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Massive point defect redistribution near semiconductor surfaces and interfaces and its impact on Schottky barrier formation

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ABSTRACT

Nanoscale depth-resolved cathodoluminescence spectroscopy calibrated with deep level transient spectroscopy of native point defects and capacitance–voltage measurements of free carrier densities, all at the same metal–semiconductor interface, demonstrate that native point defects can (i) increase by order-of-magnitude in densities with tens of nanometers of the semiconductor surface, (ii) alter free carrier concentrations and band profiles with the surface space charge regions, and (iii) dominate the Schottky barrier formation for metal contacts to ZnO and many other single crystal compound semiconductors. The spatial redistribution of electrically active defects within the surface space charge can be understood in terms of temperature-dependent atomic diffusion enabled by low formation energies and driven by strain and electric fields as well as metal-specific chemical reactions near room temperature, consistent with first-principles calculations of interfacial segregation and migration barriers. These results underscore the importance of native point defects in charge transport and barrier formation at semiconductor interfaces.

1. Introduction

Until now, native point defects in semiconductors were not considered a significant factor in Schottky barrier formation due to their relatively low bulk densities. Instead, many theories have postulated localized states, including adsorption-induced defects, at the semiconductor surface with high enough densities to "pin" the Fermi level. It is now possible to measure the energies and densities of point defects below the semiconductor free surface and its metal interface with nanoscale precision. Using depth-resolved cathodoluminescence spectroscopy (DRCLS) of deep level emissions calibrated with deep level transient spectroscopy (DLTS) as well as capacitance–voltage (C–V) measurements of free carrier densities—all at the same interface, we can now demonstrate that native point defects can increase by order-of-magnitude in densities within tens of nanometers of the semiconductor surface, introducing localized charge sites at densities that can significantly alter free carrier concentrations and band profiles within the surface space charge region. In turn these can dominate Schottky barrier formation at metal–semiconductor interfaces.

Here we present results for metal contacts to ZnO and show how the native defect features characteristic of this interface can extend to many other single crystal compound semiconductors. Previously we used this combination of techniques to show that surface adsorbates, hydrogen donors, and sub-surface native point defects each contribute independently to interface charge transport and Schottky barrier formation [1]. Furthermore, metal deposition [2] and subsequent annealing [3] induce additional native point defects extending tens of nanometers or more below the free ZnO surface that increase tunneling, recombination, and hopping transport. These effects are orientation-dependent, with significantly higher defect and free carrier densities below the free $(000\bar{1})$ O face versus (0001) Zn face and their interfaces with many different metals [4].

Unlike many semiconductors, metal contacts to ZnO single crystal surfaces yield a wide range of Schottky barrier heights [5]. While this large variation has been attributed to ZnO's relatively large ionicity [6]; numerous studies determine large variations in Schottky barrier height for the same metal on ZnO crystals prepared under different conditions [1,7,8]. Very recently, nanoscale DRCLS studies showed that native point defects near the metal–ZnO interface [1,9] could alter Schottky barriers from Ohmic to Schottky and vice-versa. Earlier DRCLS studies showed

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that hydrogen below the surface acts as an n-type dopant [10]. Furthermore, surface adsorbates could induce surface accumulation and high conductivity. These studies also found that exposure to a remote oxygen plasma (ROP) could reduce such sub-surface hydrogen [10], sub-surface defects [1], and surface adsorbates [1]. Thus the combination of DRCLS and ROP treatment can be used to separate the effects of hydrogen doping and defects in the ZnO depletion region near the metal–semiconductor interface.

Recent DRCLS studies of clean, ordered metal–ZnO($000\bar{1}$) surfaces show that Schottky barriers are reduced and ideality factors increased by high near-surface densities of native point defects [9]. Significantly, capacitance–voltage (C–V) measurements reveal a monotonic increase in carrier concentration for hydrogen-depleted ZnO($000\bar{1}$) interfaces that correlates with DRCLS-measured deep level defect densities. These results suggest that Schottky barrier decreases may be due to *both* hopping transport through the depletion region of the barrier as well as tunneling through barriers that are substantially narrowed by high near-surface dopant densities.

The spatial redistribution of electrically active defects within the surface space charge can be understood in terms of temperature-dependent atomic diffusion enabled by low formation energies and driven by strain and electric fields as well as metal-specific chemical reactions near room temperature. Self-consistent electrostatic calculations based on sub-surface trap distributions, energies and carrier densities yield a wide range of effective Schottky barriers, in agreement with measured values for different metals on a wide array of ultrahigh vacuum clean ZnO crystals grown by various methods. These results are not unique to ZnO. Indeed, there is now considerable evidence to show that these sub-surface and near-interface native point defects dominate the Fermi level movement across the band gaps of most compound semiconductors. Here we discuss this dramatic native defect redistribution and its electronic effects using first-principles calculations of interfacial segregation [11] and migration barriers [12]. The massive accumulation and creation of native point defects at these interfaces underscore their importance in charge transport and Schottky barrier formation.

2. Experiment

The DRCLS technique provides a tool to measure the emissions from defects as a function of depth on a nanometer scale. For a description of this technique, see for example, Ref. [13]. Basically an incident electron beam of energy E_B excites secondary electrons that decay by X-ray emission, plasmon generation, and ultimately electron–hole pair creation. The free electron–hole pairs can recombine radiatively by photon or nonradiatively by phonon emission. For E_B in the range of a few keV or less, the electron cascade extends into a semiconductor by a Bohr–Bethe range R_B that is on the order of tens to hundreds of nanometers. The depth U_0 of maximum rate of energy loss due to electron–hole pair creation is a fraction of this depth such that electron–hole creation and recombination across the semiconductor band gap or between band edges and gap states occur at correspondingly shallower depths. This capability enables measurements of defect and impurity emissions as a function of depth from the bulk to within a few nanometers of the surface. DRCLS has successfully probed localized states at buried quantum well interfaces [14] and gate oxide heterostructures [15], only a few nanometers thick, and even the variations in electronic states at different semiconductor surface reconstructions [16].

In general, we prepare the ZnO crystals by a combination of chemical cleaning and ROP plasma treatment to produce atomically clean surfaces in ultrahigh vacuum (UHV) [17]. DRCL spectra are obtained both in bare areas between diodes and by excitation and detection *through* the diodes. DRCLS has shown previously that bulk defect densities in commercially grown ZnO crystals can vary by many orders of magnitude between different growth methods or even between crystals from the same vendor and growth method [18]. In turn, crystals with high defect densities exhibit large changes in defect redistribution and creation with metal contacts [19]. For the studies reported here, we used ZnO with some of the lowest native point defect densities available. These crystals exhibited defect emission intensities many orders of magnitude below those of the near-band-edge (NBE) emission as verified by DRCLS. Metallization in the form of 400 μm, 25–30 nm thick diode arrays immediately followed ROP cleaning in UHV to avoid any impurity contamination of the metal–ZnO interfaces.

We calibrated the defect intensities measured by DRCLS with gap densities measured by DLTS of the same diodes. DLTS provides trap densities and cross sections at depths corresponding to the edge of the semiconductor surface space charge region. Similarly, C–V measurements provide carrier concentrations and their variation with depth. Current leakage in forward voltage limits the measurement of trap and free carrier densities very near the semiconductor interface. However, DLTS can calibrate DRCLS emission intensities at depths over which the two techniques overlap. Assuming a linear dependence of DRCLS with trap density, DRCLS can then provide densities at shallower depths up to a few nanometers of the surface. Similarly, DRCLS can provide densities for contacts with relatively low or ohmic contacts, for which DLTS cannot provide information.

3. Results

DRCLS measurements of ZnO initially showed the one of the most common deep level defects, the "green" defect with emission centered at 2.5 eV, increased toward the surface from depths of 30–50 nm and that ROP annealing could reduce their density significantly [1]. As defect density decreased in stages by an order of magnitude, their corresponding Schottky barrier heights with the same metal contact increased from ohmic to Schottky-like and their ideality factors decreased. Similarly, ZnO with orders of magnitude decrease in bulk native point defect density produced order-of-magnitude decrease in reverse current–voltage (I–V) saturation current [19]. These results demonstrated that native point defects within the semiconductor bulk could have major effects on Schottky barrier formation.

Combined $1/C^2$–V, DLTS, and DRCLS measurements of a high barrier contact provide a correlation between carrier density, trap density, and deep level emission over the same range of depths. Fig. 1(a) illustrates DRCLS spectra obtained with three E_B corresponding to depths from the bulk to ~50 nm for a ROP-cleaned Ir–ZnO($000\bar{1}$) diode. These spectra show the NBE peak at 3.35 eV and defects with emission peaks at 2.1, 2.5, and 3 eV that vary strongly with depth. In particular, the 2.5 eV peak increases three-fold between 10 and 5 keV, corresponding to depths of ~200 and ~50 nm, respectively. For the same diode, Fig. 1(b) displays carrier concentration versus depth. Correspondingly, carrier densities increase by approximately a factor of 3 from depths of ~200 to 90 nm. Absolute carrier densities reach $10^{17}\,cm^{-3}$ at 90 nm, indicating a corresponding number of electrically active defects at this depth. Furthermore, the sharp rise in carrier density at shallow depths indicates that these densities may increase by at least another order of magnitude at even shallower depths.

Deep level optical spectroscopy (DLOS) of this diode shows the presence of multiple deep levels with energies extending across