

Unification of the electrical behavior of defects, impurities, and surface states in semiconductors: Virtual gap states in CdO

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(Received 9 December 2008; published 15 January 2009)

In contrast to conventional semiconductors, native defects, hydrogen impurities, and surface states are all found to be donors in *n*-type CdO. Using this as a model system, the electrical behaviors of defects, dopants, and surface states in semiconductors are unified by a single energy level, the charge neutrality level, giving much insight into current materials and allowing a band-structure engineering scheme for obtaining desired custom electronic properties in new compound semiconductors.

DOI: [10.1103/PhysRevB.79.035203](https://doi.org/10.1103/PhysRevB.79.035203)

PACS number(s): 71.55.Gs, 73.20.At, 73.61.Ga, 78.66.Hf

I. INTRODUCTION

The presence of even small concentrations of native defects or impurities in semiconductors has a profound effect on their bulk electronic properties. For example, hydrogen almost always counteracts the prevailing conductivity.¹ Similarly, surface electronic properties are generally dominated by a small number of charged surface states of acceptorlike character in *n*-type semiconductors and donorlike character in *p*-type semiconductors, leading to a depletion of charge carriers at the surface. In some cases, however, such native defects, impurities, and surface states can be donors in *n*-type material or acceptors in *p*-type material.²⁻⁵ Understanding this unconventional behavior is crucial to advancing the functionality of current and future semiconductors.

The group-II oxide materials represent a rapidly emerging class of semiconductor compounds, where recent advances in growth resulting in high quality single-crystalline material present opportunities for their use in a wide range of device applications. Research in these materials has largely focused on ZnO, which, with its similar band gap to GaN but substantially larger exciton binding energy, has enormous promise for devices such as light-emitting diodes.⁶ However, the smaller band-gap compound CdO ($E_g \sim 2.2$ eV at the Brillouin-zone center⁷) has received far less attention, despite its importance when alloyed with ZnO to extend the operation of ZnO-based devices into the visible spectral range.⁸

In this work, surface states and intentionally introduced impurities and native defects are all shown to be donors in *n*-type CdO. While these properties have important consequences for CdO's use in practical applications, more importantly it serves as an excellent model system in which to probe the fundamental origins of bulk and surface electronic properties. In particular, we show that the electrical behavior of native defects, hydrogen, and surface states can all be understood from the position of a single energy level, unifying bulk, surface, and interface electronic properties of semiconductors, and giving insight into possibilities for future engineering of materials with specific electrical characteristics.

II. EXPERIMENTAL DETAILS

Single-crystalline CdO(001) samples were grown by metal-organic vapor phase epitaxy (MOVPE).⁹ The electron

density and mobility of the as-grown samples were $\sim 1.5 \times 10^{20} \text{ cm}^{-3}$ and $\sim 60 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. Particle irradiation was performed with 1 MeV $^4\text{He}^+$ ions. The displacement damage dose¹⁰ (product of the calculated nonionizing energy loss and the particle fluence) ranged from 5.6×10^{13} to $7.4 \times 10^{16} \text{ MeV/g}$. Atomic hydrogen diffusion into nominally undoped CdO was performed by annealing samples at ~ 350 °C in an ultrahigh-vacuum (UHV) system at a background pressure of 5×10^{-6} mbar of molecular hydrogen passed through a thermal gas cracker (cracking efficiency of $\sim 50\%$).

Single-field Hall-effect measurements were performed in the Van der Pauw geometry. Optical transmission and 35° specular infrared (IR) reflectivity measurements were performed using a Perkin-Elmer Lambda 25 UV-visible spectrophotometer and Spectrum GX Fourier transform IR spectrometer, respectively. High-resolution x-ray photoemission spectroscopy (XPS) measurements were performed using a Scienta ESCA300 spectrometer with a monochromated rotating anode Al $K\alpha$ x-ray source ($h\nu = 1486.6$ eV). The Fermi level (zero of the binding-energy scale) was calibrated from an ion-bombarded silver reference sample. All measurements were performed at room temperature. Nonparabolic carrier-statistics and space-charge layer calculations were performed as described elsewhere¹¹ using the CdO material parameters from Ref. 7.

III. CHARGE NEUTRALITY LEVEL POSITION

Figure 1 shows the evolution of electrical properties of CdO when native defects are introduced by high-energy particle irradiation, as determined by IR reflectivity and Hall-effect measurements. Initially, the electron concentration increases with increasing displacement damage dose: the defects introduced are predominantly donors in nominally undoped, although already heavily *n*-type, CdO. With further increase in damage dose, the carrier concentration stabilizes at $n = 2.2 \times 10^{20} \text{ cm}^{-3}$, corresponding to a bulk Fermi level 2.57 eV above the Γ -point valence-band maximum (VBM). This is in agreement (within experimental error) with optical absorption of the most heavily irradiated sample (Fig. 1(a), inset), where the Fermi level is determined to lie 2.52 ± 0.05 eV above the Γ -point VBM. From the average

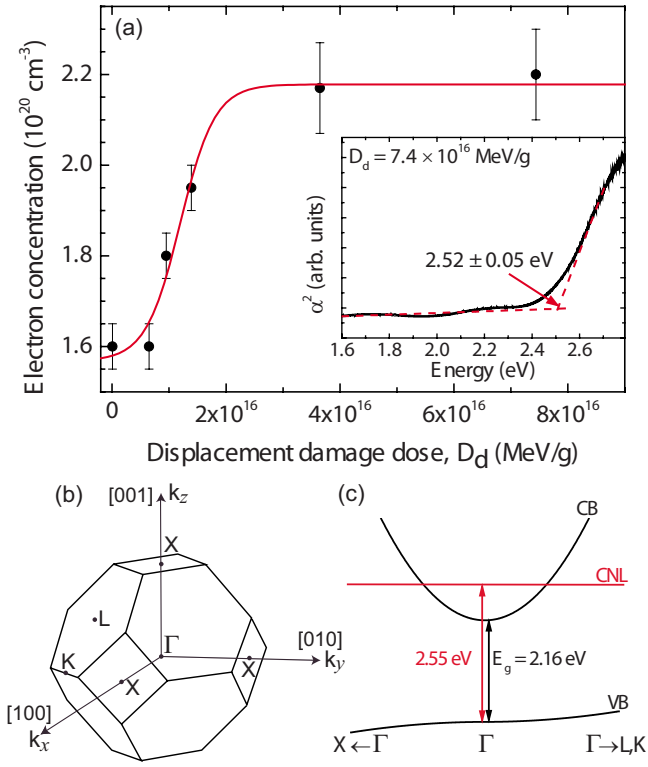


FIG. 1. (Color online) (a) Electron concentration of $^4\text{He}^+$ ion irradiated CdO as a function of displacement damage dose D_d , with a sigmoidal fit to guide the eye. Inset: square of the optical-absorption coefficient for the most heavily irradiated sample; (b) Brillouin zone for the rocksalt crystal structure; (c) schematic representation of the CNL position, conduction-band (CB) and valence-band (VB) edges in CdO close to Γ .

of these values, the Fermi level is therefore determined to stabilize $2.55 \pm 0.05 \text{ eV}$ above the Γ -point VBM, and hence above the conduction-band minimum (CBM) [$E_g(\Gamma) = 2.16 \text{ eV}$ (Ref. 7)] following extremely heavy irradiation.

Within the amphoteric defect model, the formation energy for donor (acceptor) native defects, such as anion (cation) vacancies, increases (decreases) with increasing Fermi level, as shown in Fig. 2(a), such that formation of donor (acceptor) native defects is most favorable when the Fermi level is below (above) an energy level known as the Fermi-level stabilization energy.¹² The behavior of such native defects can, more generally, be considered from the charge character of the associated virtual gap states (ViGS), which exist wherever the perfect periodicity of the crystal lattice is broken. The level of local charge neutrality (CNL) occurs at the branch point of the ViGS, marking the energy at which their character changes from predominantly donorlike (valence-band character) below the CNL to predominantly acceptorlike (conduction-band character) above the CNL.¹³ Consequently, the formation energy for donor and acceptor native defects will be equal at the branch point of the ViGS, and the Fermi-level stabilization energy can be equated with the CNL of the material.

In the majority of semiconductors, the CNL is located close to the middle of the fundamental band gap. Ion irradiation therefore preferentially produces donor defects in p -type

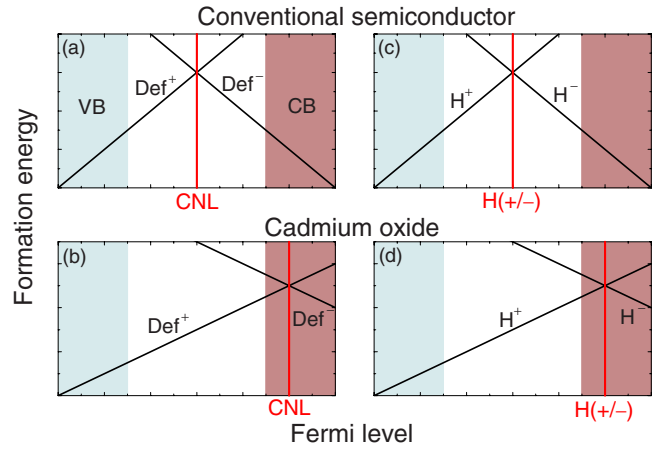


FIG. 2. (Color online) Schematic representation of the formation energy as a function of Fermi level for [(a) and (b)] irradiation-induced donor (Def $^+$) and acceptor (Def $^-$) defects, relative to the CNL, and [(c) and (d)] donor (H $^+$) and acceptor (H $^-$) hydrogen, relative to the H(+/-) level, in [(a) and (c)] conventional semiconductors and in [(b) and (d)] CdO. The conduction bands (CB) and valence bands (VB) are represented by shading.

material, whereas for n -type material, acceptor defects have lower formation energy [Fig. 2(a)]. However, donor defects are created here in already heavily n -type samples, indicating that the CNL must be located substantially above the CBM in CdO [Fig. 2(b)]. After sufficient irradiation, the Fermi level will move to the CNL, at which point the formation energy for creating donor and acceptor native defects is equal; no net change in carrier density will occur upon further creation of native defects, resulting in the Fermi level stabilizing at the CNL.¹⁴ Thus, the CNL is determined to lie $2.55 \pm 0.05 \text{ eV}$ ($0.39 \pm 0.05 \text{ eV}$) above the Γ -point VBM (CBM), as illustrated schematically in Fig. 1(c). The formation energy for compensating acceptor (donor) defects to form when n -type (p -type) doping CdO will therefore be relatively high (low) for Fermi levels above the CBM (below the VBM) [Fig. 2(b) compared with Fig. 2(a)], allowing CdO to be extrinsically doped heavily n -type, as has been observed experimentally,¹⁵ whereas p -type doping will be difficult.

As ViGS are gap states, it seems counterintuitive that the CNL can lie outside of the fundamental band gap. However, they are very localized in real space, and so have an extended k -space character, derived from the complex band structure across the *entire* Brillouin zone, rather than just the Γ point. Consequently, the CNL lies close to the midgap energy averaged across the Brillouin zone. Due to the significant size and electronegativity mismatch of Cd and O, the CBM at the Γ point is significantly lower than across the rest of the Brillouin zone in CdO, as confirmed by previous band-structure calculations.¹⁶ Additionally, for the octahedral point symmetry of CdO's rocksalt structure, a p - d interaction between the Cd $4d$ and O $2p$ orbitals, which pushes the VBM to higher energies, is symmetry forbidden at Γ , causing a positive valence-band dispersion away from the zone center in the $\Gamma \rightarrow L, K$ directions,¹⁷ shown schematically in Fig. 1(c). The resulting midgap energy averaged across the Brillouin zone is therefore high compared to the band edges at Γ , explaining why the CNL lies above the CBM.

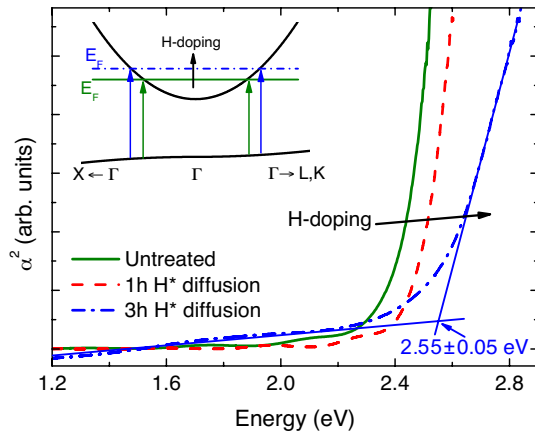


FIG. 3. (Color online) Squared optical-absorption coefficient for untreated CdO and CdO following diffusion of atomic hydrogen for 1 and 3 h. An increased Burstein-Moss shift is evident with increased hydrogen doping, represented schematically in the inset.

IV. HYDROGEN

Similar to the native defects discussed above, hydrogen forms a very localized impurity center; it is therefore appropriate to also consider this within the ViGS framework. Indeed, Van de Walle and Neugebauer¹ argued that hydrogen in the positive charge state can be associated with the creation of a cation dangling bond, whereas for hydrogen in the negative charge state, an anion dangling bond will exist. From the discussions of native defects above, the H(+/-) transition should therefore occur at the CNL of the material. To investigate this experimentally, atomic hydrogen was diffused into nominally undoped CdO for 1 and 3 h, as described above. The incorporation of hydrogen within the semiconductor causes an increased Burstein-Moss shift of the optical-absorption edge (Fig. 3), associated with the Fermi level moving to higher energies in the conduction band (Fig. 3, inset), consistent with the results of Dakhel.¹⁸ This is supported by Hall-effect measurements which reveal an increase in carrier concentration from 1.4×10^{20} to $2.2 \times 10^{20} \text{ cm}^{-3}$ upon diffusion of hydrogen. Following the 3 h diffusion, the measured carrier density equates to a Fermi level 2.57 eV above the Γ -point VBM, in agreement with the value of $2.55 \pm 0.05 \text{ eV}$ determined from optical absorption.

Hydrogen therefore forms an electrically active donor, even in highly n -type CdO, in contrast to most materials where hydrogen forms as an acceptor (H^-) in n -type or a donor (H^+) in p -type material,¹ as shown in Fig. 2(c). In rare cases however, perhaps most notably in ZnO, hydrogen has been predicted to act solely as a donor.² As for ZnO, the H(+/-) transition must be above the CBM in CdO [Fig. 2(d)]. Further, the Fermi level is located at the same energy as the CNL after significant diffusion of hydrogen, providing the first experimental evidence of the equality of the CNL and the H(+/-) level, indicating a common origin governing the electrical behavior of both native defects and hydrogen in semiconductors.

Hydrogen is therefore a probable candidate for the unintentional dominant donor giving rise to the high n -type conductivity of the MOVPE-grown nominally undoped CdO

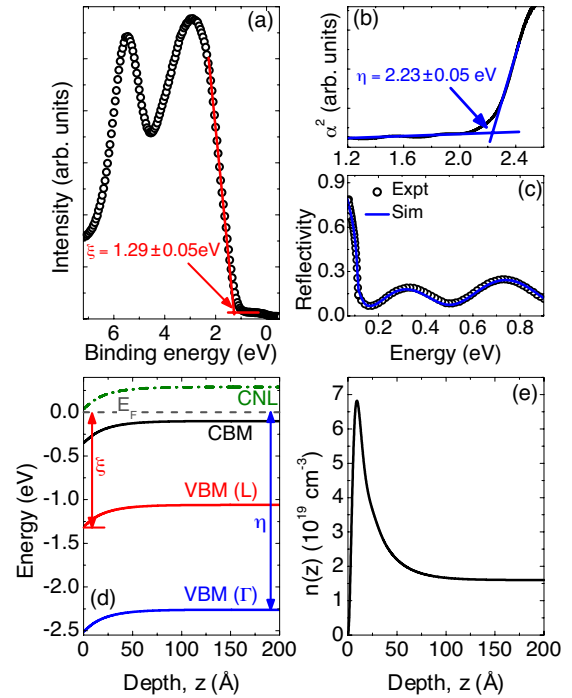


FIG. 4. (Color online) (a) Valence-band photoemission, (b) squared optical-absorption coefficient, and (c) measured (points) and simulated (line) IR reflectivity spectra for an undoped CdO sample following annealing at 600°C in UHV for 2 h. (d) Band bending [CBM, indirect (L -point) and direct (Γ -point) VBMs] and (e) carrier concentration as a function of depth below the surface in the electron accumulation layer.

samples investigated here, with thermal debonding and removal of hydrogen a likely cause of the dramatic improvement in electrical properties with annealing in UHV observed in previous investigations.⁷ This was also observed here for a 570-nm-thick sample annealed in UHV at 600°C for 2 h, before (after) which the carrier concentration and mobility were determined from Hall-effect measurements to be $1.7 \times 10^{20} \text{ cm}^{-3}$ ($1.6 \times 10^{19} \text{ cm}^{-3}$) and $59 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ($106 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), respectively. The carrier density determined by Hall-effect measurements following annealing is in agreement with the bulk Fermi level determined from optical-absorption measurements and the bulk plasma frequency determined from IR reflectivity measurements, shown in Figs. 4(b) and 4(c), respectively, suggesting that the removal of hydrogen is fairly uniform throughout the film. In all materials where the CNL, and consequently the H(+/-) level, is above the CBM, hydrogen must certainly be considered as a potential cause of unintentional n -type conductivity in addition to donor-type native defects. Conversely, when the CNL lies below the VBM, hydrogen is a plausible candidate for unintentional p -type conductivity.

V. SURFACE ELECTRONIC PROPERTIES

To probe the importance of the CNL in determining surface electronic properties, the surface space-charge region of the CdO sample prepared by annealing in UHV at 600°C for 2 h (discussed above) was investigated. Valence-band

XPS measurements [Fig. 4(a)] give the L -point (indirect) VBM to surface Fermi-level separation as $\xi = 1.29 \pm 0.05$ eV, consistent with previous results.¹⁹ From Hall effect ($n = 1.6 \times 10^{19}$ cm⁻³, $\mu = 106$ cm² V⁻¹ s⁻¹), optical absorption and IR reflectivity measurements [Figs. 4(b) and 4(c)], the Γ -point VBM to bulk Fermi-level separation was determined as $\eta = 2.23 \pm 0.05$ eV. Taking the separation of the Γ point and L point of the valence band as 1.2 eV,¹⁶ the Fermi level lies higher relative to the band extrema at the surface than in the bulk, implying a downward bending of the bands at the surface of 0.26 eV. The calculated band bending is shown in Fig. 4(d). Below the CNL, surface states can be described by ViGS which are predominantly donor like. As the surface Fermi level pins slightly below the CNL value determined above [Fig. 4(d)], a number of these donor-like ViGS are unoccupied, and therefore ionized, leading to a positive surface charge. As the CNL is above the CBM in CdO, these ViGS are able to donate their electrons directly into the conduction band, maintaining charge neutrality and leading to a large accumulation of electrons in the near-surface region [Fig. 4(e)]. The CNL lying above the CBM can therefore be understood as the overriding mechanism driving surface electron accumulation in CdO.

VI. IMPLICATIONS FOR OTHER MATERIALS

The above investigations have shown that a single energy level, fundamentally deriving from the bulk band structure, dictates the favorable charge state for native defects, hydrogen impurities, and surface states in semiconductors. When the Brillouin-zone averaged midgap energy, and hence the CNL, lies in the conduction band, as for CdO investigated here, the material exhibits properties such as: donor nature of hydrogen; high unintentional n -type conductivity; ease of n -type but difficulty of p -type doping; and surface electron accumulation. Similar properties would be expected for other semiconductors with a large size and electronegativity mismatch between the cation and anion, leading to particularly low Γ -point CBMs lying below the CNL. This explains, for example, why the oxide materials such as ZnO, In₂O₃, SnO₂, and indeed CdO can have very high n -type conductivities, despite being optically transparent. Conversely, in a material such as GaSb, the critical points of the conduction-band edge are all located at similar energies, whereas the downward dispersion of the valence bands away from Γ is rather pronounced.²⁰ Consequently, the CNL would be expected to lie below the VBM in this material, explaining its propensity for unintentional p -type conductivity, surface hole accumulation,²¹ and the recent theoretical predictions of the acceptor nature of hydrogen even in p -type material.³ Another interesting example is the Cu-containing delafossite

materials. In these, the very high Cu p -orbital energy pushes the VBM upward in energy, and so the CNL will lie close to the VBM. High p -type conductivity can therefore be achieved, even in wide band-gap materials, as has previously been observed experimentally,²² explaining the use of Cu in p -type transparent conducting oxide semiconductors.

Band-gap engineering of semiconductors involves the alloying of several compounds in order to control basic optoelectronic and structural properties (for example, the band gap and lattice constant). Using the insights gained here, this can be extended to tailor the electrical properties of the material by considering not only the band gap and lattice constant of the constituent compounds, but also the position of the band extrema relative to the CNL. For example, if an alloy is formed incorporating a material with a low Γ -point CBM, elements with low s -orbital energies, or dilute impurities which cause an anticrossing interaction lowering the conduction-band edge,²³ the CBM of the alloy will be pushed down with respect to the CNL, increasing its tendency toward n -type conductivity and surface electron accumulation. If, on the other hand, a high Γ -point VBM material is used, elements are incorporated with high p -orbital energies or a valence-band anticrossing interaction²⁴ is introduced pushing the VBM upward with respect to the CNL, the proclivity toward acceptor defects, impurities, and surface states will be increased.

VII. CONCLUSIONS

The nature of the charge state of native defects, hydrogen, and surface states has been unified via a single energy level, the charge neutrality level, deriving from the bulk band structure. In CdO, this was shown to lead to such centers being donors even in n -type material, with the charge neutrality level determined as lying ~ 0.4 eV above the conduction-band minimum. This facilitates a general understanding of the electronic properties of all semiconductors, and allows the possibility of engineering materials with specific electrical properties.

ACKNOWLEDGMENTS

We are grateful to N. Peng of Surrey Ion Beam Centre, U.K., and to D. Law and G. Beamson of the National Centre for Electron Spectroscopy and Surface analysis, Daresbury Laboratory, U.K., for technical assistance. We acknowledge the Engineering and Physical Sciences Research Council (U.K.), and the Spanish Government for financial support under Grants No. EP/E010210/1 and No. EP/G004447/1 (Warwick) and No. EP/E025722/1 (NCESS), and Grant No. MAT2007-66129 (Valencia), respectively.

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