Direct Measurement of the Band Structure of a Buried Two-Dimensional Electron Gas

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We directly measure the band structure of a buried two dimensional electron gas (2DEG) using angle resolved photoemission spectroscopy. The buried 2DEG forms 2 nm beneath the surface of p-type silicon, because of a dense delta-type layer of phosphorus n-type dopants which have been placed there. The position of the phosphorous layer is beyond the probing depth of the photoemission experiment but the observation of the 2DEG is nevertheless possible at certain photon energies where emission from the states is resonantly enhanced. This permits direct access to the band structure of the 2DEG and its temperature dependence.

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Buried two dimensional electron gases (2DEGs) have recently attracted considerable attention as a testing ground for both fundamental physics and quantum computation applications. Such 2DEGs can be created by phosphorus delta (δ) doping of silicon, a technique in which a dense and narrow dopant profile is buried beneath the Si surface [1–3]. The band structure of the δ-layers has been studied intensely using different theoretical methods [4–9], but it has hitherto not been possible to directly compare these predictions with experimental data. Here, we report measurements of the electronic band structure of a δ-doped layer below the Si(001) surface by angle resolved photoemission spectroscopy (ARPES). Our measurements confirm the layer to be metallic and give direct access to the Fermi level position. Surprisingly, the direct observation of the states is possible despite them being buried far below the surface.

In order to probe the electronic structure of the δ-layer states, samples were prepared by substitutionally incorporating $1/4$ of a monolayer of phosphorus atoms on a clean Si(001) surface and burying this structure under 2.0 ± 0.6 nm of silicon [10]. Control samples were fabricated by similarly growing silicon on the clean surface, without the incorporation of a phosphorus layer. Figures 1(a), 1(b), 1(e), and 1(f) show ARPES measurements (performed at MAXlab) at two photon energies (36 and 113 eV) of a control sample and a δ-doped sample, respectively. Both samples show several similar structures that can be ascribed to silicon bulk and surface states, but the δ-doped sample clearly shows sharp additional states that are missing on the control sample (enclosed in yellow). Most strikingly, we observe a state at the Fermi energy ($E_b < 0.2$ eV), immediately confirming the predicted metallic nature of the δ-doped layers. Other additional states are found at a binding energy $E_b \approx 1$ eV with a character similar to the bulk Γ valence band states.

Figures 1(c) and 1(d) show the photoemission intensity in normal emission ($k_x = k_y = 0$) for the control sample and δ-doped sample, respectively. The horizontal axis has been converted from photon energy to $k_\perp$ assuming free electron final states [10]. The marked states in Figs. 1(b) and 1(f) are clearly identified as two-dimensional by their lack of dispersion as the photon energy is changed. Furthermore, they can be distinguished from the genuine surface states or surface resonances (emphasized by white contours at $E_b \approx 0.5$ and 2.0 eV) of Si(001), since these are present on both samples. Note that the surface states appear quite broad. This is ascribed to crystalline imperfection in the surface of the overlayer, grown at low temperature to minimize dopant segregation.

The ARPES measurements in Figs. 1(c) and 1(d) are plotted together with the calculated bulk band structure for Si (after Ref. [11]) and the agreement is very good. The $k_\perp$ values for reaching the bulk X high symmetry point are found to correspond to photon energies of 36 and 113 eV. Although the bulk state dispersion is essentially unchanged by δ-doping, the surface Fermi level is shifted toward the top of the band gap by ≈ 0.23 eV. This results in a shift of the entire band structure (shallow bulk and surface states) to a higher binding energy as seen, for example, by comparing Figs. 1(a) and 1(b).

The new electronic states in the δ-doped sample can be mapped in the plane parallel to the surface. Figure 2 shows the dispersion in two high-symmetry directions [Figs. 2(a) and 2(d)], as well as the Fermi contour [Fig. 2(c)]. The map directly reveals the periodicity of the dispersion parallel to the surface as corresponding to a (2×2) structure. This is to be expected because of the two rotational domains of (2×1) reconstruction present on a Si(001) surface. Note that this periodicity parallel to the surface does not necessarily imply the same periodicity in the δ-layer or in the bulk; it is anyway expected due to surface-umklapp

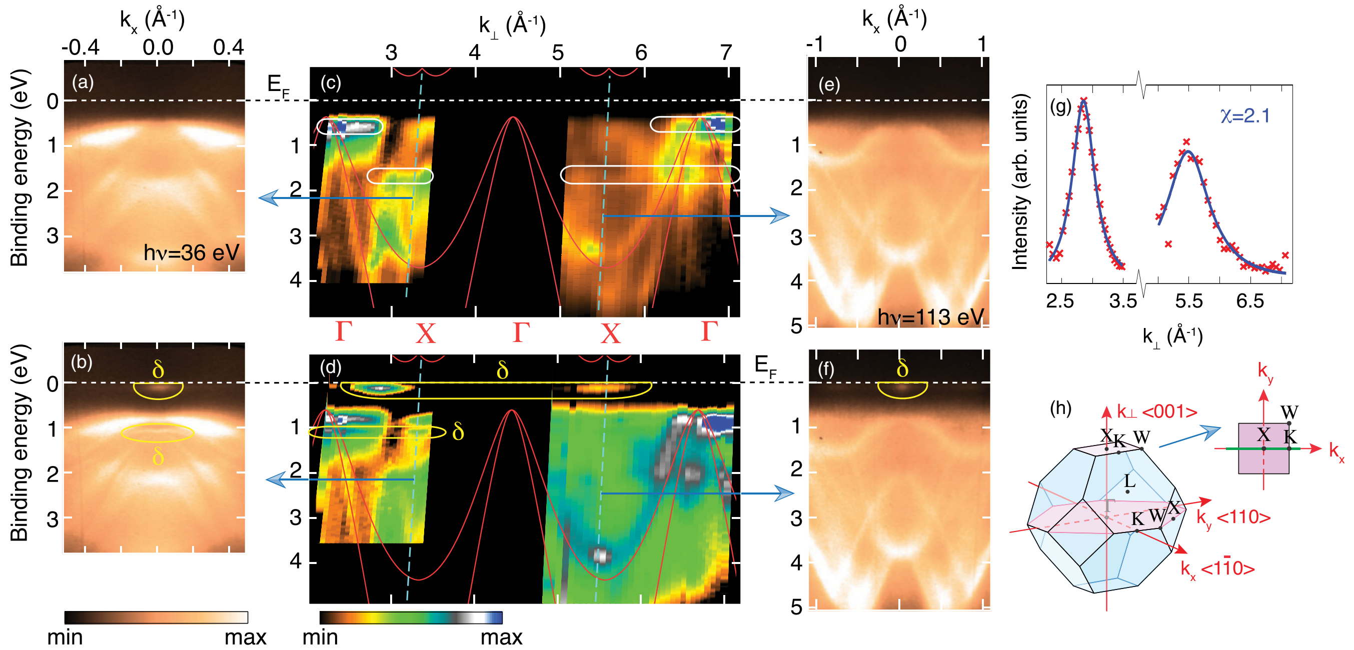

FIG. 1 (color online). (a) and (b) ARPES measurements at $h\nu = 36$ eV for the control sample and δ-doped silicon, respectively. The additional states due to the δ-layer are enclosed in yellow and marked. (c) and (d) The photoemission intensity at normal emission, plotted as a function of $k_\perp$ for the same samples with the calculated bulk band structure [11] overlaid in red. δ-layer states are marked as before and surface states are enclosed in white in (c). (e) and (f) ARPES measurements taken at $h\nu = 113$ eV for the control sample and the δ-doped sample, respectively. (g) The intensity of the δ state nearest the Fermi level (red markers) and a fit (blue traces) after Ref. [14]. (h) Bulk Brillouin zone and the definition of the axes $k_\perp$, k_x, and k_y, with the plane through the bulk X point extracted. The green solid line along k_x corresponds to the bulk directions probed in (a), (b), (e), and (f).

scattering [10]. The Fermi contour appears to be streaked along the k_x and k_y directions. The streaks can be related to the different appearance of the state along the two cuts shown. In the $k_x = k_y$ direction in Fig. 2(a), the δ-layer state appears as a sharp structure around $k_\parallel = (k_x^2 + k_y^2)^{0.5} = 0$, whereas it is always observable along the $k_x = 0$ and $k_y = 0$ directions [see Figs. 2(c) and 2(d)]. The detailed reason for this is difficult to determine because the states are only barely visible at the Fermi energy and the full dispersion is not accessible. The dispersion could be anisotropic with a higher effective mass along k_x and k_y than along the diagonal direction. It is also conceivable that states lying closely above the Fermi level, such as the predicted 1Δ state (see, for example, Ref. [5] and Fig. 2(b)) contribute intensity to the Fermi surface. However, since the 1Δ state is predicted to have its minima in the $k_\parallel = (k_x^2 + k_y^2)^{0.5} = 0$ direction, this would produce streaking rotated 45° to that observed here. Streaking would also be expected if step edges, or the rotated (2×1) domains on the surface, are restricted in the x and y directions. Similar limited domain sizes in the δ-layer could also play a role but the present observations do not require the existence of new periodicities (such as $4 \times n$) in the δ-layer [4].

Theoretical studies of δ-doped Si have focused on the electronic states close to the Fermi energy, as these are relevant for transport [4–9]. A common prediction is the formation of impurity bands below the bulk conduction band minimum. The lowest lying states, called 1Γ and 2Γ, derive from the projection of the conduction band minimum states onto the surface plane. These states are nondegenerate, and different theoretical approaches have resulted in different calculated separation energies between them at $k_\parallel = 0$, referred to as valley splitting [4,5]. Even for the present dopant concentration of 1/4 monolayer, the Fermi level position of the 1Γ band minimum and the valley splitting are dependent on factors such as the dopant distribution [5]. These values also vary between theoretical approaches; however, for the present case binding energies of 300–500 meV for the 1Γ band minimum are typical [5].

Our observed metallic states can be assigned to the 1Γ states and possibly also the 2Γ states, depending on the size of the valley splitting. The observed occupation of the states is, however, much lower than predicted and appears to be <200 meV. The most important reasons for this discrepancy is that the calculations assume an intrinsic Si bulk, in contrast to our strongly p-doped samples, and a symmetric potential around the δ-layer. It is nonetheless interesting to overlay calculated δ-layer states on the experimental data. This is shown in [Fig. 2(b)] using the 1Γ, 2Γ, and 1Δ states from Fig. 10(d) of Ref. [5]. The Fermi level has been shifted by 140 meV in order to facilitate the

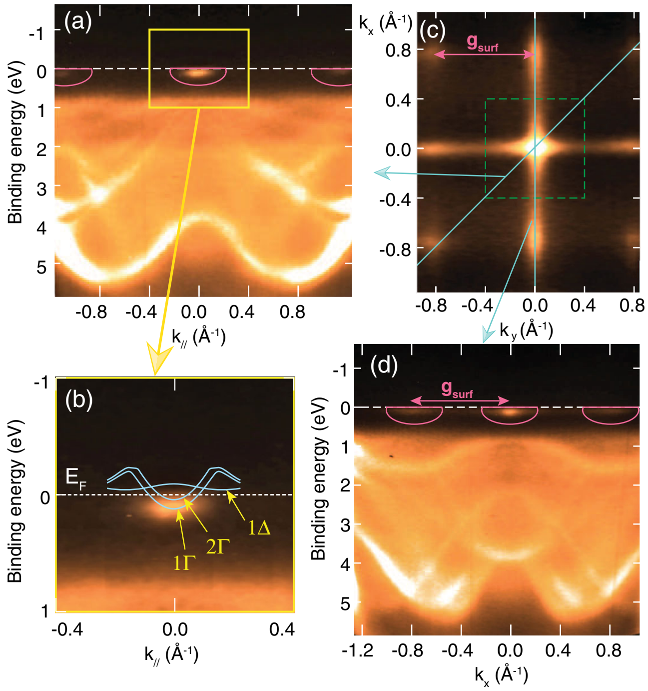

FIG. 2 (color online). (a) and (d) ARPES measurements along $k_x = k_y$ and $k_y = 0$, respectively, for the δ-doped sample at $h\nu = 113$ eV with the δ-layer states enclosed in pink. (b) Detail of the δ-layer state [yellow box in (a)] with the calculated 1Γ, 2Γ, and 1Δ states (after Fig. 10(d) of Ref. [5]) overlaid. (c) A constant energy map at the Fermi level. The 2×2 surface unit cell is indicated by a green dashed box and the pale blue lines and arrows indicate where the band maps (a) and (d) have been extracted. The length of the surface reciprocal lattice vector $\mathbf{g}_{\mathbf{surf}}$ is indicated.

comparison. The width, depth, and general shape of the measured state is consistent with the calculation. However, only one state is observed. This could be due to the limited experimental resolution or to a valley splitting that is slightly larger than calculated such that the 2Γ state remains unoccupied. In any event, it appears safe to assume that the next band, the 1Δ state, is sufficiently separated in energy to be unoccupied, precluding its observation.

The δ-layer states at a binding energy of ≈ 1 eV [Fig. 1(b)] are interpreted as valence band-derived impurity bands. A comparison to theoretical work is not possible at present for lack of published calculations in this energy range. Such a comparison would, however, give valuable information on the electronic structure of the δ-layers.

It is surprising that the electronic structure of the δ-layers should be observable by ARPES at all. A simplistic view of photoemission suggests that the mean free path of the photoelectron is so short (< 1 nm) that the photoemission intensity becomes vanishingly small for layers buried by just a couple of unit cells [12]. Indeed, this is what happens to the photoemission intensity from the P $2p$ core level that is entirely attenuated after 6 minutes of Si dosing, indicating negligible segregation of the dopants [13] and allowing us to calibrate the Si overlayer thickness to be at least 1.4 nm for this evaporation time. The δ-layer states in the valence band and conduction band, on the other hand, are still observable for Si overlayer thicknesses in excess of 5 nm. The reason for this behavior is the extended nature of these δ-layer states. While they are strongly confined to the region close to the δ-layer [7], their wave function still has a very small amplitude at the surface.

Whilst states such as surface states and buried or surface 2DEGs are fundamentally two-dimensional, their wave function exists over a finite distance perpendicular to the plane. Further, they are derived from three-dimensional bulk states and the perpendicular part of their wave function is not merely an exponential decay but includes a periodic, Bloch-like part. Photoemission from such states involves a final state that also has a periodicity in this perpendicular direction. The photoemission matrix element that couples the initial and final state is thus resonantly enhanced for particular photon energies, or values of $k_\perp$, when the periodicity of the final state matches that of the initial state. More specifically, the intensity profile is expected to take the form $(\chi - 1)^2/[1 + \chi^2 - 2\chi \cos(k_\perp a - \pi)]$, where a is the reciprocal unit cell size and χ is a free parameter [14]. In the present case, the intensity of the buried 2DEG state lying closest to the Fermi level has maxima in intensity [Fig. 1(d)]. This intensity variation has been extracted and plotted as Fig. 1(g), and is well-described by the aforementioned expression, where χ is found to be 2.1 ± 0.1 (note that the ARPES data have been normalized to the total intensity of each image). The maximum intensity occurs near to the bulk X point, consistent with the fact that the 1Γ and 2Γ states are derived from the conduction band minimum. This resonant enhancement of the intensity allows the buried 2DEG to be directly observed, even though the maximum of its wave function lies far beneath the surface.

Being able to directly probe the states of the δ-layer, relative to the surface and bulk states allows the band alignment in this region to be measured. The position of the Fermi level at the surface is directly measured and the presence of the δ-layer leads to a shift of ≈ 0.23 eV with respect to the surface of uniformly doped Si. The positions of the δ-layer states themselves were found to be independent from the thickness of the Si overlayer for a thickness range of nominally 2 to 5 nm. Note, however, that there is a significant uncertainty in the absolute Si overlayer thickness [10]. The band alignment on the bulk side of the δ-layer cannot be directly probed here, but it is reasonable to expect alignment back to the bulk Fermi level. A schematic representation of the room temperature band alignment is given in Fig. 3(b). Note that this scenario is more complex than the situation usually assumed in calculations of the δ-layer's properties [4–9]. First of all, the bulk Si used is strongly p-doped, fixing the Fermi level on one side of the potential well. The Fermi level at the surface is largely dictated by the surface states (even though the presence of the δ-layer leads

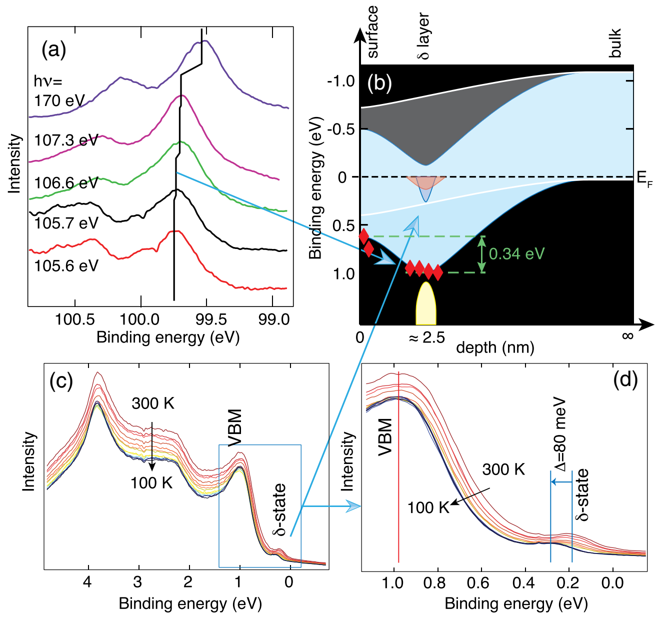

FIG. 3 (color online). (a) Low kinetic energy measurements of the Si $2p$ core level (after subtraction of a polynomial background) at normal emission for a range of photon energies. $h\nu = 105.6$ eV corresponds to a E_k of just ≈ 1.3 eV. (b) Schematic representation of the band bending; the pale blue band indicates the silicon band gap. The red diamonds show the VBM position as extracted from the core level measurements (uncertainty in energy <50 meV). The δ-layer state within the band gap is indicated in red ($T = 300$ K) and blue (100 K). The δ-layer state at deeper binding energy is indicated schematically in yellow. The band bending for the same substrate, without the δ-layer, is overlaid as a transparent white band. (c) Temperature dependent measurements of the valence band at normal emission and $h\nu = 113$ eV, and (d) the same data expanded to show the detail of the δ-layer state near the Fermi level and VBM.

to a shift), such that the near surface region is seen to be n-type. Such details are important for the theoretical modeling of the δ-layer's electronic structure and ultimately for the operation of δ-layer based devices [1–3].

The schematic band bending near the surface can be confirmed by core level spectroscopy. To this end, Si $2p$ core level spectra were measured as a function of photon energy and thus, electron kinetic energy E_k [Fig. 3(a)]. Since the mean free path λ of the photoemitted electron has a dependence on E_k, the sampling depth is also dependent on E_k, with $E_k \approx 70$ eV corresponding to a minimum in λ of ≈ 0.6 nm. A large increase in λ can be achieved with very low E_k [15]. It is possible to collect the Si $2p$ core level from $E_k < 2$ eV ($\lambda \approx 2.5$ nm [15]) to $E_k > 70$ eV ($\lambda \approx 0.6$ nm), corresponding to depths within the region of strongest band bending, as illustrated in Fig. 3(b). Although there is significant uncertainty in estimating the sampling depth, this allows measured values of the band bending to be overlaid on Fig. 3(b) (red diamonds).

As an example of the possibilities opened by the direct measurement of δ-layer states, we report the temperature dependence of the state close to the Fermi level. Figures 3(c) and 3(d) reveal that this state moves to higher binding energy as the temperature is reduced. Between 100 and 300 K, the δ-layer state is seen to shift (reversibly) by around 80 meV, whilst the valence band maximum is essentially unchanged. This observed behavior is somewhat different from the prediction of an almost constant position with respect to the Fermi level [8], something that is probably caused by the aforementioned differences in bulk doping and shape of potential well between our experiment and most calculations. The important point is that the experimental approach presented here allows this temperature dependence to be directly measured, opening the possibility to test different calculational approaches.

The experimental approach presented here utilizes a resonant enhancement of the photoemission intensity from a buried state such that the small fraction of its wave function which exists near the surface, is strong enough to be directly measured. Since such resonances are a general feature of two-dimensional states, we emphasize that the approach presented here is not limited to buried phosphorus dopants in silicon. δ-doping of other semiconductors (such as GaAs [16] and Ge [17]), boron (p-type) δ-layers [18] as well as metal oxide interfaces [12,19] could be similarly studied. In addition to a plethora of such materials, a wealth of further information should also be extractable from such experimental data; we have already been able to discuss the temperature dependence to the δ-layer pinning, but more detailed studies should reveal parameters such as the effective mass [6] and the strength of the electron-phonon interaction [20,21]. Finally, the resonant enhancement of the photoemission from buried states might be an alternative to increasing the electron inelastic mean free path by doing ARPES at very high or very low energies [22].

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