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Energy band offsets of SiGeC heterojunctions [1]

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Abstract

We report on conduction and valence band offsets in thick, relaxed Ge-rich $Si_{1-x-y}Ge_xC_y$ alloys grown by solid source molecular beam epitaxy on (100) Si substrates. X-ray photoemission spectroscopy was used to measure the valence band energies with respect to atomic core levels, and showed that C increased the valence band maximum of SiGeC by +48 meV/%C. The bandgap energies were obtained from optical absorption, and were combined with the valence band offsets to yield the conduction band offsets. For SiGeC/Si heterojunctions, the offsets were typically 0.6 eV for the valence band and 0.38 eV for the conduction band, with a staggered type II alignment. These offsets can provide significant electron and hole confinement for device applications. © 1997 Elsevier Science S.A.

Keywords: Band structure; Heterostructures; Semiconductors; X-ray photoelectron spectroscopy (XPS)

1. Introduction

Alloys of $Si_{1-x-y}Ge_xC_y$ are exciting candidates for the heterojunction devices expected in future integrated circuits. The bandgaps and the energy offsets of the conduction and valence bands at heterointerfaces are important parameters for device design [1,2], but are not well known for the SiGeC system. Electrical measurements performed directly on heterojunctions may be misleading because of interface charges caused by defects and impurities. Although no measurement technique is without difficulties, it is generally acknowledged that X-ray photoelectron spectroscopy (XPS) gives unambiguous results [3–5].

We used XPS to measure the valence bands offsets that would exist in heterojunctions of $Si_{1-x-y}Ge_xC_y$ alloy layers. The energies of the valence band maxima (VBM) were measured with respect to the atomic core levels of Si and Ge. The conduction band offsets were determined by including the bandgap energies obtained from optical transmission measurements. The layers were grown by molecular beam epitaxy (MBE) on (100) Si substrates and were unusual in having Ge-rich compositions with up to 2 at% C. Single, relaxed epitaxial layers exceeding the critical thickness were measured to avoid ambiguities that may occur in pseudomorphic heterojunctions caused by interface defects and the degree of strain.

2. Experimental details

The MBE technique used to grow the $Si_{1-x-y}Ge_xC_y$ alloys was described elsewhere [6,7]. Solid thermal sources were used for the Si and Ge, and the C was sublimated from a resistively heated filament. Substrates were 75 mm diameter (100)-oriented Si wafers 750 μm thick. Substrates were degreased and etched ex-situ followed by an HF dip, and were immediately loaded into the MBE chamber for outgassing for 1 h at 250 °C. The SiGeC alloys were grown at a substrate temperature of 600 °C at a rate of 0.1 $\mu m\ h^{-1}$. Prior to growth, reflection high-energy electron diffraction (RHEED) showed the (2 × 1) reconstructed surface of Si, and after growth indicated flat crystalline layers. Visual inspection showed the layer surfaces were specular and smooth. X-ray diffraction indicated that the layers were single crystalline with (100) orientation.

The XPS system used an SSX-100 spectrometer with Al Kα radiation, as described elsewhere [4]. Pure Si, Ge and C (thin film diamond) samples were used for calibration. The relative intensities of the Si 2p, the Ge 3d, and the C 1s core levels indicated that the compositions agreed with Rutherford backscattering (RBS) measurements using the

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C resonance at 4.265 MeV to enhance the C signal [8].

The offsets were determined from the relative differences between the VBM and the Si 2p and the Ge 3d core levels. Atomic core level positions were determined by Gaussian fits to the intensities. Variations in chemical bonding with alloy composition may slightly shift the core levels for different samples. Analysis of $Ge_{1-y}C_y$ alloys indicated that the Ge 3d core level energy shifted by at most $900y$ meV for C fraction y [4]. Therefore, our assumption of fixed core levels may contribute 9 meV/%C of error. Additional sources of error include composition-dependent wavevector selection rules and interface effects [3].

The optical absorption coefficient and the bandgap energies were determined from optical transmission using Fourier transform infrared spectroscopy (FTIR), as described elsewhere [9]. Alloy measurements were referenced to blank Si substrates, and interference fringes were curve-fitted to determine the onset of fundamental absorption. Absorption coefficients were calculated by matching data to transmittance and reflectance equations.

3. Results and discussion

Fig. 1 shows the valence band energy distribution functions, proportional to the valence band density of states (DOS), for a SiGeC alloy and pure Si. The intensity peaks are related to critical points in the valence band DOS. Fig. 2 shows the valence band offset for a SiGeC alloy compared with Si. As a graphical construction, the offset between two compositions was determined from the amount of relative shift in the energy scales needed to align the valence band edges as in the Fig. 2 inset. This graphical determination avoids errors that may occur when estimating the VBM by extrapolating the band edge slopes to the different background intensities of each sample.

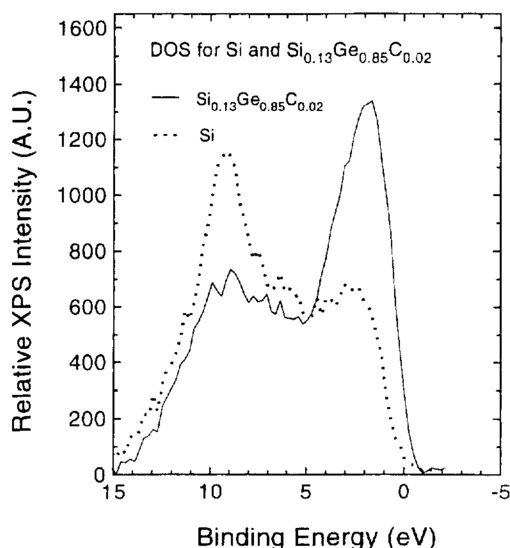

Fig. 1. Measured XPS intensity versus binding energy showing valence band energy distribution functions of $Si_{0.13}Ge_{0.85}C_{0.02}$ and of Si. Intensity peaks reflect variations in the valence band structure of the materials.

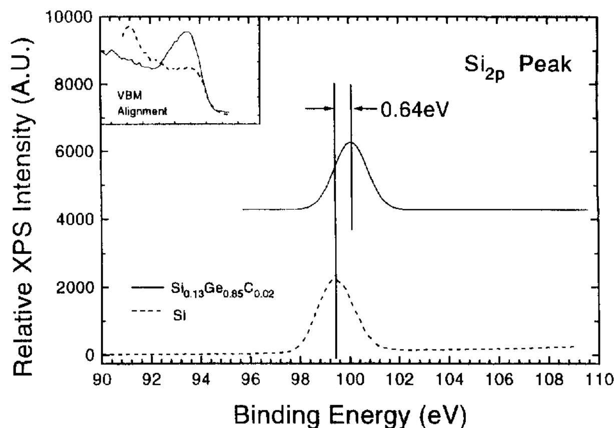

Fig. 2. Valence band offset energy between $Si_{0.13}Ge_{0.85}C_{0.02}$ and Si, illustrating our technique of shifting the binding energy scales to align the valence band edges as shown in the inset. The offset energy corresponds to the amount of the shift, determined by comparing core level positions. The energy scale is not absolute because it was shifted to align the valence bands.

Table 1 summarizes the effects of C on the valence band offsets for SiGeC alloys with similar Si and Ge contents but slightly different C fractions. To adjust for the different Si and Ge compositions between samples, we used the published value of 7.8 meV/%Ge for the valence band offset [3], resulting in a VBM shift of +48 meV/%C for our Ge-rich SiGeC alloys. The error per C percentage is estimated to include 4 meV due to uncertainties in the Ge fraction plus 9 meV due to chemical shifts. The offsets reported here were not adjusted for strain because our alloys greatly exceed the critical thickness for dislocation formation, and the residual biaxial strain was measured by X-ray diffraction to be less than 2×10^{-3}.

The measured optical absorption coefficient α is shown in Fig. 3 for a SiGeC alloy having a bandgap of 0.88 eV. For the SiGeC alloys measured here, α varied as the square of photon energy, indicating that the energy gaps were indirect in $\boldsymbol{k}$-space.

Table 1
Measured properties of SiGeC alloys including composition, bandgap (E_g), valence band offsets (ΔE_v) and conduction band offsets (ΔE_c) with respect to Si and to Ge. Positive offset values indicate higher energies of the alloy band energies with respect to Si or Ge. Negative offsets indicate lower energies of the alloy bands

Sample	SGC-67	SGC-68	SGC-70
Composition	$Si_{0.13}Ge_{0.85}C_{0.02}$	$Si_{0.11}Ge_{0.88}C_{0.01}$	$Si_{0.10}Ge_{0.89}C_{0.01}$
Thickness (μm)	0.22	0.18	0.19
E_g (eV)	0.889	0.866	0.854
ΔE_v on Si (eV)	+0.64	+0.62	+0.62
ΔE_c on Si (eV)	0.409	0.366	0.354
ΔE_v on Ge (eV)	+0.01	−0.01	0.00
ΔE_c on Ge (eV)	+0.229	+0.186	0.184

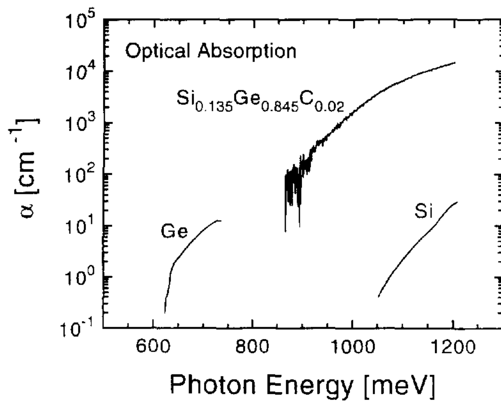

Fig. 3. Optical absorption coefficient versus photon energy of $Si_{0.13}Ge_{0.85}C_{0.02}$ and Si, showing the bandgap absorption edge. The bandgap of SiGeC lies below that of Si because of relatively high Ge content. Analysis indicated that alloy energy bands are indirect.

The conduction band offsets in Table 1 were obtained by adding the measured bandgaps to the valence band offsets. Our results show the band alignments to be staggered type II for SiGeC/Si heterostructures, as shown in the flat band diagram of Fig. 4. The valence band offsets for heterostructures of SiGeC alloys on Ge were much smaller than on Si. The valence band offset of pure Ge on Si can be obtained by subtracting the offsets for SiGeC on Ge from that of SiGeC on Si. The result for our samples yields 0.63 eV, which is smaller than the value of 0.78 eV reported for Ge on Si [3]. We ascribe this difference to experimental error, and to possible departures from transitivity [5].

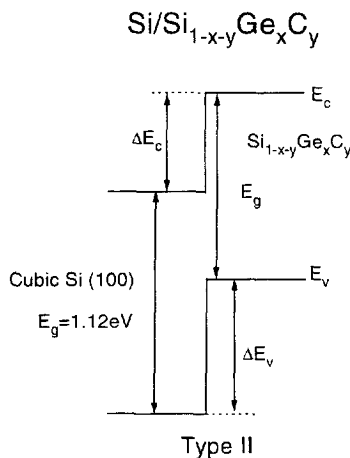

Fig. 4. Flat band diagram of SiGeC/Si heterojunction based on the data of Table 1. Energy band alignment is staggered, type II.

Using XPS, we have measured the valence band energies of thick bulk-like SiGeC alloys. Unlike previous studies, we report on Ge-rich compositions. We found that the addition of C shifts the VBM to higher energies. The conduction and valence band offsets between SiGeC and Si were large enough for significant confinement of both electrons and holes. This would not occur if the offsets were smaller than the thermal energy kT. Therefore SiGeC/Si heterojunctions can be useful for controlling both p-type and n-type conduction in device and circuit applications.

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