Bandgap and band discontinuity in wurtzite/zincblende GaAs homomaterial heterostructure

Ron Gurwitz,[1] Asa Tavor,[1] Liran Karpeles,[1] Ilan Shalish,[1,a)] Wei Yi,[2,b)] Georgiy Seryogin,[2,c)] and Venkatesh Narayanamurti[2]
[1]*Department of Electrical Engineering, Ben Gurion University of the Negev, Beer Sheva, Israel*
[2]*School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA*

(Received 28 January 2012; accepted 21 April 2012; published online 9 May 2012)

A wurtzite GaAs epilayer grown on a zincblende GaAs substrate by metalorganic chemical vapor deposition is studied by surface photovoltage spectroscopy. The wurtzite structure of the epilayer is disclosed by scanning electron microscope images of surface pits, where the pits are seen to change their structure from a rectangular into a hexagonal shape. The wurtzite phase is also revealed in x-ray diffraction showing a ⟨0002⟩ diffraction alongside the main (200) diffraction, suggesting a "c" lattice constant of 0.668 nm. A comparison of room temperature surface photovoltage spectra taken from the epilayer sample and from an epilayer-etched substrate suggests a *type II* heterostructure with valence band difference of about 15 meV and bandgap difference of about 70 meV between the zincblende and the wurtzite GaAs polytypes. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4712562]

Wurtzite GaAs is gaining much interest recently, for being commonly observed in GaAs nanowires.[1–9] Metastable polytype inclusions are more likely to form in nanowires, probably because the small nanowire diameter allows a stacking fault to easily complete a layer, which stabilizes the structure. However, the alternating nature of stacking faults in nanowires results in random lengths, some of which are small enough to actually form quantum dots, possibly with blue-shifted optical transitions. In addition, generated electron-hole pairs will tend to diffuse to the lower bandgap material, and the luminescence will thus detect only the smaller bandgap. Alternatively, in the case of type II heterojunction, recombination is likely to take place at the junction emitting photons with energy smaller than the smallest bandgap. Hence, as long as a bulk of pure wurtzite GaAs is not available, attempts to define the bandgap by luminescence are likely to remain controversial.[10] Controversy also exists among theorists, with some *ab-intio* calculations suggesting a wurtzite bandgap larger than that of the zincblende (ZB)[11–13] and others suggesting the opposite relation.[14,15] In this study, we examine a relatively thick wurtzite GaAs epilayer (∼100 nm) on a zincblende substrate, which is large enough to avoid effects of quantum confinement.

The epilayer was grown by metalorganic chemical vapor deposition on an n-type zincblende GaAs(100) substrate. Apparently, at an early growth stage, a stacking fault took place, forming a different phase that, for an unknown reason, remained stable for the rest of the growth. We emphasize that this growth was by all means a "lucky accident" and not a result of any reproducible process. Figure 1(a) shows a scanning electron microscope image of a typical pit. A very high density of such pits ($7.4 \times 10^7\,\mathrm{cm}^{-2}$) was observed all over the epilayer. As can be seen, the bottom of the pit is rectangular, as is commonly observed on zincblende GaAs surfaces. However, at a certain depth, the cross-section of the pit becomes hexagonal. In Figure 1(b), we outline the edges on the same image to aid the eye. Figure 1(c) is a three dimensional sketch of a cross-section of the pit. Likely, the abundance of these defects is what actually enabled the metastable wurtzite phase to form and stabilize. The image clearly suggests that the wurtzite layer grew in the ⟨0001⟩ direction.

To obtain another independent verification for the presence of a wurtzite phase, we removed most of the substrate by reactive ion etching with 30 sccm of 1:1 Ar:Cl_2 at 20 W in several consecutive steps and used x-ray diffraction after

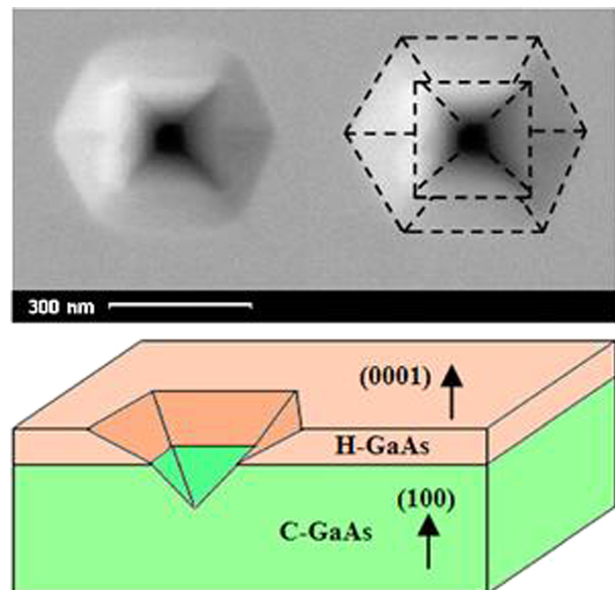

FIG. 1. Scanning electron microscope image of a surface pit (a). Many such pits of the exact same structure were observed all over the wafer area. The inner structure of the pit is outlined (b) and illustrated (c) showing how at a certain height it changes over from a rectangular to a hexagonal shape.

[a)]Author to whom correspondence should be addressed. Electronic mail: shalish@ee.bgu.ac.il.
[b)]Present address: Hewlett-Packard Labs, Palo Alto, California 94304, USA.
[c)]Present address: Nexx Systems, Billerica, Massachusetts 01821, USA.

 © 2012 American Institute of Physics

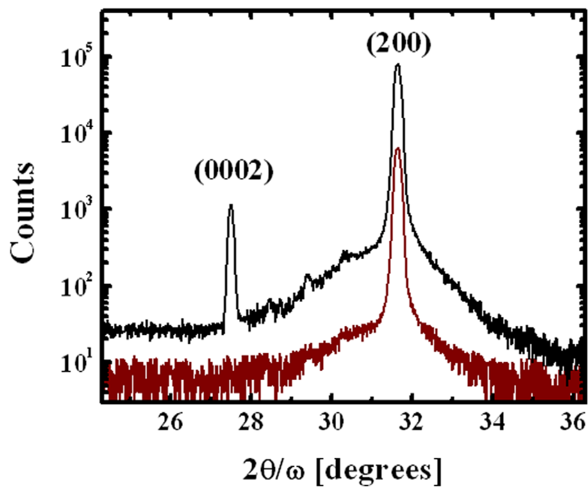

FIG. 2. Symmetric 2θ–ω x-ray diffraction before (red) and after (black) substrate etch. The peak at 27.8° appeared only after etching away most of the substrate.

each step, until the GaAs⟨0002⟩ diffraction could be detected. Figure 2 shows a 2θ-ω symmetric x-ray diffraction from the sample after the removal of most of the substrate. A semi-logarithmic plot is used because of a two-order of magnitude difference between the diffraction from the thin epilayer (estimated to be 100 nm thick) and that from the substrate, which volume still accedes that of the epilayer. The diffraction shown was the last to be acquired before the sample was completely etched. The emerging peak at 27.5° corresponds to d-spacing of 0.334 nm. As the layer grew in the c-axis direction (see pit structure in SEM image), this diffraction is likely to be the expected (0002) diffraction, which suggests that the c lattice constant in our epilayer is 0.668 nm. *Ab initio* calculations of the c lattice constant for the 2 H GaAs polytype by Yeh *et al.* and by Panse *et al.* yielded 0.644 and 0.651, respectively.[11,16]

Perhaps the most intriguing question about the wurtzite form of GaAs is its bandgap. To this end, using emission spectroscopies, such as photoluminescence may not always be conclusive, because the generated pairs are bound to diffuse and be trapped in the lower gap layer, or diffuse to the junction, before they recombine and emit photons of lower energy than that of the wider gap. Thus, if the wurtzite polytype is indeed of a wider bandgap as is generally expected, an adjacent zinc-blende phase will render it invisible to luminescence spectroscopies. To avoid this obstacle, we used surface photovoltage spectroscopy, which is an absorption spectroscopy, i.e., reflects the effect of light absorption rather than emission.

To measure changes in the surface voltage, we used a Kelvin probe in a dark Faraday cage with the typical setup commonly used for surface photovoltage spectroscopy.[17] The samples were illuminated using a monochromatized and filtered halogen light source. The results are given in the form of contact potential difference (CPD). The photovoltage is defined as the difference between the dark CPD and the CPD under illumination.[18] Under illumination with above-bandgap photons, electron-hole pairs are generated in densities that are greatest at the surface and diminish into the substrate. These electron hole pairs are separated by electric field at the space charge regions in the sample, giving rise to

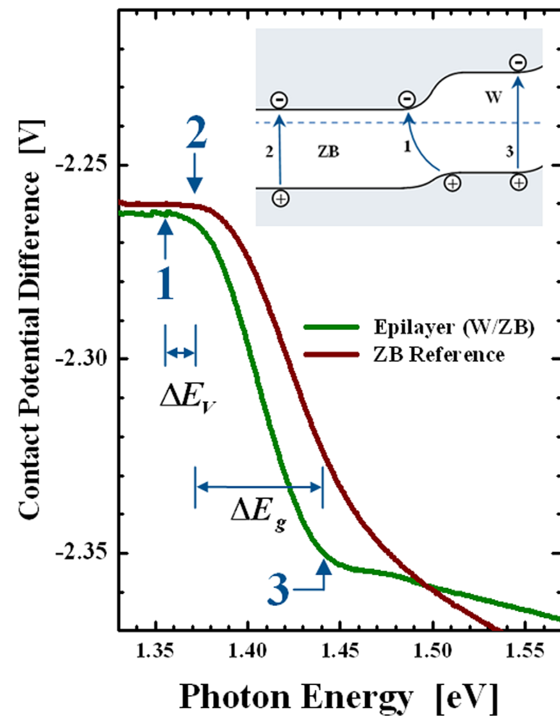

FIG. 3. Above bandgap surface photovoltage spectra taken from a reference sample comprised of zincblende phase only (red) and from our study sample comprised of a wurtzite epilayer atop a zincblende substrate (green). The three transitions marked on the curves are also shown on a band diagram (inset).

charging that is reflected in the contact potential. Another reason for charging is the inward diffusion of the pairs. Since electron mobility is always higher than that of holes, electrons diffuse faster giving rise to a positive photovoltage, in a process known as the *Dember effect*.[19] In an n-type semiconductor, this usually results in a reduction of the surface band bending. Therefore, when the photon energy is scanned from low to high energy, a sharp CPD drop is typically observed when a photon energy equal to the lowest band gap in the structure is reached. When the photon energy reaches the next bandgap in the structure, the CPD may either rise or fall depending on the ratio of minority carrier diffusion lengths between the two materials or between two different band *extrema* of the same material.

Figure 3 compares two photovoltage spectra obtained from our structure with and without the epilayer. The photovoltage reflects changes in the band bending in both interfaces of the epilayer: the interface with air and the interface with the zincblende substrate. When the epilayer is removed, the substrate alone has only one interface: the surface. Its photovoltage shows a single feature at about the zincblende GaAs fundamental gap. A sharp CPD decrease is observed as the photon energy approaches the zincblende GaAs band edge energy of 1.42 eV at room temperature. This transition is denoted with arrow 2 at 1.371 eV. The direction of this transition agrees with the n-type conductivity of the sample. A more moderate decrease in the CPD follows this point, which can be explained by the interplay between the increase of the density of states (DOS), as states deeper in the conduction and valence bands are made available by the increasing photon energies, and the relaxation of deep levels as the absorption depth decreases.

A similar decrease is observed in the spectrum of the epilayer structure. However, the CPD decrease sets in about 15 meV earlier in energy than the parallel decrease in the reference spectrum, denoted with arrow 1 at 1.355 eV. To obtain a smaller transition in the epilayer structure requires a type II heterojunction between the two polytypes, where the transition between the valence band of one semiconductor and the conduction band of the other semiconductor is smaller than the lower gap by the amount of the valence band offset. The inset in Fig. 3 shows this transition on a hypothesized band structure model, where we assumed the wurtzite to possess a larger bandgap than the zincblende and form a type II heterojunction. This feature is followed by a drop in the CPD which levels off at the next feature, about 81 meV higher in energy, denoted with arrow 3 at 1.440 eV. Since no higher band feature of the zincblende phase is expected below photon energy of 1.7 eV (In n-type semiconductors, above gap photovoltage senses van Hove singularities in the valence band structure[20]), and since both theory and experiment suggest the difference between zincblende and wurtzite does not exceed 150 meV, we can safely relate this feature to the bandgap of the wurtzite phase previously identified. From this point and on to higher photon energies, the rate of decrease in the CPD is made smaller. The observed rate change may be accounted for by a decrease in the minority carrier diffusion length in the wurtzite phase compared with the zincblende phase.

Since electron-hole generation always sets in slightly below the band edge, due to the Franz-Keldysh effect,[21] the onset of band edge transition in surface photovoltage spectra always precedes the actual gap energy and, therefore, is not an accurate measure to define bandgap energy. However, the energy difference between the two gaps is accurate, because the same effect takes place in both materials, and therefore, cancels in the subtraction.

As an alternative to the above interpretation, we may consider the photovoltage transition denoted as "1" to reflect the wurtzite bandgap, which, in this case, is smaller than that of the zinc-blende. In this case, the junction must be a type I heterojunction, and the photovoltage transition denoted as "3" would have to reflect the next valence band maximum at the Γ symmetry point in the wurtzite phase being about 90 meV below the top valence band. However, no such band feature may be expected according to reported calculations of the wurtzite (WZ) GaAs band structure, while there is a broad consensus that the WZ-ZB heterojunction in GaAs exhibits a type-II band alignment.

Finally, a word of caution is due as to the use of the term "wurtzite." While the term "zinc-blende GaAs" is well defined to be the single polytype 3C-GaAs, there are several possible polytypes that may go under the definition of "wurtzite GaAs," e.g., 2H-,4H-, or 6H-GaAs. Each of these polytypes is a wurtzite but at the same time their bandgaps may vary. Both this work and most of the reports to date fall short of this fine identification. However, it is likely that stability differences make nature always choose a specific one of these polytypes, eliminating the others for their low stability.

The advantage of this work is twofold: (1) The structure under test is a layer which is an advantage over nanowires, where the smallness may blue-shift optical transitions and (2) the band structure is studied by photon absorption rather than emission. Absorption takes place both in the wurtzite and in the zinc-blende at the same time, whereas emission is more elusive, because charge carriers will first move around to minimize their energy and only then recombine.

This work was funded by a Converging Technology grant from the Israeli Science Foundation – VATAT. The NSF funded Nanoscale Science and Engineering Center (NSEC) at Harvard University is acknowledged for partial support, and the use of the facilities of the Center for Nanoscale Systems (CNS) at Harvard University is also acknowledged.

[1] A. I. Person, M. W. Larsson, S. Stenstorm, B. J. Ohlsson, L. Samuelson, and L. R. Wallenberg, Nature Mater. **3**, 677 (2004).
[2] I. P. Soshnikov, G. E. Cirlin, A. A. Tokikh, Yu. B. Samsonenko, V. G. Dubovskii, V. M. Ustinov, O. M. Gorbenko, D. Litvinov, and D. Gerthsen, Phys. Solid State **47**, 2213 (2005).
[3] T. B. Hoang, A. F. Moses, H. L. Zhou, D. L. Dheeraj, B. O. Fimland, and H. Weman, Appl. Phys. Lett. **94**, 133105 (2009).
[4] P. Caroff, K. A. Dick, J. Johansson, M. E. Messing, K. Deppert, and L. Samuelson, Nat. Nanotechnol. **4**, 50 (2009).
[5] D. Spirkoska, J. Arbiol, A. Gustafsson, S. Conesa-Boj, F. Glas, I. Zardo, M. Heigoldt, M. H. Gass, A. L. Bleloch, S. Estrade, M. Kaniber, J. Roessler, F. Peiro, J. R. Morante, G. Abstreiter, L. Samuelson, and A. Fontcuberta i Morral, Phys. Rev. B **80**, 245325 (2009).
[6] T. B. Hoang, A. F. Moses, L. Ahtapodov, H. L. Zhou, D. L. Dheeraj, A. T. J. van Helvoort, B. O. Fimland, and H. Weman, Nano Lett. **10**, 2927 (2010).
[7] J.-M. Jancu, K. Gauthron, L. Largeau, G. Patriache, J.-C. Harmand, and P. Voisin, Appl. Phys. Lett. **97**, 041910 (2010).
[8] B. Ketterer, M. Heiss, M. J. Livrozet, A. Rudolph, E. Reiger, and A. Fontcuberta i Morral, Phys. Rev. B **83**, 125307 (2011).
[9] B. Ketterer, M. Heiss, E. Uccelli, J. Arbiol, and A. Fontcuberta i Morral, ACS Nano **5**, 7585 (2011).
[10] U. Jahn, J. Lähnemann, C. Pfüller, O. Brandt, S. Breuer, B. Jenichen, M. Ramsteiner, L. Geelhaar, and H. Riechert, Phys. Rev. B **85**, 045323 (2012).
[11] C.-Y. Yeh, Z. W. Lu, S. Froyen, and A. Zunger, Phys. Rev. B **46**, 10086 (1992).
[12] M. Murayama and T. Nakayama, Phys. Rev. B **49**, 4710 (1994).
[13] T. Cheiwchanchamnangij and W. R. L. Lambrecht, Phys. Rev. B **84**, 035203 (2011).
[14] A. De and C. E. Pryor, Phys. Rev. B **81**, 155210 (2010).
[15] M. Heiss, S. Conesa-Boj, J. Ren, H.-H. Tseng, A. Gali, A. Rudolph, E. Uccelli, F. Peiró, J. R. Morante, D. Schuh, E. Reiger, E. Kaxiras, J. Arbiol, and A. Fontcuberta i Morral, Phys. Rev. B **83**, 045303 (2011).
[16] C. Panse, D. Kriegner, and F. Bechstedt, Phys. Rev. B **84**, 075217 (2011).
[17] L. J. Brillson, Surf. Sci. Rep. **2**, 123 (1982).
[18] L. Kronik and Y. Shapira, Surf. Sci. Rep. **37**, 1 (1999).
[19] H. Dember, Phys. Z. **32**, 554 (1931).
[20] I. Shalish, Phys. Rev. B **66**, 165214 (2002).
[21] C. M. Wolfe, N. Holonyak, and G. E. Stillman, *Physical Properties of Semiconductors* (Prentice-Hall, Englewood Cliffs, NJ, 1989).