Electric Field-Driven Point Defect Pile-up Near ZnO Polar Surfaces

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Abstract

Electric fields in near-surface space charge regions influence the spatial distribution of charged defects, with implications for the efficiency of photocatalysts and gas sensors. Through isotopic oxygen diffusion experiments on both Zn-terminated ZnO (0001) and O-terminated ZnO (000 $\bar{1}$), the present work better delineates the quantitative relationship of defect pile-up to the degree and direction of near-surface band bending, the rate of defect injection, and the temperature. The two terminations exhibit dramatic differences in behavior from each other, especially in the temperature dependence. The results suggest that the amount of fixed charge at the surface directly affects the injected flux.

Keywords: ZnO, defect diffusion, space charge, polar surface

The spatial distribution of native point defects and substitutional dopants near solid-gas and solid-solid boundaries of semiconductors affects the operational efficiency of photovoltaic [1, 2], photocatalytic [3, 4], and microelectronic [5, 6, 7] devices. During fabrication steps that require heating, dopant atom segregation or precipitation [8] can occur due to a combination of misfit elastic strain [9], chemical potential gradient [10, 11, 12] and electrostatic drift [10, 13, 14]. Pile-up of native defects is also possible, and those associated with energy levels deep in the bandgap usually affect device performance adversely [15]. The published literature has focused primarily on electrostatic mechanisms [10, 13, 14] by which fixed charge on surfaces influences the spatial distribution of nearby charged defects. This laboratory has reported [14] experimental evidence for a distinct mechanism involving field-induced changes in the motion of rapidly mobile defects such as interstitials, coupled with their exchange into a station-

ary reservoir such as the host crystal lattice. Subsequent modeling demonstrated [16] that these effects enhance or diminish the concentration of the mobile defects within the surface space charge region (SCR), leading to a pile-up or depletion of the corresponding species exchanged into the reservoir - depending upon the direction of the field and the sign of the defect's charge.

The experimental results underlying that work involved $^{18}\text{O}_2$ gas exchange with rutile $\text{TiO}_2(110)$, wherein pile-up of substitutional isotopic oxygen was observed within several nanometers of the surface. However, the results were not sufficiently precise to establish the quantitative relationship of pile-up to the degree and direction of near-surface band bending, the rate of defect injection, or the temperature. The present work employs similar experimental methods with *c*-axis ZnO, both Zn-terminated (0001) and O-terminated (000 $\bar{1}$), in tandem with the mathematical model [16], to examine these relationships. The two terminations exhibit dramatic differences in behavior from each other, especially in the temperature dependence. Taken together, the results suggest that the amount of fixed charge at the surface may

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Figure 1: Isotopic-labeled oxygen (^{18}O) diffusion profiles in Zn-ZnO (and O-ZnO inset) samples annealed in $^{18}\text{O}_2$ gas (5×10^{-5} Torr) at 540°C, 600°C, 650°C and 700°C for 105 min. The near-surface profile shows pile-up of the isotopic marker within ~ 10 -35 nm of the surface. The exponential profile beyond the pile-up zone represents bulk diffusion.

exert a direct influence on the injected flux.

As discussed previously [14, 16], mobile defects formed at the surface and injected into the bulk undergo Fickian diffusion. For downward band bending in the SCR of natively *n*-type materials such as TiO_2 and ZnO, the near-surface field $\epsilon(x)$ points into the bulk, which induces field drift of negatively charged defects such as O_i^{2-} toward the surface and impedes migration into the bulk. The prolonged residence time of these defects in the SCR increases the degree to which they exchange with the reservoirs that exist there, such as the lattice via kick-in. In an isotopic oxygen (^{18}O) gas-solid exchange experiment, the labeled O marker replaces the existing lattice O over time. Since ^{18}O and ^{16}O are chemically alike, they are thermodynamically interchangeable in the lattice; the ^{18}O represents an isotopic rather than a chemical defect. The resultant pile-up (or valley) can be measured with secondary ion mass spectrometry (SIMS).

The present experiments employed an apparatus described previously [14]. Single crystals of wurtzite

ZnO with polar (0001) Zn-terminated (Zn-ZnO) or (000 $\bar{1}$) O-terminated (O-ZnO) surfaces were exposed to isotopically-labeled oxygen gas ($^{18}\text{O}_2$) at elevated temperatures (540-700°C) under O-rich conditions ($P_{\text{O}_2} \sim 5 \times 10^{-5}$ Torr) for 105 min. Before isotopic exposure, the specimens were degreased *ex situ* as described in Ref. 14, and then heated in natural abundance O_2 to equilibrate the native defect concentrations at the same temperature and pressure as the subsequent isotopic exposure. After that exposure, ^{18}O concentration profiles were measured *ex situ* with time-of-flight SIMS using a PHI-TRIFT III instrument [14] and electron flooding. To ensure that the near-surface profiles are not complicated by measurement artifacts [17], low depth profiling rates were employed and data points at or very near the surface were discarded (Figure 1). Additionally, multiple measurements were performed at different spots on the sample to check for reproducibility of the pile-up profile. Special care was taken to maintain instrumental base pressures that minimized mass interferences from H_2^{16}O , which has a mass similar to ^{18}O . In Figure 1, the near-surface profiles change dramatically and systematically with annealing conditions. If the existence of pile-up were an artifact of the SIMS measurements, the annealing conditions would not exert any systematic effect on the profiles.

Figure 1 (and inset) shows example ^{18}O diffusion profiles for Zn-ZnO (and O-ZnO). The profiles qualitatively resemble those obtained in rutile $\text{TiO}_2(110)$ [14, 16], with two distinct regimes: (1) near-surface (~ 10 -35 nm) pile-up of the isotopic O marker, and (2) deeper profile extensions into the bulk. Unlike TiO_2 , for which pile-up was typically small, shallow (< 10 nm) and poorly reproducible, Zn-ZnO exhibits pile-up that is often large, deeper (up to 35 nm), and straightforward to reproduce among various specimens. O-ZnO exhibits smaller and shallower pile-up, but the reproducibility is still good. As in the case of TiO_2 , the profiles in the deeper bulk (> 35 nm) have very shallow, but non-zero, slopes. The migration of isotopic marker into the bulk is perhaps more evident in Figure 1 from the large increase in overall ^{18}O concentration throughout the entire deep bulk. Extensive analysis of this section of the profile has been reported elsewhere [18], and is not a focus of

this work except where noted below for the purposes of near-surface profile analysis.

Previous work [14] has quantified the amount of pile-up (P) as the total integrated area between the near-surface pile-up profile and the deep-bulk profile extrapolated to the surface, shown as shaded regions in Figure 1. For this extrapolation, an exponential function was used (linear on the semilogarithmic scale of Figure 1) as in the case of TiO_2 [14, 16]. The width of the pile-up region for a given profile was determined as the depth at which the profile begins to deviate substantially from the exponential function used for extrapolation. These widths are marked in Figure 1 as vertical lines. For Zn-ZnO, both this width and P itself increase with temperature from 540°C to 700°C. For O-ZnO, the width and P both remain roughly constant with increasing temperature. Regardless of temperature or termination, P accounts for <1% of the total number of ^{18}O injected into the bulk - corresponding to the behavior in rutile TiO_2 [14]. In this small-perturbation limit, it is a good mathematical approximation [16] to analyze the pile-up and deeper-bulk regions separately.

Substantial evidence suggests that the oxygen interstitial O_i mediates oxygen diffusion in TiO_2 under clean-surface conditions [14]. That evidence includes the elevated magnitude of the observed O diffusivity compared to the literature, the exponential (rather than error-function) shapes of the profiles, the existence and behavior of near-surface pile-up [14], and the predictions of quantum calculations[19] that O_i^{2-} is thermodynamically more stable than other O-related native defects. The analogous body of published evidence for ZnO is smaller, and rests mainly on quantum calculations [20, 21] and diffusion experiments [18] that point to O_i^{2-} as the most stable O-related native defect.

The ZnO used in this work is almost certainly n -type because of incorporated hydrogen donors [22, 23], with the charge density set by the hydrogen concentration. The existence of pile-up in the profiles of Figure 1 (contrasted with a “valley”) indicates an electric field directed opposite to the diffusional flux, which in n -type material implies the existence of an accumulation-type space charge region with downward band bending [24]. Our previously-developed

Figure 2: (a) Arrhenius temperature dependence of V_s for the Zn-ZnO (red) and O-ZnO (blue) at 5×10^{-5} Torr. The activation energy for buildup of V_s is ~ 1.7 eV for the Zn-ZnO surface. V_s remains almost constant at the O-ZnO surface. (b) Widening of the pile-up width (L_{sc}) with temperature for Zn-ZnO and O-ZnO surfaces.

analytical expressions [16] can be used to estimate the surface potential V_s from the surface concentration $C_{S,1}$, using the equation:

$$C_{S,1} - C_{S0}|_{x=0} = \frac{Ft}{\lambda} \chi_1 \quad (1)$$

where F is the flux of mobile species injected at the surface, λ the mean diffusion length of that species before exchange with the reservoir, C_{S0} the background concentration of natural abundance marker in the material, t the diffusion time, and χ_1 a dimensionless factor. Extrapolation of the deep bulk profile to the surface yields a hypothetical zero-field

concentration equal to Ft/λ [16]. For drift directed oppositely to diffusion, the surface concentration of marker is always enhanced by a factor of χ_1 . With λ and F calculated from the deep bulk profile, χ_1 can be calculated from Eq. (1). From χ_1 , the magnitude of the surface electric field $\epsilon(x)$ can be determined from the relation [16]:

$$\chi_1 = \sqrt{\left(\frac{\alpha\epsilon_1\lambda}{2}\right)^2 + 1} - \frac{\alpha\epsilon_1\lambda}{2} \quad (2)$$

where $\alpha = q/k_B T$, q is the charge on the mobile species, and k_B is Boltzman's constant. The value of ϵ_1 permits the estimation of the surface potential V_s from classical electrostatic relations involving the background carrier concentration of the material and its dielectric constant. The pile-up region has approximately the same width L_{SC} as the SCR. Evidence that the donor concentration remains constant with T comes from the fact that both L_{SC} and χ_1 remain independent of T for O-ZnO.

Fitting an Arrhenius temperature dependence to λ for the Zn-ZnO surface yields a pre-exponential factor of 105.36 ± 0.73 nm and an effective activation energy $E_\lambda = 0.28 \pm 0.13$ eV. A similar procedure for F yields an activation energy $E_{Flux} = 1.67 \pm 0.32$ eV [14]. For O-ZnO, E_λ is similar in magnitude to that of Zn-ZnO, while E_{Flux} is roughly T -independent. The similar values of E_λ for Zn-ZnO and O-ZnO point to the same O diffusion species and mechanism in both cases.

With the assumption of a -2 charge state for O_i , Eqs. (1) and (2) may be applied to the profiles of Figure 1 to yield V_s as a function of temperature, as shown in Figure 2(a). The magnitude of V_s in Figure 2(a) is on the order of only a few meV, which highlights the sensitivity of the near-surface pile-up profile to built-in electric fields in the SCR. Conventional measurement techniques such as Kelvin probe microscopy are not sensitive enough to resolve surface potentials of the order of few meV at most [25]. At the typically high temperatures used in the diffusion experiments, thermalization of charge carriers tends to significantly flatten band bending in the SCR, which can explain the small values of V_s in Figure 2(a).

Figure 3: A linear fit to a semi-logarithmic plot of surface potential (V_s) vs. pile-up width (L_{SC}) confirms that the widening of the space charge region with temperature is in response to the increasing V_s in an accumulation-type space charge.

On the Zn-ZnO surface, V_s increases exponentially by almost an order of magnitude from ~ 0.1 meV at 540°C to ~ 3.8 meV at 700°C . The activation energy E_{V_s} for the variation of V_s is 1.7 ± 0.3 eV with a pre-exponential factor of 109.4 ± 1.6 meV. For O-ZnO, the pile-up profile does not appreciably change with temperature so V_s is also roughly constant with temperature. Figure 2(b) shows the temperature dependence of L_{SC} . The value remains constant near 10 nm for O-ZnO; it increases exponentially with T for Zn-ZnO - similar to the V_s buildup. Note that the electric field in an accumulation region decays exponentially in space, as opposed to quadratic decay in a depletion region [18]. For an accumulation-type space charge region, a semi-logarithmic plot of V_s versus L_{SC} should therefore be approximately linear as contrasted with quadratic for a depletion region. The linearity of a semi-logarithmic plot of V_s versus L_{SC} for the Zn-ZnO surface, shown in Figure 3, confirms the exponential functional form and thereby the existence of an accumulation region as discussed above. This confirmation gives confidence that the mathematical model derived in Ref. 16 accurately describes the behavior of pile-up in its various aspects.

The correspondence in the general behavior of E_{V_s} and E_{Flux} for Zn-ZnO and O-ZnO is notable. The presence of the accumulation-type space charge in an n -type semiconductor implies the presence of excess electrons in the SCR compared to the bulk, which in conjunction with polar effects [18] could be responsible for enhancing the adsorption and dissociation of O_2 as well as the subsequent charging of the injected O interstitial species. Indeed, recent first-principles calculations [26] highlight the propensity of adsorbed O and O_2 , as well as O_i , to soak up nearby electrons even when no excess is available.

That such an influence of V_s on F is plausible may be established as follows. From the context of gas sensors, adsorption of O_2 is already known to withdraw electrons from ZnO and thereby affect V_s [27]. It is therefore reasonable to suppose that, for surfaces wherein the surface Fermi energy is pinned, the value of V_s and the corresponding availability of conduction-band electrons could influence the amount of O_2 (or O) adsorption. As adsorption is the first step in the kinetic sequence leading to O_i injection, changes in the amount of injectable oxygen at the surface would translate into changes in F . Similarly, the value of V_s in some semiconductors affects the average charge state of near-surface point defects whenever an ionization level is favorably situated within the band gap [5, 16]. The ionization levels for O_i in ZnO are not known, although the possibility of multiple charge states has not been excluded.

Evidence for the influence of V_s on F may be found in the fact that V_s and L_{SC} increase with temperature for Zn-ZnO, which increases the concentration of electrons in the SCR and also leads to increased O injection flux [18]. Correspondingly, V_s and L_{SC} remain constant with temperature for O-ZnO, as does the injected flux. The differences in behavior between Zn-ZnO and O-ZnO undoubtedly arise from the distinct surface reconstructions and atomic geometries for the two terminations [26]. However, we do not ascribe significance to the exact numerical correspondence between E_{V_s} and E_{Flux} . E_{Flux} for Zn-ZnO has been linked directly to the elementary-step injection barrier for O_i , while for O-ZnO, E_{Flux} appears to represent a balance between the injection barrier and the concentration of injectable oxygen. The physical

mechanism for a direct correspondence between E_{V_s} and E_{Flux} is not clear.

The findings of this work give important confirmation of the mathematical treatment of Ref. 16 as a basis for interpreting pile-up in isotopic exchange experiments, and also suggest that the amount of fixed charge at the surface exert a direct influence on the injected flux. This coupling is likely to be more pronounced for polar semiconductor surfaces than for nonpolar, as the need for stabilization mechanisms to avoid thermodynamic instability [28, 29, 30, 31] are more likely to support charged oxygen species that facilitate injection into the bulk as charged O_i . For cases in which direct control over the spatial distribution of near-surface point defects is desired, this coupling between fixed charge and flux may complicate the task.

Acknowledgments

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