Determination of the valence band offset of a $\mu c\text{-C}/c\text{-Si}(100)$ heterojunction using low energy yield spectroscopy

Determination of the valence band offset of a μc-C/c-Si(100) heterojunction using low energy yield spectroscopy

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Abstract. The valence band offset developed in the heterostructure formed by depositing carbon on a Si(100) substrate was determined using a combination of low energy yield spectroscopy and x-ray photoemission spectroscopy. The spontaneous formation of an SiC layer between the crystalline silicon substrate and the carbon film was observed. Valence band offsets of 0.77 ± 0.08 eV at the SiC/c-Si interface and 1.55 ± 0.08 eV for the μc-C/SiC interface were found. Taking into account the band bending at the SiC layer after the microcrystalline graphite layer formation, the valence band offset between the silicon substrate and the carbon layer was evaluated to be 0.63 ± 0.08 eV, with the valence band edge of the carbon film being at higher energy than that of the silicon.

1. Introduction

One of the most interesting characteristics of amorphous carbon films is the variability of their electronic, optical and mechanical properties. They are governed by the relative concentration of the three different carbon bond configurations, sp^1, sp^2 and sp^3, that can exist simultaneously in a carbon film. During preparation, it is possible to vary this ratio, thereby tailoring the material for various important technological applications. The characteristics of the heterojunctions made by depositing amorphous carbon on crystalline silicon (c-Si) are a subject of increasing interest because of their potential application in a variety of electronic devices [1–4]. A fundamental problem is that of understanding the way in which the band gaps of the constituent semiconductors are aligned when the junction is formed. This problem has been investigated extensively both theoretically and experimentally [5]. Theories developed for the understanding of the band alignment can be divided into two general classes [6]: the *linear models*, where the band offset is given as a difference between two bulk energy levels referred to a common reference level, and the *interface dipole models*, where charge transfer, polarization and screening at the interface are explicitly considered. Due to the large difference in electronegativity between silicon and carbon atoms, the Si/C interface is also a key test of the band alignment theories because the predictions for the offset in the two theoretical schemes differ drastically and should be distinguishable experimentally.

Among the experimental techniques used to determine the valence band offset, low energy yield spectroscopy operating in constant final state mode (LEYS–CFS) has proved to be a powerful technique for determining valence band offsets directly from the interface spectrum [7, 8]. In this paper is presented for the first time the evaluation of the valence band offset present

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in the interface at the μc-C/c-Si heterojunction using LEYS–CFS and x-ray photoemission spectroscopy (XPS). Because of the spontaneous formation of a SiC layer between the silicon substrate and the microcrystalline graphite film (μc-C), it was necessary to determine the valence band offset at the SiC/c-Si and at μc-C/SiC interfaces. Both valence band offsets were determined using just the LEYS–CFS spectra. The valence band offsets obtained are compared with the reported calculated values [6].

2. Experimental details and results

The heterojunctions were grown *in situ* by RF glow-discharge decomposition of a CH_4/H_2 mixture on mirror-polished p-type ($\rho = 5\,\Omega$ cm) single-crystal silicon wafers heated to $950\,^\circ$C. The substrates were previously cleaned in a UHV preparation chamber using ohmic heating at $1100\,^\circ$C in an H_2 atmosphere. Substrate contamination was below the XPS detection limit. The samples were characterized *in situ* by XPS, LEYS–CFS and reflection high energy electron diffraction (RHEED) and *ex situ* by Raman spectroscopy.

XPS measurements were performed with a system (PHI model 3057) equipped with a hemispherical electron-energy analyser. The photon source was a monochromatized Al Kα line ($h\nu = 1486$ eV). The resolution of the system (source + analyser) was 0.35 eV. Based on the evolution of Si 2p and C 1s core level XPS spectra shown in figure 1, the μc-C growth, for the growth parameters used, can be divided into three different growth stages. The first stage begins with the clean silicon substrate. The corresponding Si 2p spectrum (figure 1(a)) shows the Si 2p$_{3/2}$, 2p$_{1/2}$ spin–orbit doublet. This stage finishes with the formation of a c-Si/SiC interface. The Si 2p spectrum (figure 1(b)) associated with the interface is made up of a chemically shifted component at 101 eV as well as the substrate component at 99.32 eV. The interface component is associated with the presence of a thin SiC layer on the top of the silicon substrate [10]. The C 1s spectrum (figure 1(b')) exhibits only one component. It is situated 182.1 eV above the SiC component of the Si 2p core level line, at a binding energy of 283.1 eV. This relative peak position is in agreement with the value reported in the case of single crystal c-SiC samples [9]. The second growth stage is characterized by the development of a thick SiC layer. The corresponding Si 2p spectrum (figure 1(c)) consists of a predominant component at 101 eV associated with the SiC layer and another smaller one that appears as a tail on the low energy side related to the silicon substrate emission. Its C 1s spectrum (figure 1(c')) has the same behaviour as the one in the previous stage. To evaluate possible charging effects a long series of Si 2p and C 1s core level spectra as a function of the deposition time was recorded. During the SiC overlayer growth, the SiC component of the Si 2p core level remained at the same binding energy until the beginning of the development of the μc-C overlayer, whereupon a small shift was observed. Thereafter, the component remained at the same binding energy until it finally disappeared due to the further growth of the μc-C overlayer. The behaviour of the SiC component shows that charging effects can be ignored. Further results concerning these two stages, in which there is the spontaneous formation of a SiC layer, have already been discussed in a previous paper [10], and will be discussed in more detail in a forthcoming publication [11].

After the saturation of the SiC layer growth [10], the third growth stage begins with the formation of the μc-C/SiC interface and finishes with the development of a thick μc-C layer. At the end of this stage there is no further contribution to the XPS spectrum from the c-SiC layer emission. Figure 1(d') shows the C 1s spectrum for this last growth stage. Compared to the spectra of the previous stages ((b') and (c')) a shift of 1.1 eV in the binding energy of C 1s component and an asymmetry can be seen. These two observations are in accordance with the results reported for a μc-C sample, which indicates that the carbon film formed in
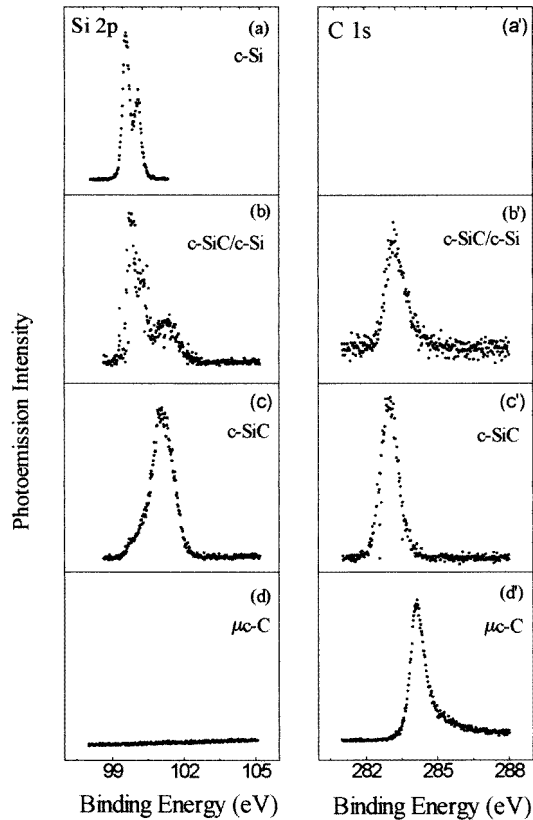
Figure 1. Left panels, Si 2p core level XPS spectra. Right panels, C 1s core level XPS spectra. (*a*) XPS spectrum of a crystalline Si sample with hydrogenated (100) surface. (*b*), (*b'*) XPS spectrum of the c-Si/c-SiC heterojunction. (*c*) (*c'*) XPS spectrum of a thick spontaneous SiC layer. (*d'*) XPS spectrum of a thick μc-C layer.

the third growth stage can be considered to be a microcrystalline carbon film. To confirm this assumption Raman measurements were performed since this technique is well known to give the 'fingerprint' of any carbon film. The Raman spectra of these microcrystalline graphite films were recorded at room temperature using a Spex 1403 1 m double pass spectrometer equipped with a cooled low noise photomultiplier tube using the 336 nm line of an Ar laser with an output of 300 mW. The resolution of the Raman spectrum is about 5 cm^{-1}. A typical Raman spectrum is shown in figure 2. The spectrum displays two features, one centred approximately at 1550 cm^{-1} corresponding to the G line associated with the optically allowed E$_{2g}$ zone centre modes of graphite and the other at 1350 cm^{-1} corresponding to the D line associated with disorder-allowed zone edge modes of graphite. Both peaks are in agreement with those reported for microcrystalline graphite films [12]. The RHEED patterns of our microcrystalline graphite films consisted of rings, which confirms their microcrystallinity.

In graphite films, carbon atoms are mainly in the three-fold coordinated sp^2 configuration where three of the four valence electrons are in σ bonds and the fourth lies in a π orbital that is weakly bonding, so that the states (π-states) associated with it lie closest to the Fermi level (E_F) [13]. The aim of this work is to determine the band alignment between the top of the π states in the microcrystalline graphite valence band and the top of silicon valence band.
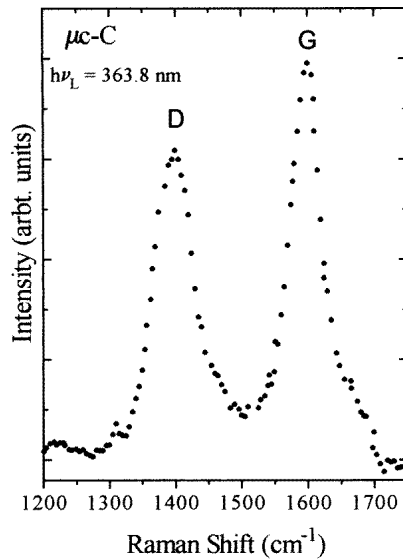
Figure 2. Raman spectrum of μc-C. The G peak has been assigned to scattering by optical zone-centre phonons in graphite. The D peak has been interpreted by scattering of disorder activated optical zone-edge phonons [3].

In the LEYS–CFS [7] experiments, the emission of an Xe lamp monochromatized by a double grating monochromator was used. The incident photons were in the 3.5–6.5 eV energy range. The photoemitted electrons were analysed by a double pass cylindrical mirror analyser (CMA PHI model 15-255 G). The system resolution was 80 meV. Because of the formation of the SiC layer between the silicon and the μc-C layer, the evaluation of the valence band offset at the μc-C/c-Si interface was made using a three step procedure. First the valence band offset $\Delta E_{V(SiC/Si)}$ at the SiC/c-Si interface was determined for a sample in an early growth stage, i.e. one in which only a thin SiC layer had developed. The thickness of this layer was such that it permits a fraction of photoelectrons generated in the substrate to be transported through the overlayer. In the second step, the valence band discontinuity $\Delta E_{V(C/SiC)}$ at the μc-C/SiC interface was determined. This determination was made using a sample on which a thin [14] microcrystalline graphite layer had developed over the SiC layer. Finally, the valence band alignment between the silicon substrate and the microcrystalline graphite film $\Delta E_{V(C/Si)}$ was determined by the difference between $\Delta E_{V(SiC/Si)}$ and $\Delta E_{V(C/SiC)}$, corrected for the rigid shift of the bands due to the band bending in the SiC layer after the microcrystalline graphite layer had developed [18]. Their shift (β) was obtained from the change in the position of the Si 2p core level in the SiC layer after the thin microcrystalline graphite layer had developed.

The method used to extract the valence band offset value from the LEYS–CFS spectrum was the following: the heterojunction spectrum was fitted with a linear combination of the experimental substrate spectrum and an overlayer spectrum obtained from a thick film, by using the relative energy shift and weight of the two spectra as the only fitting parameters, the energy shift giving the valence band offset directly [8].

In previous work [10] using LEYS–CFS we inferred a valence band offset equal to 0.77 ± 0.08 eV for the SiC/c-Si interface. Figure 3 shows the LEYS–CFS spectrum for the SiC/μc-C interface. In the μc-C film there is a high density of states near the Fermi level associated with the high sp^2 concentration. The top of the valence π band is at $E = E_F$
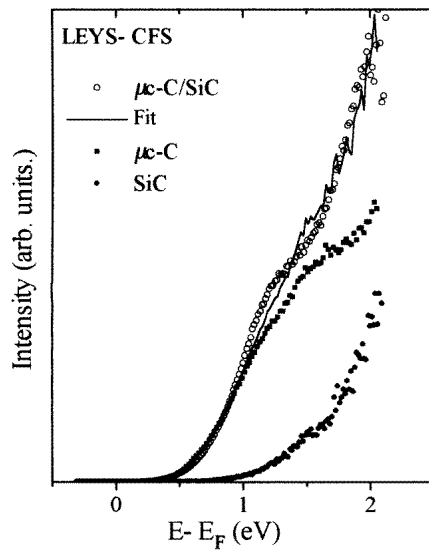
Figure 3. LEYS–CFS spectrum of the μc-C/SiC interface. The spectra of SiC and μc-C thick layer samples are also shown. The interface spectrum was fitted with a linear combination of the two thick layer spectra.
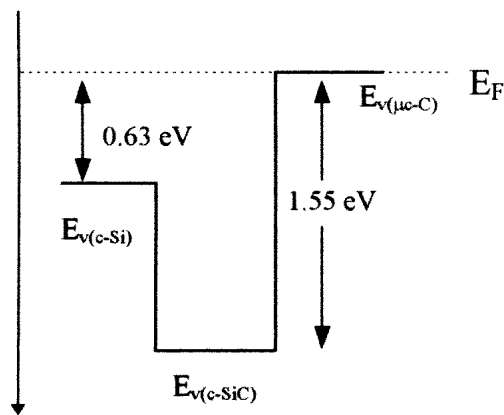
Figure 4. Schematic band diagram of the interface after the formation of the μc-C layer.

[13]. As shown in figure 3 the heterojunction spectrum was fitted with a linear combination of experimental c-SiC and μc-C spectra obtained from thick samples. A small discrepancy between fit and data was found in the defect state region of the SiC overlayer. This result can be explained by the difference in the defect density in the heterojunction and in thick films [8]. The inferred valence band offset was 1.55 ± 0.08 eV. The SiC valence band edge is at a lower energy than that of the other constituents of the interface, as shown in the diagram of figure 4. The β parameter was 0.15 eV, yielding $\Delta E_V = 0.63 \pm 0.08$ eV between c-Si and μc-C, with the valence band edge of the microcrystalline graphite film being at a higher energy than that of the silicon (figure 4).

3. Discussion

Theoretical predictions for the valence band offsets at the interfaces studied here are scanty. Robertson [6] evaluated the valence band offset for the a-C/c-Si interface and for the c-SiC/c-Si interface using both classes of theoretical model [15–17]. In this evaluation he considered a carbon film with a sp^2 component that dominates the gap states. In the tight binding approach introduced by Harrison [15] (*linear model*) he obtained the values 2.65 eV and 2.5 eV for c-SiC/c-Si and c-C/c-Si interfaces respectively. Using the Tersoff model [16, 17] (*dipole models*) the values calculated were 0.85 eV and 0.6 eV respectively.

Comparing these theoretical values with those obtained here (table 1) it is apparent that the valence band offset evaluated for the c-SiC/c-Si interface using the dipole model is in a range that is in accordance with the measured results. This agreement indicates that the effect of the interface dipoles needs to be considered in order to account for the measured discontinuity. On the other hand for the μc-C/c-Si interface the valence band offset evaluated using either model does not agree with the measured value. This difference can be explained by the very high density of π states in our film which could lead to a different localization of the top of the π states from the calculated one.

Table 1. Valence band discontinuities of the investigated heterojunctions.

Interface	Linear model	Dipole model	Experiment
c-Si/SiC	2.65	0.85	0.77
SiC/μc-C			−1.55[a]
c-Si/μc-C			−0.63[a]
c-Si/a-C	2.5	0.60	

[a] The minus means that the valence band edge of the SiC layer is at lower energy than the other interface constituents.

In summary, a valence band offset of 0.63 ± 0.08 eV was found for the μc-C/c-Si interface and 1.55 ± 0.08 eV for μc-C/c-Si, with the valence band edge of the SiC layer being at a lower energy than the other interface constituents. It was shown that the effect of interface dipoles needs to be considered in order to account for the measured discontinuity in the c-SiC/c-Si valence band.

Acknowledgments

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[14] In the context of this work, a thick overlayer means that the thickness is such that only the electrons generated on the film contribute to the LEYS–CFS spectrum. Since the escape depth of the electrons generated at the low energies used is nearly 40 Å, a thick overlayer is one with thickness greater than 40 Å. In contrast a thin layer is one which permits the contribution of the electrons generated in both sides of a heterojunction to the LEYS–CFS spectra. In this case an optimal layer thickness is around 15 Å.

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