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Measurements of the energy band offsets of $Si_{1-x}Ge_x/Si$ and $Ge_{1-y}C_y/Ge$ heterojunctions

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Abstract

Discontinuities in the energies of the conduction and valence bands at semiconductor heterojunctions are important parameters for device design. We describe experiments using X-ray photoelectron spectroscopy with measurements of valence-band energies with respect to core-levels of metastable, coherently strained $Si_{1-x}Ge_x$ alloy layers and of thick $Ge_{1-y}C_y$ alloy layers. For strained $Si_{1-x}Ge_x$ alloys on Si, we have found that the valence band offset increased with the Ge fraction x with most of the offset in the valence band. We obtained a valence band offset of 0.22 eV for $x = 0.23$, in good agreement with theoretical calculations. For $Ge_{1-y}C_y$ alloys, we found very little shift in the valence band energies with the C fraction y. Since the optical bandgap of GeC increased with the C fraction y, most of the offset for $Ge_{1-y}C_y/Ge$ heterojunction was in the conduction band. Based on the measurements of the energy band offsets of $Si_{1-x}Ge_x/Si$, we infer that the major portion of bandgap discontinuity of $Ge_{1-y}C_y$ on Si is in the valence band. $Ge_{1-y}C_y$ alloys are new metastable materials that open up a new region for group IV heterostructures.

Knowledge of the band offsets at heterointerfaces is important for assessing the degree of carrier confinement, and therefore is important for high-speed optoelectronic device operation. Many theories have reported calculations of valence-band offsets at heterojunctions. For examples, Tersoff [1] and Cardona and Christensen [2] calculated semiconductor band offsets using interface dipole theory and dielectric midgap energy theory, respectively. Frensley and Kroemer [3] proposed a pseudopotential model to predict the semiconductor band offsets. For certain heterojunction systems, the above theories yield fairly different results.

Several experimental techniques have been studied during the last few years for the quantitative determination of semiconductor band offsets at heterojunctions [4–6]. Among them, X-ray photoelectron spectroscopy (XPS) of the atomic core-levels represents the most reliable method for obtaining valence-band offsets (ΔE_v) [7]. The valence band energies can be measured with respect to deep atomic core levels which are relatively unaffected by the heterointerface. If the bandgap E_g is known, the

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conduction band offsets can also be determined, and thus whole band structure will be clear.

In this paper, we present and discuss the results of an XPS investigation of $Si_{1-x}Ge_x/Si$ and $Ge_{1-y}C_y/Ge$ heterojunction valence-band offsets (VBO) by using metastable, coherently strained $Si_{1-x}Ge_x$ alloys on Si and thick $Ge_{1-y}C_y$ alloys on Si. The $Si_{1-x}Ge_x/Si$ system is well-known and there are many theoretical and experimental results regarding to its valence-band offsets. We compared our measurements of $Si_{1-x}Ge_x/Si$ to published data to check our XPS data analysis method which was proposed by Shih and Spicer [8]. Our interest was to find the band energies at the heterointerface of $Ge_{1-y}C_y$ and Ge with respect to Si by measuring the band energy position using thick $Ge_{1-y}C_y$ and Ge layers. $Ge_{1-y}C_y$ alloys are a novel material system for the physics and device of group IV semiconductors [9]. In principle, it can be lattice matched to Si substrates by adjusting the composition. Its optical bandgap (E_g) depends on the C fraction y [10].

In order to avoid the demands posed by XPS core-level spectroscopy such as preparing good interface quality samples and ensuring negligible band bending over the portion of the sample probed, we followed the potentially simplified method proposed by Shih and Spicer [8]. They postulated that the core-level positions were approximately independent of alloy composition, thus they substituted bulk samples for the actual interface to study valence-band offsets. They tested their method by deducing the VBO in the HgTe–CdTe system and obtained an accurate lineup. This approach was also studied in a theoretical analysis by Wei and Zunger [11] with good results. By using this technique, we can easily determine the band offsets without performing a measurement located precisely at the heterointerface.

In our study, we used the Si_{2p} core-level as a reference level for the $Si_{1-x}Ge_x/Si$ system, and the Ge_{3d} core-level for the $Ge_{1-y}C_y/Ge$ system. Before any heterostructure data analysis, we first estimated the core-level shifts due to the alloy composition, and justified the approximation of core-level constancy.

Strict and consistent calculation of core-level shifts due to the alloy composition requires using a Born–Haber cycle calculation which is used to relate binding-energy shifts to changes of bond energies due to the excitation of core electrons [12]. However, Morar et al. used a model based on linear-response theory [13] to estimate the shift of the Si_{2p} core-level energy in $Si_{1-x}Ge_x$ alloys due to different Ge composition. They found that for strain-free $Si_{1-x}Ge_x$ alloys with $x \leq 0.3$, the maximum Si_{2p} core-level shift was ~ 15 meV. We used the same approach to estimate the Ge_{3d} core-level shift of $Ge_{1-y}C_y$ alloys due to adding small amount of carbon. Energetic shifts in the core levels are interpreted in terms of changes in the total valence charge surrounding each atom. They can be directly associated with the electronegativity and ionicity. The hydrostatic component of strain can also cause core-level shifts. Because the strain configuration depends on details of the growth conditions for the different samples, we can determine the band offsets without these strain effects first, and then add the tetragonal distortion caused by strain for the particular sample later if strain is present. Thus the total core-level shift ΔE_{core} can be written as:

$$\Delta E_{core} = n_C \Delta,$$

$$\Delta = \Delta_d + (r_{GeC} - r_{Ge\,bulk}) \frac{dE_{CL}}{dr} = \Delta_r + \Delta_d,$$

and where n_C is the number of C neighbors of each Ge atom, Δ_d is the electronic shift of the core-level corresponding to the dielectric response to a first-order local perturbation, r_{GeC} is the bond length for $Ge_{1-y}C_y$ alloys, and $r_{Ge\,bulk}$ is the bulk Ge covalent bond length. Δ_r is the core-level shift associated with the atomic displacement. With consisting of a superposition of spherical atomic density [14], we obtained $\Delta_d \sim -83.45$ meV and $dE_{CL}/dr \sim 630$ meV/Å, giving $\Delta \sim 225$ meV. The total core-level shift for $Ge_{1-y}C_y$ is $4y\Delta$. For a small amount of C (1–3% for our SGC samples), the maximum shift is ~ 27 meV. Therefore we conclude that the core-level is approximately constant for our GeC alloys to within ± 27 meV.

Two groups of molecular beam epitaxy grown samples were used for this study. The first was metastable strained $Si_{1-x}Ge_x$ alloys on Si substrates, and the second was thick $Ge_{1-y}C_y$ alloys on Si substrates. The $Si_{1-x}Ge_x$ samples were grown in a VG-80 solid source MBE system using e-beam evaporation for Si and a thermal effusion cell for Ge. The

$Ge_{1-y}C_y$ alloys were grown by solid source in an EPI 620 MBE system. The base pressure of the GeC growth chamber was below 5×10^{-11} Torr, and growth pressures were typically near 5×10^{-9} Torr [10]. The Ge beam was produced by thermal evaporation from a solid polycrystalline Ge source in a pyrolytic boron nitride crucible, and the C beam was produced by sublimation from a pyrolytic graphite filament carbon source. The substrates used in the $Ge_{1-y}C_y$ experiments were p-type (100) Si wafers ($\rho = 13$–$17\ \Omega$ cm) that had been chemically cleaned before being inserted into the vacuum chamber. Details of growth conditions are given in [10]. The substrate temperature during the film growth was 570°C.

XPS measurements were performed using an SSX-100 spectrometer with a monochromatic Al Kα X-ray source ($h\nu = 1487$ eV). The background base pressure for the analysis chamber was $T = 10^{-9}$ Torr. Because of exposure to air, samples were sputtered with Ar^+ ions of energy 2 keV for 30 min to remove surface oxidation.

We determined the absolute valence band maximum (VBM) position by finding the relative difference between the VBM and the core-level in each material. We decided not to fit theoretically calculated density of valence-band energy distribution states to the complete XPS spectrum since the calculated theoretical critical points of the density of states of GeC are not yet well known. Near the valence-band maximum, the density of states varies as the square root of energy. Assuming that Vegard's law is valid for the interpolation of alloy hole effective masses of the endpoint compositions near the VBM, we can compare the VBM of these alloys accurately after dividing out the characteristic hole effective mass. The inset in Fig. 1 and Fig. 2 shows the measured alignment of the VBM for $Si_{1-x}Ge_x$ and $Ge_{1-y}C_y$ samples respectively. For $Si_{1-x}Ge_x$ alloys, we compare the VBM of metastable, coherently strained $Si_{0.92}Ge_{0.08}$ and $Si_{0.77}Ge_{0.23}$ alloy layers with the VBM of bulk Si substrate. For $Ge_{1-y}C_y$ alloys, we compare the VBM of thick $Ge_{0.984}C_{0.016}$ and $Ge_{0.968}C_{0.032}$ alloy layers with the VBM of a thick pure Ge layer. The core-level energy positions were defined as the center of the peak width at half of the peak maximum height. After alignment of the adjusted valence band edges of these materials, the relative positions of the core-level binding energies referred to the VBM can be determined very precisely to within 30 meV (systematic errors can be canceled) [8]. This change reflects the movement of

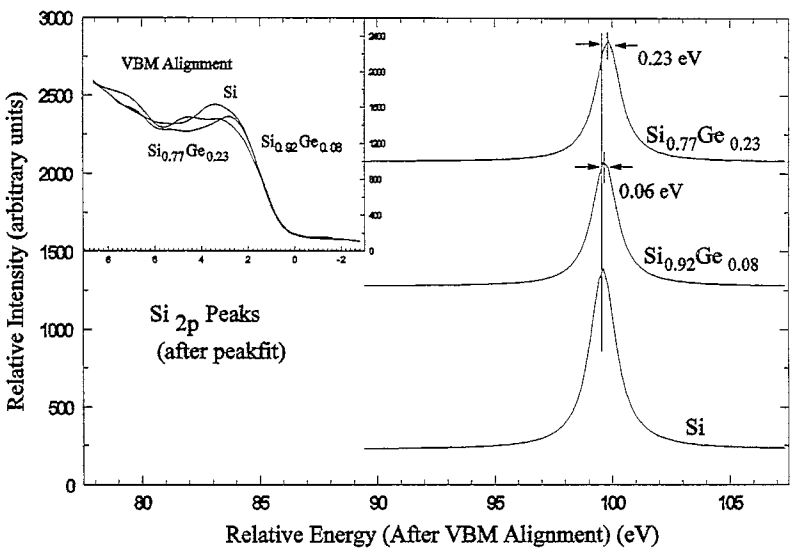

Fig. 1. The Si_{2p} core-level of Si, $Si_{0.92}Ge_{0.08}$, and $Si_{0.78}Ge_{0.22}$ with the valence band maximum (VBM) taken as zero binding energy. Inset: Alignment of the VBMs by shifting energy scales after counting the effects of characteristic hole effective mass for each material. Energy shifts near peaks are the VBO with respect to Si.

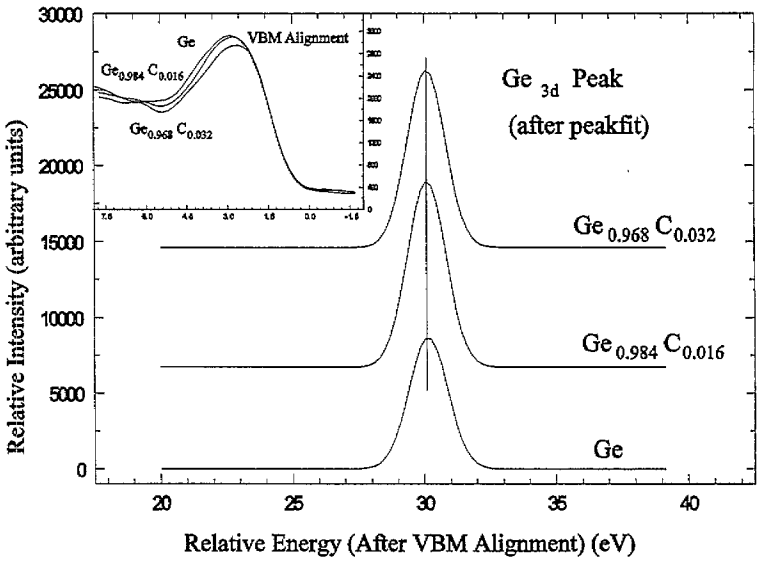

Fig. 2. The Ge_{3d} core-level of Ge, $Ge_{0.984}C_{0.016}$, and $Ge_{0.968}C_{0.032}$ with the valence-band maximum (VBM) taken as zero binding energy. Inset: Alignment of the VBMs by shifting energy scales after counting the effects of characteristic hole effective mass for each material. No VBO was found for $Ge_{1-y}C_y$ on Ge.

the VBM with alloy composition if we neglect the contribution from core-level shift, thus the VBO can be deduced. Results for VBO of SiGe/Si and GeC/Ge system of different alloy composition can be read directly from Fig. 1 and Fig. 2. Fig. 3 shows our VB offset results for $Si_{1-x}Ge_x/Si$ system compared with the theoretical prediction of $\Delta E_v = 740x$ meV where x is the Ge fraction [15] and with

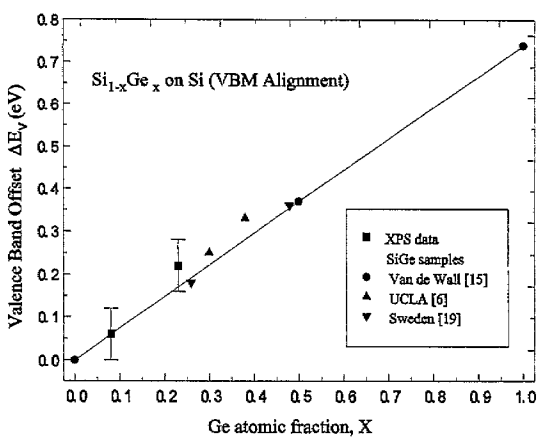

Fig. 3. Valence band offsets in strained $Si_{1-x}Ge_x$ on Si substrate heterostructures: the solid line indicates theoretical prediction of $0.74x$ eV.

experimental data done by different research groups using various techniques. On the other hand, our results of VB offsets for $Ge_{1-y}C_y/Ge$ indicated that there was almost no valence band discontinuity between $Ge_{1-y}C_y$ as the C fraction varied from 0.01 to 0.03. This was surprising at first, but, using the diamond bandgap of 5.45 eV [16,17], and by applying the electron-affinity Anderson–Shockley model to Ge/C, we note that Ge and C indeed lineup across the heterointerface theoretically. This prediction was consistent with our XPS results and with measurements by other groups [18]. Fourier transform infrared spectroscopy (FTIR) optical absorption data showed that the optical bandgap of the $Ge_{1-y}C_y$ alloys varied linearly with composition throughout the composition range investigated [10]. For $y =$ 0.032 (SGC32), the bandgap E_g increased by 250 meV with respect to the bulk Ge bandgap. Combining the results from XPS and FTIR, the conduction band alignment of unstrained $Ge_{1-y}C_y$ and Ge heterojunction was determined. Fig. 4 shows the whole band structure of GeC/Ge heterojunction system. As previously, the core-level shifting was assumed to be zero in this picture. Combining the results of band alignment for Ge/Si and $Ge_{1-y}C_y/Ge$ gives the alignment of $Ge_{1-y}C_y$ on Si which is also shown in

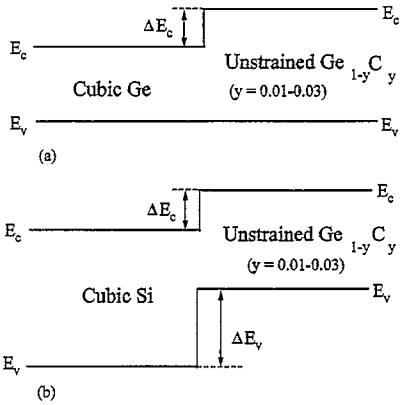

Fig. 4. Flat-band diagram showing the bandgap alignment for (a) thick $Ge_{1-y}C_y$ on Ge, and (b) thick $Ge_{1-y}C_y$ on Si. The major portion of bandgap discontinuity of $Ge_{1-y}C_y$/Ge system is in the conduction band, whereas the major discontinuity of $Ge_{1-y}C_y$/Si is in the valence band. Numerical values of the offsets for our samples are given in Table 1 and Table 2.

Fig. 4. If we count the core-level shifting calculated previously, the precision of the results of this study is ± 60 meV.

In conclusion, we used the XPS method and a data analysis approach proposed by Shih and Spicer to deduce energy band lineups in $Si_{1-x}Ge_x$/Si and $Ge_{1-y}C_y$/Ge systems. Convenient core levels (Si_{2p} and Ge_{3d}) serve as reference levels. The results obtained for $Si_{1-x}Ge_x$/Si are in good agreement with pseudopotential calculations [3], and experimental data. The $Ge_{1-y}C_y$/Ge VB offsets are approximately constant for C fractions y between 0.01 and 0.03. The optical bandgap increases with C fraction y, implying that the major portion of bandgap discontinuity of $Ge_{1-y}C_y$/Ge system is in the conduction band. So it has type III (one band continuous) band-edge lineups. Combining the results of band alignment for $Si_{1-x}Ge_x$/Si and $Ge_{1-y}C_y$/Ge, we infer that the major portion of bandgap discontinuity

Table 1
Sample properties and valence-band offsets for $Si_{1-x}Ge_x$

Sample i.d.	Ge atomic fraction	Thickness (Å)	Measured ΔE_v (meV)	Theoretical calculation (meV)
IBM27	0.08	2075	60 ± 60	59
IBM28	0.23	915	220 ± 60	170

Table 2
Sample properties and valence-band offsets for $Ge_{1-y}C_y$

Sample i.d.	C atomic fraction	Thickness (Å)	Measured ΔE_v (meV)
SGC10	0	6240	—
SGC30	0.016	4300	10 ± 60
SGC32	0.032	3500	20 ± 60

of $Ge_{1-y}C_y$/Si is in the valence band and it has type II (staggered) band-edge lineups. Our measurements are the first experimental determination of VB offsets for $Ge_{1-y}C_y$/Ge systems. The $Ge_{1-y}C_y$/Ge and $Ge_{1-y}C_y$/Si heterostructures have high potential for carriers confinement on band-engineered devices.

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