −0.9 V yielded Ohmic contacts. We also note that, despite the large difference in work functions of our substrates ($\Phi_{Au}=5.1$ eV, $\Phi_{Pt}=5.7$ eV),[22] barrier heights of the electrodeposited junctions on these different substrates show a much smaller spread (0.8±0.1 eV). Furthermore, using Eq. (2) to estimate an effective substrate work function, we find a value of 4.5±0.1 eV which is on par with the work func-

tion reported for Zn (4.4 eV).[22] Thus, the rectifying response in electrodeposited ZnO heterojunctions is consistent with contacts at a Zn metal interface.

We established a more definite link between Schottky behavior and the presence of a Zn-based prelayer at the buried interface using scanning electron microscopy (SEM) (FEI Quanta 400) with energy dispersive x-ray (EDX) analysis. ZnO/substrate interfaces were exposed by mechanically detaching films from their substrates by cooling epoxy-coated films in liquid nitrogen. EDX data show higher Zn content at the ZnO/substrate interface relative to the ZnO film's air interface. EDX investigations on the stainless steel substrates after ZnO film removal show no evidence of Zn content, suggesting that the Zn-based prelayer contributing to the Schottky response is strongly adhered to the ZnO film. Contrast variations in the backscattered electron images from the ZnO/substrate interface suggest that the Zn-based prelayer may have thickness inhomogeneities, which would be consistent with multiple conduction pathways[7] implied by our films' high ideality factors.

In summary, potentiostatic electrochemical deposition of ZnO on metal substrates provides selectivity between Ohmic contacts and Schottky junctions, with no need for annealing. This selectivity can be attributed to potential-dependent formation of a Zn-based interface between the substrate and ZnO electrodeposit, thereby yielding barrier heights consistent with ZnO–Zn contacts. The electrodeposited junctions compare well with ZnO Schottky diodes synthesized using more resource-intensive synthesis methods, offering an opportunity for greater economy and control over ZnO heterojunctions for device applications.

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