Surface Band-Gap Narrowing in Quantized Electron Accumulation Layers

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An energy gap between the valence and the conduction band is the defining property of a semiconductor, and the gap size plays a crucial role in the design of semiconductor devices. We show that the presence of a two-dimensional electron gas near to the surface of a semiconductor can significantly alter the size of its band gap through many-body effects caused by its high electron density, resulting in a surface band gap that is much smaller than that in the bulk. Apart from reconciling a number of disparate previous experimental findings, the results suggest an entirely new route to spatially inhomogeneous band-gap engineering.

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The interface between some semiconductors [1] and even insulators [2] can be designed to support a quasi-two-dimensional electron gas (Q2DEG), in which the electrons move freely parallel to the interface, but are otherwise confined. Such 2DEGs have not only shown a plethora of fascinating fundamental phenomena, for example, the integer and the fractional quantum Hall effect [3,4] and two-dimensional superconductivity [5], but also have enormous technological importance [6]. While there is a depletion of charge carriers close to the surface of most semiconductors, a particular class of materials [7], where the so-called charge neutrality level lies within the conduction band, have been shown to support an intrinsic Q2DEG (electron accumulation) at their surfaces [7–10]. Its surface-localized nature opens up a unique opportunity to spectroscopically probe a Q2DEG system.

In this Letter, we report such an investigation. We show that the conventional one-electron picture of surface space-charge in semiconductors is inconsistent with the electronic structure that we observe directly from angle-resolved photoemission spectroscopy (ARPES), indicating that many-body interactions play an unexpectedly large role in these materials. We show that such interactions lead to a depth-dependent shrinkage of the semiconductor band gap, resulting in a surface band gap which differs from its value in the bulk of the material.

InAs(111)*B* and CdO(001) samples were grown by molecular-beam epitaxy and metal-organic vapor phase epitaxy, respectively. The InAs was Si-doped to $n = 6 \times 10^{17}$ cm^{-3}, while the CdO was nominally undoped, with a residual background concentration of $n = 2 \times 10^{19}$ cm^{-3}. The InAs was terminated by an amorphous As cap following growth, which was removed *in situ* by annealing at 350 °C, while the CdO was prepared by annealing at 600 °C. Sharp (2×2) low energy electron diffraction patterns were observed for all samples following surface preparation. Photoemission measurements were performed on the undulator beam line SGM-3 of the ASTRID synchrotron, Denmark [11]. All photoemission spectra discussed in this work are referenced to the Fermi level determined from a polycrystalline gold film in electrical contact with the sample.

The electronic structure of a surface Q2DEG [Fig. 1(a)] can be measured directly by ARPES [12,13]: such measurements, performed here for CdO(001), are shown in Fig. 1. Both the parallel dispersion [Fig. 1(b)] and constant energy contours [Fig. 1(c)] of these states (vertical and horizontal "slices" through their two-dimensional electronic structure [Fig. 1(a)]) were measured, revealing two rapidly dispersing states centered at the $\bar{\Gamma}$ point of the surface Brillouin zone. The positive dispersion of these states confirms their electron character, resulting from the Q2DEG that exists at the surface of this material [7], while the concentric circular contours reveal the highly isotropic in-plane nature of these states. Such states result from a pronounced downward bending of the electronic bands relative to the Fermi level when approaching the surface of the material [Fig. 1(d)]. This creates a confining potential well for electrons, causing the conduction-band states to become quantized into two-dimensional subbands having dispersion within the surface plane [Figs. 1(a)–1(c)].

InAs also supports a surface accumulation of electrons [8]. A conventional measure of the associated downward band bending is given by the difference in the valence-band maximum (VBM) to Fermi level separation at the surface and in the bulk. The former quantity can be determined

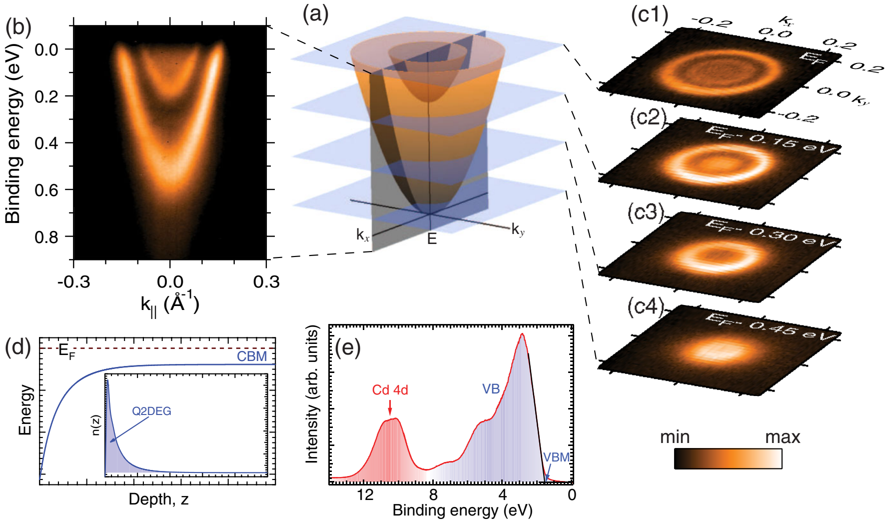

FIG. 1 (color online). (a) Quantized conduction-band subbands of a surface Q2DEG. (b) E vs $k_{\|}$ and (c) constant energy cuts through the subband dispersions measured by ARPES, shown here for a CdO(001) surface recorded with a photon energy of $h\nu = 30$ eV at room temperature. The constant energy cuts are integrated over ± 3 meV about (c1) the Fermi level and (c2) 0.15, (c3) 0.30, and (c4) 0.45 eV below the Fermi level, respectively. (d) Schematic of downward bending of the conduction band and (inset) corresponding increase in free-carrier density within the semiconductor surface electron accumulation layer (Q2DEG). (e) AIPES measurements of the valence bands and Cd 4d core levels in CdO, recorded at a photon energy of $h\nu = 120$ eV.

directly from the onset of valence-band photoemission, or from the difference between the measured core-level binding energy (α) and the known VBM to core-level separation (β) [14], as shown inset to Fig. 2(a). Photoemission measurements of the In 4d core-levels of InAs are shown in Fig. 2(a). These were fitted by two spin-orbit split d components ($\Delta E_{\mathrm{so}} = 0.855$ eV) to account for the bulk core-level peak and a shifted component from the surface atoms. The separation of the bulk and surface components was 0.28 eV, in agreement with previous studies of InAs(111)$B - (2 \times 2)$ [15]. The bulk component occurs at a binding energy of 17.46 ± 0.05 eV. Comparison with the VBM to In 4d separation determined previously [15] allows the Fermi level to be located 0.56 ± 0.05 eV above the VBM at the surface. A valence-band photoemission spectrum, recorded in the normal emission geometry at a photon energy chosen to probe the center of the bulk Brillouin zone [16], is shown in Fig. 2(b). From this, the onset of valence-band photoemission can be estimated to occur ~0.6 eV below the Fermi level, in agreement with the VBM to surface Fermi level separation determined from the core-level analysis.

Coupled with knowledge of the bulk Fermi level and bulk band gap, these valence and core-level PES measurements confirm a downward band bending of the valence band of ~0.1 eV; quantized surface conduction-band subbands would also, therefore, be expected [16]. ARPES measurements confirming this for InAs(111) are shown in Fig. 3(c) and 3(d). The density of the surface Q2DEG can be estimated from its Luttinger area, $N_{2\mathrm{D}} = k_F^2/2\pi$, where k_F is the Fermi wave vector. Taking k_F directly from the measured ARPES data gives $N_{2\mathrm{D}} \approx 3.8 \times 10^{12}$ cm^{-2}. While this is higher than the often quoted value of the surface state density of InAs of $\sim 1 \times 10^{12}$ cm^{-2} [16], it is in good agreement with recent multiple-field Hall effect measurements [17], which determined an electron accumulation density of $\sim 4 \times 10^{12}$ cm^{-2}.

Given the valence-band bending, and assuming the same bending for the conduction band, both the Q2DEG density and positions of the quantized subbands can be inferred from nonparabolic coupled Poisson-Schrödinger (PS) calculations [18]. Taking a value for this band bending of 0.1 eV, determined above for the valence-band bending of

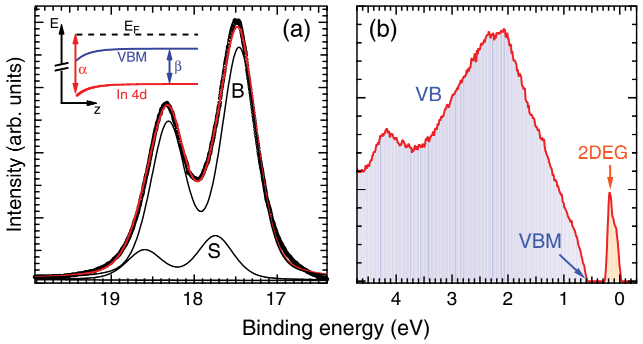

FIG. 2 (color online). (a) In 4d core-level photoemission from InAs, recorded with a photon energy of $h\nu = 70$ eV at a temperature of 60 K, and its deconvolution into bulk (B) and surface (S) components. A schematic representation of the core-level and valence-band bending is shown in the inset. (b) Valence-band ARPES spectrum recorded in the normal emission geometry with a photon energy of $h\nu = 20$ eV at a temperature of 60 K. The 2DEG states can also be seen above the VBM.

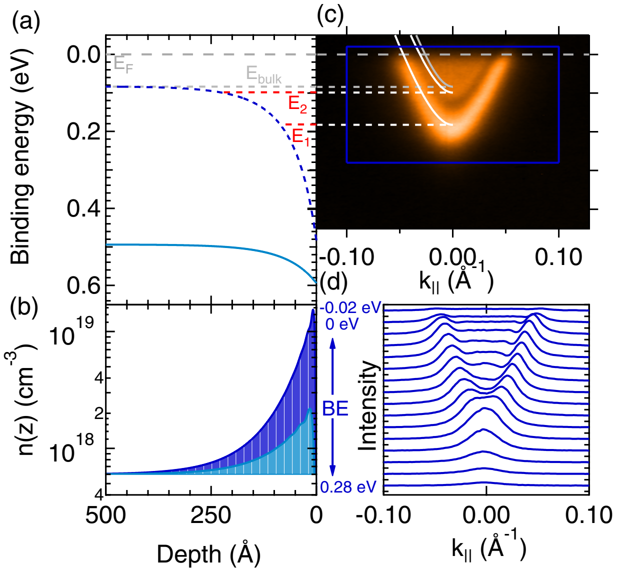

FIG. 3 (color online). (a) Downward band bending at the surface of InAs of 0.1 eV (light blue solid line) and 0.4 eV (dark blue dashed line) determined from analysis of the valence band and conduction band, respectively, and (b) corresponding near-surface carrier density variation. (c) Parallel dispersions of the quantized states measured by ARPES, recorded with a photon energy of $h\nu = 20$ eV at a temperature of 60 K. Calculated subband positions and dispersions are shown as red [white] lines in (a) [(c)]. (d) A set of momentum distribution curves from within the blue box of (c), confirming a clear rapidly dispersing outer band and a much weaker inner band.

InAs, such calculations yield only a single subband, located ~ 0.1 eV below the Fermi level [Fig. 4(a)], and a corresponding Q2DEG density of only 1×10^{12} cm^{-2}. This is inconsistent with the electronic structure of the Q2DEG determined directly from the ARPES measurements (Fig. 3): The single calculated subband lies ~ 0.1 eV above the lower of *two* measured subbands, which of course also leads to a significant underestimation of the electron density.

Consequently, there is a discrepancy between the Q2DEG density determined by probing the valence-band bending and the conduction-band bending in InAs. A similar discrepancy can be identified for the materials CdO and InN. Angle-integrated (AI) PES measurements of the valence bands and Cd 4*d* core levels from CdO are shown in Fig. 1(a). From a linear extrapolation of the leading edge of the valence-band photoemission to the baseline, the VBM to surface Fermi level separation is estimated here as 1.55 ± 0.05 eV. The Cd 4*d* levels are very shallow in this material, and so hybridize with the valence-band structure [19], preventing spectral fitting to yield their exact binding energy using conventional lineshapes, as was performed for InAs above. However, by comparison of these spectral features with previous measurements [19], the VBM to surface Fermi level separation determined from the core-level peak positions can be estimated as 1.6 ± 0.1 eV, in good agreement with that determined from valence-band photoemission. Coupled with knowledge of the bulk Fermi level and bulk band gap, these AIPES measurements allow the downward bending of the valence band to be estimated as ~ 0.25 eV.

When this band bending is used to calculate the Q2DEG density, the result is again significantly lower than the Luttinger area density estimated directly from the measured ARPES data ($\sim 1 \times 10^{13}$ cm^{-2} instead of 4.4×10^{13} cm^{-2}). Meanwhile, a downward bending of the conduction band by 1.1 eV is required to obtain agreement between coupled PS calculations and the ARPES measurements: Indeed, as in the case of InAs, PS calculations assuming the smaller, valence-band derived, value for the band bending of 0.25 eV yield a single conduction-band subband, located 0.2 eV below the Fermi level, and so 0.31 eV above the bottom subband observed in the ARPES measurements [Fig. 4(b)].

Similar effects can also be seen in the previous InN ARPES measurements of Colakerol *et al.* [12]. PS calculations require a downward band bending of 1.1 eV to simulate the conduction-band subband energies and dispersions, much higher than the value of ~ 0.65 eV that can be estimated from valence-band AIPES measurements performed on similar samples [20,21]. The calculated subband position for this smaller amount of downward band bending again lies ~ 0.3 eV above the lower measured subband position, as shown in Fig. 4(c). Further, while the Q2DEG density inferred from the valence-band photoemission results is $\sim 1.6 \times 10^{13}$ cm^{-2}, the ARPES measurements reveal a higher density of $\sim 4.5 \times 10^{13}$ cm^{-2}. This is, in fact, in better agreement with multiple-field Hall effect measurements of the surface Q2DEG density [22,23], as for the case of InAs discussed above.

We argue that the above discrepancies can be understood by considering many-body interactions within the semiconductor electron accumulation layer. In the bulk of

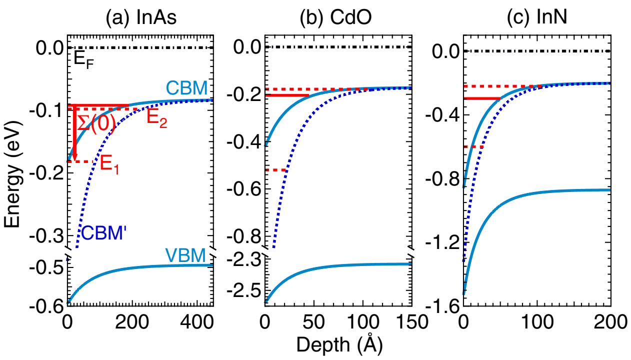

FIG. 4 (color online). One-electron (solid line, determined from core-level and valence-band photoemission) and schematic renormalized (dashed line, determined from ARPES of the conduction-band subbands) band bending at the surface of (a) InAs, (b) CdO, and (c) InN, and corresponding calculated one-electron (solid) and measured renormalized (dashed) subband energies.

degenerately doped semiconductors, such interactions between the free carriers are known to lead to a renormalization of the semiconductor electronic structure, resulting in a shrinkage of the band gap [24], effects which should be more pronounced in reduced dimensionality systems [25]. Our results suggest that a nonhomogeneous band renormalization occurs in the systems studied here, with increased band-gap shrinkage occurring within the electron accumulation layer due to its high electron density, as compared to in the bulk of the material. Such a band-gap shrinkage leads to a smaller band gap at the surface of the semiconductor than in the bulk: This effectively increases the depth of the Q2DEG potential well, causing the quantized states observed by ARPES to occur at higher binding energies than would be expected by considering the Hartree potential neglecting these many-body interactions (determined from valence-band and core-level photoemission).

In such a description, the conduction-band subband should be renormalized to lower energies by the real part of the electron self energy at the band edge [26]. Calculations of the electron self energy were performed here within the random phase approximation incorporating both electron-phonon (*e*-ph) and electron-plasmon (*e*-pl) interactions, following the method derived by Jalabert and Das Sarma [27], yielding a subband renormalization of 0.09, 0.34, and 0.32 eV for InAs, CdO, and InN, respectively. These calculations are in good agreement with the shift in energy between the subband position calculated within the Hartree approximation (using the valence-band bending determined from valence-band and core-level photoemission) and the observed position of the lower subband in the ARPES measurements (see Fig. 4).

This supports our conclusion of a surface band-gap narrowing due to many-body interactions within the quantized electron accumulation layer, reconciling previous disparate electrical and spectroscopic results on surface space-charge in semiconductors. Consequently, the band gap of a semiconductor is not necessarily constant, but can exhibit a striking variation with depth below the surface. Furthermore, being localized at the surface, the Q2DEGs investigated here provide a model system in which to spectroscopically investigate the fundamental properties of many-body interactions in solids. In particular, the density of the Q2DEG could be varied by adsorption of minute quantities of alkali metals on the surface [28], allowing a novel opportunity to spectroscopically probe the carrier density and temperature dependence of electron-phonon and electron-plasmon interactions, and indeed coupling between these modes, without changing the properties of the host material. Beyond fundamental studies, these findings offer potential for novel density-controlled band-engineering schemes in electronic devices.

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[1] R. Dingle *et al.*, Appl. Phys. Lett. **33**, 665 (1978).
[2] A. Ohtomo and H. Y. Hwang, Nature (London) **427**, 423 (2004).
[3] K. von Klitzing, G. Dorda, and M. Pepper, Phys. Rev. Lett. **45**, 494 (1980).
[4] D. C. Tsui, H. L. Stormer, and A. C. Gossard, Phys. Rev. Lett. **48**, 1559 (1982).
[5] N. Reyren *et al.*, Science **317**, 1196 (2007).
[6] T. Ando, A. B. Fowler, and F. Stern, Rev. Mod. Phys. **54**, 437 (1982).
[7] P. D. C. King *et al.*, Phys. Rev. B **79**, 035203 (2009).
[8] M. Noguchi, K. Hirakawa, and T. Ikoma, Phys. Rev. Lett. **66**, 2243 (1991).
[9] I. Mahboob *et al.*, Phys. Rev. Lett. **92**, 036804 (2004).
[10] P. D. C. King *et al.*, Phys. Rev. Lett. **101**, 116808 (2008).
[11] S. V. Hoffmann *et al.*, Nucl. Instrum. Methods Phys. Res., Sect. A **523**, 441 (2004).
[12] L. Colakerol *et al.*, Phys. Rev. Lett. **97**, 237601 (2006).
[13] L. F. J. Piper *et al.*, Phys. Rev. B **78**, 165127 (2008).
[14] F. J. Himpsel, G. Hollinger, and R. A. Pollak, Phys. Rev. B **28**, 7014 (1983).
[15] L. Ö. Olsson *et al.*, Phys. Rev. B **53**, 4734 (1996).
[16] L. Ö. Olsson *et al.*, Phys. Rev. Lett. **76**, 3626 (1996).
[17] Y. Lin *et al.*, Appl. Phys. Lett. **93**, 062109 (2008).
[18] P. D. C. King, T. D. Veal, and C. F. McConville, Phys. Rev. B **77**, 125305 (2008).
[19] P. D. C. King *et al.*, Phys. Rev. B **79**, 205205 (2009).
[20] P. D. C. King *et al.*, Appl. Phys. Lett. **91**, 092101 (2007).
[21] P. D. C. King *et al.*, Phys. Rev. B **77**, 045316 (2008).
[22] C. Swartz *et al.*, J. Cryst. Growth **269**, 29 (2004).
[23] T. B. Fehlberg *et al.*, J. Electron. Mater. **37**, 593 (2008).
[24] K. F. Berggren and B. E. Sernelius, Phys. Rev. B **24**, 1971 (1981).
[25] G. Tränkle *et al.*, Phys. Rev. Lett. **58**, 419 (1987).
[26] S. Das Sarma, R. Jalabert, and S.-R. E. Yang, Phys. Rev. B **39**, 5516 (1989).
[27] R. Jalabert and S. Das Sarma, Phys. Rev. B **40**, 9723 (1989).
[28] V. Y. Aristov *et al.*, J. Vac. Sci. Technol. B **12**, 2709 (1994).