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New method to study band offsets applied to strained $Si/Si_{1-x}Ge_x(100)$ heterojunction interfaces

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A new method based on x-ray photoelectron spectroscopy measurements in combination with ion-beam doping during molecular-beam-epitaxy growth has been developed to study band offsets for $Si/Si_{1-x}Ge_x(100)$ heterostructures. Both ΔE_c and ΔE_v have been determined experimentally at abrupt heterojunction interfaces with a Si layer thickness of ~ 35 Å on a $Si_{1-x}Ge_x$ alloy layer. Significant differences in band lineup have been observed for heterostructures grown on different buffer layers, which are consistent with previous theoretical calculations of strain effects.

Band lineups and band offsets have recently received much attention not only in theoretical studies but also in experimental work, since they are directly associated with the electronic transport behavior of heterostructures.[1,2] During the last few years, several experimental techniques have been reported for quantitative determination of band offsets at hererojunction interfaces.[1-6] Photoelectron spectroscopy has been considered as probably the most reliable method among these for obtaining valence-band discontinuities.[1,2] However, previous investigations using these technique have relied on measurements of the valence-band-edge position, which for several reasons can be very difficult to determine. First, the shape of the photoemission spectra near the valence-band edge is photon-energy dependent because of contributions from direct transitions in the bulk. Second, emission from surface states can give strong contributions near the band edge.

The observation, first, of two-dimensional charge-carrier gases both of electrons and of holes in $Si/Si_{1-x}Ge_x$ strained-layer heterostructures,[7,8] and, second, the strain-induced band-gap reduction in $Si_{1-x}Ge_x$ alloys,[9] has stimulated a growing interest in $Si/Si_{1-x}Ge_x$ heterojunctions and superlattices. Recent theoretical calculations of the strain dependence of band lineups,[10,11] predicting a straddling lineup for certain configurations of strain and a staggered for others, are consistent with the earlier experiments showing formation of two-dimensional hole and electron gases. However, no photoelectron spectroscopy studies of the band offsets in $Si/Si_{1-x}Ge_x$ heterostructures have been reported up until now.

In this Rapid Communication we report an experimental method for the determination of band offsets, which is based on x-ray photoelectron spectroscopy (XPS) measurements made *in situ* in a Si/Ge molecular-beam-epitaxy (MBE) system with possibilities for ion-beam doping of n^+ and p^+ layers. We have used this new method in a study of band gaps and band lineups of strained $Si/Si_{1-x}Ge_x$ heterostructures. The results obtained agree well with published theoretical calculations on the Ge-concentration dependence as well as the strain dependence of band gaps and band offsets.

The absolute value of the binding energy of an electronic level E_B in a semiconductor can be referred to the Fermi level E_F (see Fig. 1). In the XPS experiment, we have the following energy-conservation requirement:

$$E_B = h\nu - E_k - \Phi = (E_F - E_v) + E_{B,0} , \quad (1)$$

where $E_{B,0}$ is the binding energy relative to the valence-band edge (E_v), $h\nu$ is the photon energy, E_k is the measured kinetic energy of the emitted electron, and Φ is the work function of the energy analyzer. By varying the doping of the semiconductor from p^+ to n^+, it is possible to move the Fermi level in the bulk from an energy close to the valence-band edge to an energy close to the conduction-band edge, that is to change E_B from $E_{B,0}$ to $E_{B,0}+E_g$, where E_g is the semiconductor band gap. The energy window defined by the shift of a bulk core level as the doping is changed from n^+ to p^+ can thus in principle be used to assess the band gap of the semiconductor. In our present study of band offsets we also use the fact that for samples with arbitrary doping the energy position of the core level, relative to this window, is a direct monitor of the position of E_F relative to the band edges, as seen in Fig. 1.

Since an XPS experiment probes the binding energies throughout a small volume within a probing depth deter-

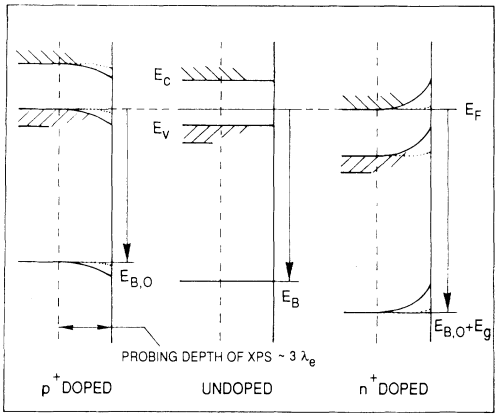

FIG. 1. Energy diagrams showing the energy levels near the surface of differently doped semiconductors. The dotted lines show schematically the reduction in band bending observed with In and Sb overlayers on p^+ and n^+ samples, respectively.

mined by the photoelectron mean free path, λ_e (λ_e is ≈ 25 Å,[5] as the kinetic energy of the emitted electrons is ~ 1400 eV in our measurements) it is essential that the energy levels do not change significantly within this volume. For a clean surface of a moderately or heavily doped semiconductor this is generally not the case, as the presence of localized surface states in the gap pins the Fermi level at the surface and induces band bending below the surface. In order to avoid this problem, we have used a method similar to the one previously described in Ref. 12. 1–2 monolayers (ML) of Sb or In were evaporated onto the n^+ and p^+ doped semiconductors, respectively, directly after the semiconductor growth to take away the surface states from the gap. This treatment successfully eliminated the Fermi level pinning and created a nearly flat band situation in both cases, as illustrated by dotted lines in Fig. 1.

The alignment of the band gaps at interfaces has been measured on thin undoped $Si/Si_{1-x}Ge_x$ heterostructures grown on different buffer layers. For these undoped structures (the background doping $N_B \leq 1\times10^{15}$ cm^{-3}) the band bending lengths are much greater than the XPS probing depth, and the presence of surface states will only give a uniform shift of all energy levels measured by XPS in both semiconductors. Figure 2 shows a schematic drawing of the energy levels that have been used to determine the alignment of the band gaps. The energy diagram can also be interpreted as showing the band edges at the interface. The discontinuities in the conduction band ΔE_c and the valence band ΔE_v can be expressed as follows:

$$\Delta E_c = (E_c - E_F)_{Si_{1-x}Ge_x} - (E_c - E_F)_{Si}$$
$$= (E^c_{Ge\,3d} - E^i_{Ge\,3d}) - (E^c_{Si\,2p} - E^i_{Si\,2p}) \ , \qquad (2)$$

$$\Delta E_v = (E_F - E_v)_{Si} - (E_F - E_v)_{Si_{1-x}Ge_x}$$
$$= (E^i_{Si\,2p} - E^v_{Si\,2p}) - (E^i_{Ge\,3d} - E^v_{Ge\,3d}) \ , \qquad (3)$$

where $E^i_{Si\,2p}$ is the core-level position in the topmost Si layer, and $E^i_{Ge\,3d}$ the core-level position in the lower-lying

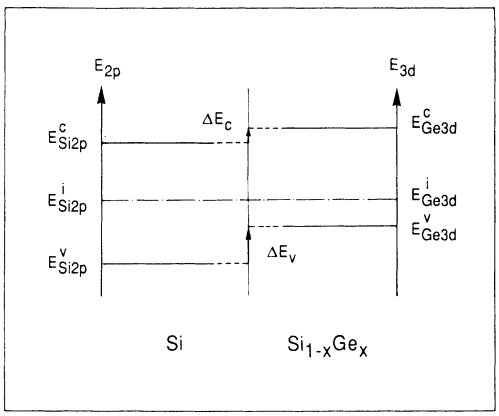

FIG. 2. A schematic diagram of the energy levels that were measured and used in the determination of the band lineup at an abrupt heterojunction interface.

$Si_{1-x}Ge_x$ alloy layer as measured on an undoped thin heterostructure. $E^c_{Si\,2p}$, $E^v_{Si\,2p}$, $E^c_{Ge\,3d}$, and $E^v_{Ge\,3d}$ are the core-level energies measured on heavily n- and p-doped reference samples of Si and $Si_{1-x}Ge_x$, respectively.

All experiments were performed in a VG-80 Si MBE system equipped with electron-beam-heated sources for Si and Ge evaporation, and facilities for XPS using Al $K\alpha$ radiation (1486.6 eV), Auger electron spectroscopy (AES), reflection high-energy electron diffraction (RHEED), and low-energy electron diffraction (LEED). Both Sb and In low-energy ion-beam sources, which are able to enhance efficiently the incorporation probability of the dopants during Si and $Si_{1-x}Ge_x$ growth by MBE,[13] were employed for n^+ and p^+ doping. The substrates used in the present experiments were lightly n-doped mirror-polished Si wafers ($\sigma = 10$ Ω cm, $N_D = 5\times10^{14}$ cm^{-3}) that had been chemically cleaned before insertion into the vacuum chamber. The thicknesses of the layers and the Ge content of $Si_{1-x}Ge_x$ alloys were calibrated both by a quartz crystal monitor and by AES. The substrate temperature during the film growth was 570 °C as monitored by a calibrated infrared pyrometer. The undoped $Si/Si_{1-x}Ge_x$ double-layer structures used to measure the band lineups were grown in the following way. After heating the substrate to 950 °C for 30 min to remove the surface oxide, a thick ≈ 2500-Å buffer layer was deposited, followed by a ≈ 80-Å $Si_{1-x}Ge_x$ layer and a ≈ 35-Å Si layer. The object of the thick relaxed buffer layer was to introduce a given strain in the following unrelaxed layers.[14] The heavily doped reference layers were made 80-Å thick onto relaxed buffer layers, i.e., thin enough to ensure the same strain in the reference layers as in the corresponding layer in the heterojunctions,[14] still thick enough to eliminate the influence of band bending near the interface to the buffer layers. Dopant concentrations of 2.5×10^{19} Sb atoms/cm^3 and 2×10^{19} In atoms/cm^3 were chosen for the reference layers, which places E_F very close to the band edges.[12]

XPS spectra of the $2p$ core level of unstrained Si, heavily doped (n^+ or p^+) with additional Sb or In overlayers, are shown in Fig. 3 together with one spectrum for an undoped heterostructure. The shift of the Si $2p$ core-level binding energy from n^+ to p^+ doped Si, which was measured between the centers of the peak widths at half the peak height, was 1.06 eV. As a comparison for samples with the same doping levels but without metallic overlayers the shift of the Si $2p$ level was only 0.3 eV. This suggests that the surface was efficiently passivated by the adsorbed Sb or In atoms, i.e., the density of surface states in the gap was significantly reduced, allowing us to move E_F close to the band edges also at the surface. The ~ 60-meV deviation between our measured core level shift and the full Si band gap (1.12 eV) is consistent with experimental and theoretical values for the band-gap narrowing in heavily doped semiconductors.[15] Other factors that could lead to a reduced shift of the core level are incomplete removal of band bending or active doping levels being lower than the dopant concentration.

The measured core-level shifts (band gaps) for strained $Si_{1-x}Ge_x$ alloys are given in Table I. The observed strain-induced band-gap reductions are in good agreement

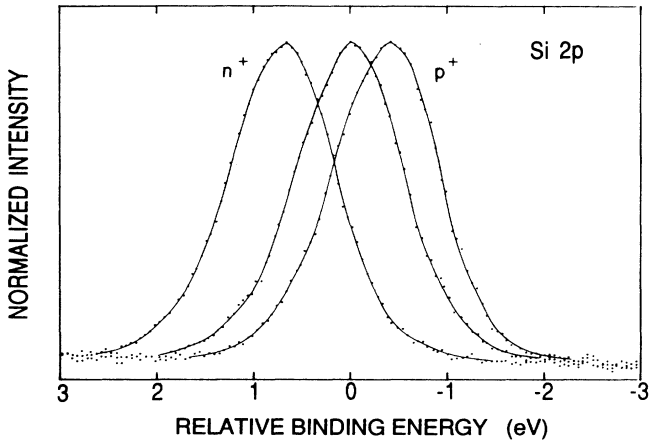

FIG. 3. Si $2p$ core-level spectra of the n^+-doped and p^+-doped reference samples with Sb and In overlayers, respectively. The middle spectrum is from the undoped $Si/Si_{0.74}Ge_{0.26}$ heterostructure on Si.

TABLE I. Values of core-level shifts (band gaps) for $Si_{1-x}Ge_x$ alloys with different strain configurations.

	Present Expt. (eV)	Theory 90 K (eV)	Estimate[a] 298 K (eV)
Si (bulk)	1.06 ± 0.03	1.17	1.12
$Si_{0.74}Ge_{0.26}$ on Si	0.88 ± 0.03	0.95[b]	0.91
$Si_{0.52}Ge_{0.48}$ on Si	0.74 ± 0.03	0.78[b]	0.75
$Si_{0.52}Ge_{0.48}$ on $Si_{0.75}Ge_{0.25}$	0.87 ± 0.03	0.89[c]	0.85
Si on $Si_{0.75}Ge_{0.25}$	0.98 ± 0.03	1.04[c]	1.01

[a]Assuming that the band structures of strained $Si_{1-x}Ge_x$ alloys are still Si-like, the values of band gaps change 4.3% from 90 to 298 K.
[b]Reference 16.
[c]Reference 11.

with data obtained from photocurrent measurements,[9] and theoretical calculations.[10,16] The estimated uncertainties given in Table I (and Table II) correspond to the reproducibility in the values of the core-level shifts. Errors because of band-gap narrowing or incomplete removal of band bending are not included, but are expected to be similar in magnitude for all $Si_{1-x}Ge_x$ alloys studied, which means that their effect on the resulting band offset values will be reduced.[17]

In order to obtain $E^i_{Ge\,3d}$ and $E^i_{Si\,2p}$, and to determine the band lineups from the undoped heterostructures, the Ge $3d$ spectra were measured at normal emission to allow for probing the energy level in the buried $Si_{1-x}Ge_x$ layer, while the Si $2p$ spectra were taken at $\sim 70°$ from the surface normal. At this high emission angle the Si $2p$ core-level signal from the $Si_{1-x}Ge_x$ layer was suppressed, and we estimate that $\sim 98\%$ of the Si $2p$ signal came from the topmost Si layer. We use the binding energies $E^i_{Si\,2p}$ and $E^i_{Ge\,3d}$ in the heterostructure in combination with the values of $E^v_{Si\,2p}$, $E^v_{Ge\,3d}$, $E^c_{Si\,2p}$, and $E^c_{Ge\,3d}$ obtained from the appropriate reference layers, to get ΔE_v and ΔE_c according to Eqs. (2) and (3). The results of the band offset measurements for the three different heterointerfaces are summarized in Table II together with calculated band offsets from Refs. 10 and 11.

In the case of $Si/Si_{1-x}Ge_x$ heterostructures on a Si buffer layer, the pseudomorphic growth forces the thin heterostructure to retain the Si lattice constant parallel to the interface. This results in a tetragonal strain field in the $Si_{1-x}Ge_x$ alloy layer, leading to a splitting of the degenerate energy levels in both the conduction band and the valence band, which in turns leads to a narrowing of the band gap, whereas the Si layer remains unstrained. For both alloys, i.e., $Si_{0.74}Ge_{0.26}$ and $Si_{0.52}Ge_{0.48}$, used in this type of structure we observed very small conduction-band edge discontinuities, while the valence-band edge discontinuity increase from 0.18 to 0.36 eV when increasing the Ge content in the alloy from 26% to 48%.

By comparing our results for $Si/Si_{1-x}Ge_x$ heterostruc-

TABLE II. Values of band offsets at $Si/Si_{1-x}Ge_x(100)$ heterojunction interfaces.

	ΔE_c (eV)			ΔE_v (eV)		
	Present exp. value	Calc. value[a] in Ref. 10	Calc. value[a] in Ref. 11	Present exp. value	Calc. value[a] in Ref. 10	Calc. value[a] in Ref. 11
$Si/Si_{0.74}Ge_{0.26}$ on Si	0.00 ± 0.06	0.00	−0.02	0.18 ± 0.06	0.17	0.15
$Si/Si_{0.52}Ge_{0.48}$ on Si	0.03 ± 0.06	−0.02	−0.02	0.36 ± 0.06	0.38	0.37
$Si/Si_{0.52}Ge_{0.48}$ on $Si_{0.75}Ge_{0.25}$	0.13 ± 0.06	0.13	0.15	0.24 ± 0.06	0.28	0.30

[a]The calculated band offsets correspond to heterostructures of $Si/Si_{0.80}Ge_{0.20}$ on Si, $Si/Si_{0.50}Ge_{0.50}$ on Si, and $Si/Si_{0.50}Ge_{0.50}$ on $Si_{0.75}Ge_{0.25}$, respectively.

tures grown on Si or $Si_{0.75}Ge_{0.25}$ buffer layers we focus on the effects of different strain. With tensile strain in the Si part of the heterostructure (i.e., grown on the $Si_{0.75}Ge_{0.25}$ buffer layer) we find an increase in ΔE_c from 0.03 to 0.13 eV, while ΔE_v decreases from 0.36 to 0.24 eV. As seen in Table II, these results are in good agreement with the calculated strain-dependent discontinuities in both the conduction and the valence band.[10,11]

In conclusion, a new experimental method has been developed for the study of the band offsets at abrupt semiconductor heterointerfaces. Large changes of the band lineups have been observed for $Si/Si_{1-x}Ge_x$ heterostructures grown on different buffer layers, and the value of the band offsets are also varied as a function of Ge content in the alloy. The experimental results are in good agreement with calculated band offsets for different Ge concentrations and strain configurations.

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[17]The presence of surface or chemical core-level shifts for the different clean and adsorbate covered surfaces will introduce some minor errors. A 0.5-eV surface shift has been reported from synchrotron radiation studies of the clean Si(100)2×1 surface [e.g., F. J. Himpsel, P. Heimann, T. C. Chaing, and D. E. Eastman, Phys. Rev. Lett. **45**, 1112 (1980)]. When taking into account the differences in electron collection geometry and mean free path, we estimate that the maximum error in the Si $2p$ position from this effect in the present study is ≈ 0.03 eV. We have not adjusted the reported band offset values for this effect, since, first, the intensity of the surface shifted core level could have been reduced by very low-level contamination during XPS measurements; second, the estimated uncertainty in the band offsets is anyhow significantly larger (± 0.06 eV). The Si $2p$ core-level shifts on Sb-covered [R. I. G. Uhrberg (private communication)] and In-covered [D. H. Rich, A. Samsavar, T. Miller, H. F. Lin, T.-C. Chiang, J.-E. Sundgren, and J. E. Greene, Phys. Rev. Lett. **58**, 579 (1987)] Si(100) surfaces are very small ($\lesssim 0.1$ eV) and their effect on our reported values for band gaps and band offsets can safely be neglected.