Antibonding State on the Ge(111):As Surface: Spectroscopy and Dynamics

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(Received 24 February 1993)

The first direct observation of the As derived empty surface state on the Ge(111):As 1×1 surface is reported. The state is first populated with a subpicosecond pulse of 2.03 eV light and then probed with equally short pulses of light at 10, 14, 18, and 22 eV which photoemit electrons from the sample. The surface band gap at 300 K is determined to be 0.83 ± 0.04 eV and compared well with a many-body calculation for this system. Photoexcited electrons are observed to rapidly scatter into the empty As derived state and are trapped for times in excess of 200 ps. The long lifetime is due to a paucity of electrically active defect states within the surface band gap.

PACS numbers: 73.25.+i, 78.47.+p, 79.60.Dp

The arsenic terminated surfaces of Ge and Si have been widely studied as prototypical "ideal" surfaces [1–4]. The thermally formed (111) surfaces of Ge and Si do not exhibit 1×1 low-energy-electron diffraction (LEED) patterns but instead reconstruct to form a $c(2\times8)$ (Ge) or 7×7 (Si) symmetry which results in significant lowering of the surface energy. By replacing the outer layer of, for instance, Ge atoms with As, the Ge attains a fourfold coordination while the As atoms are threefold coordinated, as in bulk As. The lone pair electrons on the As atom form a fully occupied band found, with photoemission [5], to lie about 0.4 eV below the valence band maximum (VBM) at $\bar{\Gamma}$, the surface Brillouin zone (SBZ) center. Arsenic termination produces a highly ordered surface, which is lower in energy, chemically passive, and stable against reconstruction. Such unique properties have spurred the use of arsenic as a surfactant to promote the growth of, for instance, Ge on Si surfaces [6]. The segregation of As to the surfaces of group IV materials grown on GaAs represents another area which has undergone active study [7]. As a result, the electronic structure of the arsenic terminated Ge and Si surfaces have been actively investigated. In particular, while the occupied surface band (resonance) has been extensively studied, the unoccupied band has not been observed although it has been predicted by theoretical many-body calculations of the surface electronic structure [8].

In this Letter we describe our subpicosecond photoemission investigations of the photoexcited As terminated Ge(111) surface. In these studies we have directly observed the normally empty As derived surface band and found its minimum to lie 0.43 ± 0.04 eV above the Ge VBM. We also find that the small effective mass of this bona fide surface state requires high angular resolution to locate the position of its minimum which is critical to the accurate determination of the magnitude of the surface band gap. Such a determination is crucial to testing the validity of many-body calculations of the form of Ref. [8] as applied to semiconductor surface systems. In addition we find that this surface possesses an extremely low density of electrically active defects. An important consequence of such a low defect density within the surface band gap is that electrons captured by the empty As derived surface state remain there for hundreds of picoseconds. Furthermore, we have applied recent advances in our laser photoemission technique to achieve tunability in our UV pulses which has allowed us to carry out photoemission at energies of 10, 14, 18, and 22 eV. Using this tunability we show that photoexcited electrons which transiently occupy the empty As state are observed at all energies, consistent with its identification as a surface state, though changes in peak intensities due to final state resonances as a function of photon energy are observed.

While the laser photoemission technique has been described in detail elsewhere [9], several significant advances have been incorporated which are mentioned here. A dye laser synchronously pumped by a mode-locked cw Nd:YAlG laser produces 0.7 ps pulses of 610 nm (2.03 eV) light. This light is amplified to 0.6 mJ per pulse at a 540 Hz repetition rate in a three stage dye amplifier pumped by the 532 nm frequency doubled output of a regenerative Nd:YAlG laser. The high repetition rate provides for good signal averaging and rapid data acquisition. The amplified 610 nm light is split into two synchronized legs. The first beam (excite), possessing 0.1 mJ of energy is directed along a variable delay line and then onto the Ge sample in our ultrahigh vacuum (UHV) chamber. The second 0.5 mJ pulse (probe) is focused with a 15 cm lens into a stainless steel tube positioned perpendicular to the laser beam and filled with 10–20 torr of Kr gas. The tube has a 200 μm hole through the walls which permits the interaction of the light with the confined gas [10]. The light intensity reaches in excess of 10^{14} W/cm^2 at the focus and the interaction of this intense laser field with the rare gas produces significant output at odd multiple harmonics. The details of the harmonic generation process have been studied by a number of workers and are not discussed here [11].

0031-9007/93/70(25)/3979(4)$06.00

Harmonics at 10 eV (5th), 14 eV (7th), 18 eV (9th), and 22 eV (11th) are produced and individually selected by a normal incidence reflection grating. Fluxes at harmonics above the 11th are insufficient for our photoemission work due to the decreasing reflectivity of the Pt coating on the grating, which will eventually be replaced by multilayer mirrors. A specific harmonic, selected by rotating the grating which resides within a differentially pumped vacuum chamber, is directed onto the photoexcited spot on the sample in the UHV chamber. A 64 anode time-of-flight detector measures the energy of the photoemitted electrons. The angular acceptance of our detector is $\pm 3°$ corresponding to a momentum resolution at $\bar{\Gamma}$ of ± 0.06 Å^{-1} for electrons with 5 eV kinetic energy. Momentum resolution here is particularly important in determining the energetic location of the empty As surface state minimum because of its predicted small effective mass [8].

The Ge samples are sputtered and annealed by resistive heating to produce a clean $c(2\times8)$ surface pattern. The samples are then transferred to a separate chamber and held at 400 °C while being exposed to a significant As_4 flux. This process has been described in detail by other workers [5] and results in a sharp 1×1 LEED pattern with low background. All measurements were carried out at 300 K.

The sample, when first photoexcited and then probed, reproducibly produces the photoemission spectra displayed in Fig. 1. Four spectra are displayed in Fig. 1, collected at photon energies of 10, 14, 18, and 22 eV with temporal coincidence of the excite and probe pulses. States below 0 eV in Fig. 1 are normally occupied. We note an occupied peak located at -1.2 eV in the 10 eV spectrum which disperses to higher binding energies with increasing photon energy. This peak is a bulk feature arising from the Λ_3 band which disperses downward in energy from Γ to L, the symmetry line in k space which is observed in our normal emission experiments. A second peak at -0.4 eV does not disperse with photon energy and derives from the As lone pair bonding band which resides 0.4 eV below the VBM. This signal is in good agreement with previous photoemission work [1].

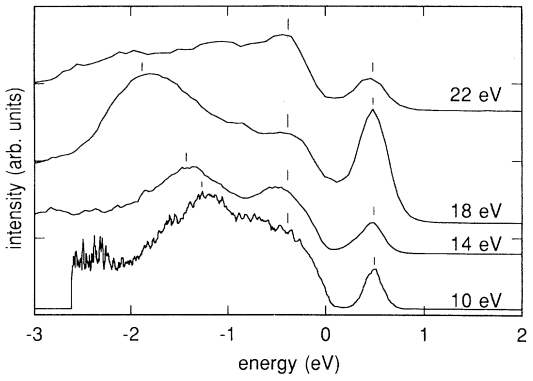

FIG. 1. Excite/probe spectra of the Ge(111):As 1×1 surface for approximate temporal overlap of the excite and probe pulses for photon energies of 10, 14, 18, and 22 eV. The vertical lines identify the occupied lone pair dangling bond and normally empty surface states of the surface. A bulk state (-1.2 eV in the 10 eV spectrum) is seen to disperse to higher binding energy with increasing photon energy. The occupied As derived surface state is observed at -0.4 eV, while the photoexcited As derived empty state is seen at $+0.43$ eV. The resolution of a time-of-flight detector worsens with increasing kinetic energy and is observed as broadening spectral features with increasing photon energy.

More interestingly, a feature 0.43 eV above the valence edge is observed when the system is photoexcited. This peak is due to the transient population of the As derived empty surface state and is observed at all four energies used in this experiment. Interestingly, we note variations in the intensity of the As derived state with photon energy. In particular, we observe a significant increase in the peak intensity at 18 eV. Such enhancements are sensitive to the nature of the band structure along the Γ-L line in k space since only final bands with significant Fourier components in the direction of the detector will contribute to the emission intensity. While the emission intensity varies with energy due to such final state effects, the energetic position of the peak does not vary, within our energy resolution. The lack of dispersion with photon energy that we observe for the occupied -0.4 and transiently excited $+0.43$ eV signals is characteristic of surface states. The wave function which characterizes a surface state is independent of $k_\perp$ (perpendicular component of the wave vector) and hence no dispersion with photon energy occurs [12]. An alternate test used to demonstrate the surface state origin of a spectral feature, the intentional contamination of the surface and subsequent reduction in the intensity of the feature, is not practical for the As terminated surface because of the unusually passive nature of this surface. Therefore the use of the tunable photon source and lack of spectral dispersion is the primary means for identifying the 0.43 eV peak as a surface state. The occupied surface state resides 0.4 eV below the VBM, resulting in a surface band gap of 0.83 ± 0.04 eV. The quoted energy uncertainty here of ±40 meV is determined by the accuracy in determining the positions of the occupied and transiently excited surface state photoemission peaks.

The size of the band gap we determine experimentally compares well with quasiparticle calculations carried out previously by Hybertsen and Louid [8] and represents a definitive test of such a theoretical approach. It is particularly desirable to compare photoemission experiments with quasiparticle calculations, which account for the electron self-energy, local fields, and dynamical screening, since electron energies measured experimentally are modified by these effects. A comparison of our energetic assignments of the occupied and empty As derived sur-

face states are given in the inset of Fig. 2 and are compared with the quasiparticle calculation for the surface band structure. We find that the occupied state is 0.1 eV lower in the energy than the predicted location at $\bar{\Gamma}$ but this is in excellent agreement when the combined experimental and theoretical uncertainties are considered. Our determination of the empty state minimum at $\bar{\Gamma}$ is in nearly complete agreement with calculation. We note as well that the density of states within the gap at the surface is extremely small (see Fig. 1). This aspect is critical to the lifetime of the transiently excited electrons since such gap states would contribute significantly to nonradiative electron-hole recombination. The low density of states within the band gap between the bulk VBM and the unoccupied As derived empty state also correlates well with our observations of extremely sharp 1×1 LEED patterns with low diffuse background.

The electron dynamics of this system can be studied in detail as shown in Figs. 2 and 3. In Fig. 2 we focus on the spectroscopic and dynamic details of the antibonding state. Three different spectra are displayed in Fig. 2 corresponding to varying delays of the photoemission probe pulse relative to the excitation pulse. At the earliest time (solid curve in Fig. 2) the 0.43 eV signal is composed of essentially two peaks consisting of the main feature and a high-energy shoulder. The main feature arises from electrons which begin to populate the As derived empty state.

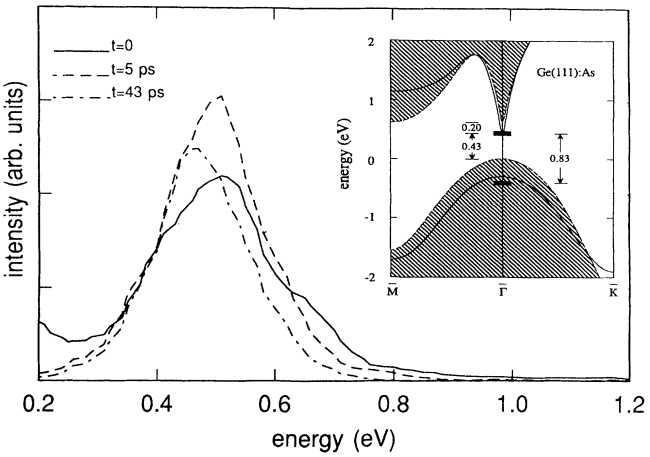

FIG. 2. Blowup of the transiently occupied As surface state. The early time, $t=0$ (solid curve), signal exhibits a shoulder 0.2 eV above the main peak due to scattering of electrons from bulk states at the surface. At later times, the shoulder disappears and a narrowing of the peak is observed. The $t=0$ peak is blown up by a factor of 6 for comparison with the later time peaks. The inset shows the projection of the bulk band structure (hatched region) onto the (111) surface while the solid curve is from a quasiparticle calculation of the As derived surface state (Ref. [8]). Horizontal bars indicate the energetic assignment of the occupied and empty As derived surface states measured here.

The bottom of the As derived surface state resides 0.2 eV below the conduction band minimum (CBM) at L and disperses rapidly to become a resonance above the CBM (see Fig. 2 inset). This was confirmed by following the surface state emission intensity as a function of emission angle and hence wave vector in the surface (not shown); by 7° from the normal, corresponding to $k_{\parallel}=0.14$ Å^{-1} (for 10 eV photons in this case) the signal intensity was reduced by a factor of 6 and shifted to slightly higher energy. This indicates that the surface band is positively dispersive. The drop in signal intensity with angle is due to the confinement of the electron gas within a relatively small region of k space (see Fig. 2 inset) [13]. Electrons confined in a band of small effective mass will be localized to a narrow region of k space, and as a result give rise to a cone of photoemitted electrons whose angle relative to the surface normal is quite small, as indicated above. While the rapid decay of the signal with emission angle prevents the accurate determination of an effective mass from our measurements, the quasiparticle calculations discussed above indicate a small value ($\sim 0.05 m_e$), consistent with our observations.

By following the detailed changes in the shape and intensity of the As derived antibonding state spectra, significant dynamic information can be obtained. In particular, the origin of the high-energy shoulder is intriguing. Since our excite pulse energy is 2.03 eV, electrons are driven into bulk states and will scatter into the conduction band states near the L minimum. Their residence time in these bulk states near the surface is expected to be exceedingly short because subsequent scattering into the As empty state further lowers their energy. For the earliest time spectrum in Fig. 2 we observe a shoulder 0.2 eV higher in energy than the centroid which then rapidly disappears at later times. Since the L point resides 0.2 eV higher than the bottom of the As derived empty state, the appearance of the shoulder indicates that electrons scatter from the bulk L minimum into the surface state at this point. That we do not see a simple isolated peak at 0.2 eV above the surface state minimum is testament to the rapid thermalization which redistributes electron population to all energetically accessible regions of the surface band. As a result, the $t=0$ signal reflects the population in the surface band from its minimum up to 0.2 eV above. In addition to the 0.2 eV shoulder, we also note that the main peak appears skewed to slightly higher energies relative to the later time spectra shown in Fig. 2. Electrons enter the surface band with 0.2 eV of excess energy resulting in a hot distribution, which cools by the emission of phonons. The skewed distribution indicates that the population, within the time resolution of our system, is still hot. As time progresses, the high-energy side of the peak retreats, all evidence of the shoulder is lost, and the entire distribution settles to lower energies. The retreat of the high-energy side of the peak is due to cooling of the electron population within the surface band

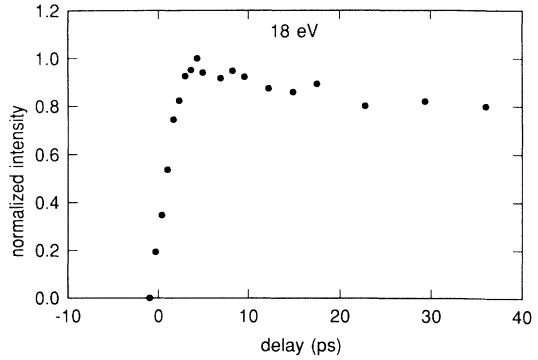

FIG. 3. Normalized intensity of the transiently occupied As state as a function of the relative delay between the excite and probe pulses. The photon energy was 18 eV for this scan.

which finally becomes degenerate. While the high-energy side of the peak displays such dynamic changes with time, the low-energy side remains essentially unchanged, as it is restricted by the band gap which is devoid of surface or bulk states. We note in Fig. 2 that even at 43 ps, while the peak is energetically narrowed, it is still intense. The narrowed distribution indicates that the electron gas has equilibrated with the lattice. That the signal is still relatively intense at this delay implies that the electrons have become trapped in the As derived antibonding state at the surface.

The time dependence of Fig. 3, which displays the normalized intensity of the 0.43 eV peak with delay time confirms that electrons are trapped by the surface state. This particular delay scan was collected with 18 eV photons but is representative of scans collected at 10, 14, and 22 eV. After an initial rapid rise the population stabilizes and decays slowly. Since the surface gap is so completely devoid of defect states, electrons become trapped and only radiative recombination between these electrons and holes at the bulk valence band maximum can remove electrons from this state. Radiative recombination requires hundreds of picoseconds or longer, and indeed fits to the time dependence beyond 10 ps yields a lifetime of between 200 and 500 ps indicating that nonradiative recombination channels are essentially nonexistent.

We can use the data discussed above to estimate the density of electrons trapped at the surface. We take the empty surface band effective mass to be $\sim 0.05 m_e$ from calculation [8]. For our excite pulse fluence, the surface photoexcited electron density is $\sim 4\times 10^{12}/\mathrm{cm}^2$ in our experiments. If we assume that any defect states within the surface band gap are localized and as a result emit isotropically and with the same emission probability as for the empty As state, then for our detection system we can set an upper limit of $\sim 1\times 10^{11}$ (defect states)/cm^2. While it has been shown that the As terminated surface is *chemically* passivated with respect to subsequent contamination, our observations address directly the *electronically* passivated nature of the surface. In addition, when electrons are captured into the As surface state, the resultant surface charge density and accompanying electrostatic field should inhibit further electron capture from the bulk. When this effect is combined with the relatively long lifetime of electrons in this state, a steady state low surface recombination velocity should result.

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