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J. Phys.: Condens. Matter **11** (1999) 3761–3768. Printed in the UK PII: S0953-8984(99)99113-0

Low-energy yield spectroscopy measurements applied to determine valence band line-up at interfaces with non-homogeneous overlayers

C Bittencourt†

Instituto de Fisica 'Gleb Wataghin', Universidade Estadual de Campinas, PO Box 6165, 13083-970, Campinas, SP, Brazil

Received 10 November 1998, in final form 1 February 1999

Abstract. The technique of low-energy yield spectroscopy is applied to determine the valence band line-up at heterojunctions in which the overlayer does not cover the substrate. It is shown that by tuning the analysis energy, the contribution made by electrons that traverse the surface in the uncovered regions can be suppressed from the interface spectrum obtained from low-energy yield spectroscopy operating in the constant-final-state mode, thus allowing the determination of the band line-up without ambiguity. The method was applied to the c-Si/c-SiC heterostructure. A value of $\Delta E_V = 0.78 \pm 0.06$ eV was found for the valence band discontinuity.

1. Introduction

The key role that heterostructures play in heterojunction devices has motivated the development of various techniques for their characterization. Among the properties of the heterojunctions a fundamental one that has been investigated extensively is the way in which the band gaps of the constituent semiconductors are aligned when the junction is formed, i.e., the band line-up. Photoemission spectroscopy has proved to be one of the most powerful tools in this investigation [1]. The main advantage of the photoemission technique is that it provides a signal which is directly proportional to the density of electronic states, and therefore the search information is obtained with only a small number of assumptions. However, it also has several shortcomings, which limit its accuracy [1]. Recently, a new version of photoelectric yield spectroscopy has been applied to determine the band line-up at the heterojunction interface [2]. The authors claim that high accuracy and reliability can be obtained with this technique in which some of the shortcomings of the photoemission method are avoided. This is based on the idea of constant-final-state (CFS) energy spectroscopy, in which the number of photoelectrons is measured as a function of photon energy ($h\nu$) for a fixed electron kinetic energy (E_R). The fundamental advantage of using a CFS mode to analyse the valence band states compared to using conventional photoemission (in which the number of photoelectrons is measured as a function of electron energy) is that in this mode the convolution of the density of initial (valence) and final (conduction) states is eliminated. Owing to this characteristic, the CFS spectrum reflects the distribution in energy of the initial states, i.e., the density of the valence band states.

† Present address: Department of Physics, University of Warwick, Coventry CV4 7AL, UK.

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The suggestion was to combine the use of low-energy photons (visible and near-UV range) as the excitation source with the analysis of the photoemitted electrons in the constant-final-state mode [2]. This version of photoelectric yield spectroscopy is called low-energy yield spectroscopy operating in the constant-final-state mode (LEYS–CFS). The use of photons in the suggested energy range generates electrons with kinetic energies that correspond to emission from a distance of up to 40–50 Å from the surface, i.e., a rather thick near-surface region. This implies that electrons generated at the valence band edges of the material both above and below a heterojunction can be identified on the same spectrum. In addition, since the effect of the secondaries can be discarded due to their low kinetic energy, the spectrum obtained provides a direct measure of the valence band discontinuity.

Topologically there are three distinct layer growth modes, each named after the researchers associated with their initial description: Frank–Van der Merwe (FV) growth, Stranski–Krastanov (SK) growth and Volmer–Weber (VW) growth. In the FV growth the overlayer grows layer by layer. VW growth is very different; three-dimensional crystallites (islands) nucleate immediately and the overlayer may not completely cover the exposed substrate surface until a great many atoms have been deposited. SK growth lies in between: a few monolayers adsorb in a layer-by-layer fashion before three-dimensional clusters begin to be formed [8].

LEYS–CFS was used to determine the band line-up of several heterojunctions, both high resolution and a high dynamical range being achieved in those measurements [2, 4]. All of the analysed heterojunctions have in common overlayers with FV growth. Indeed, the determination using several photoemission spectroscopy modes of the valence band discontinuity (ΔE_V) at interfaces with both SK and FV overlayers has been broadly discussed [1, 2, 4, 9]. In contrast, for the case in which the overlayer has VW growth, no relevant discussion can be found, probably owing to the fact that most of the photoemission measurement must be done in the early growth stage of the overlayer [1], i.e. when the substrate is not completely covered. The existence of bare substrate regions makes the photoelectron conventional spectra obscure. It is interesting to ask why this happens and whether the same problem can happen with LEYS–CFS. These questions can be answered using very basic photoemission principles. It is well known that in the absence of inelastic scattering the photoelectrons traverse the surface with kinetic energy given by

$$E_{kin} = h\nu - \phi - E_B$$

in which $h\nu$ is the photon energy, E_B the binding energy and ϕ the work function. ϕ is usually defined as the difference between the vacuum level E_{VL} and the electrochemical potential μ or Fermi level energy E_F [2]. ϕ is therefore influenced by the chemical potential, which is determined purely by the bulk properties of the solid, and by the vacuum level, which depends only on the surface properties.

In an incompletely covered substrate, the surface is formed by two different structures: one associated with the substrate and the other with the overlayer. In this case, two values of E_{VL} will coexist at the same surface and there will be two corresponding values of ϕ. This means that the photoelectrons created in the substrate in the covered and the non-covered regions by photons with the same value of $h\nu$ and having the same binding energy will experience different values of ϕ in traversing the surface, and will arrive at the analyser with different kinetic energies. This will cause ambiguity in the determination of the valence band-edge position (E_V), making it impossible to establish the correct valence band line-up between the overlayer and the substrate.

The purpose of this paper is to demonstrate that LEYS–CFS can be used to determine the valence band discontinuity (ΔE_V) at interfaces with VW overlayers; in this case, conventional photoemission is not advisable.

Silicon carbide on crystalline silicon is an interesting case of an interface showing VW growth, which has potential application in several semiconductor devices, and which has been investigated by various groups [5–7]. This interface will be used to test the use of LEYS–CFS.

2. Experimental details

The c-Si/c-SiC heterojunctions were grow *in situ* by RF decomposition of a $CH_4 + SiH_4 + H_2$ mixture on mirror-polished p-type single-crystal silicon wafers heated to 950 °C. The substrate was previously cleaned in a UHV preparation chamber using Ohmic heating at 1100 °C in a hydrogen atmosphere. The substrate contamination was below the XPS determination limit. The samples were characterized *in situ* by XPS, LEYS–CFS, UPS and reflection high-energy electron diffraction (RHEED) and *ex situ* atomic force microscopy (AFM). The AFM and RHEED analysis in the early growth stages of the SiC overlayer showed that the growth proceeds by the nucleation of cubic crystalline islands. Further details and discussion about the SiC overlayer growth mechanism with these growth parameters will be presented in a subsequent publication [10].

In the LEYS–CFS experiments, the emission of a Xe lamp monochromated by a double-grating monochromator was used. The photoelectron energies were measured using a double-pass cylindrical mirror analyser. The system resolution was 80 meV. The first step in recording a CFS spectrum using low-energy photons is to determine the energy of the vacuum level E_{VL} of the sample, since electrons are photoexcited very close to the vacuum level, as a consequence of the low energy of the photons. The vacuum level energy determination can be done via conventional photoemission spectroscopy, using photon energies around 6 eV [3]. Figure 1(a) shows a typical photoemission spectrum for E_{VL} determination; the cut-off observed at high energy is due to the presence of the vacuum level. On the basis of this spectrum, the obvious choice of analysis energy E_R is the one at which the maximum in the photoelectron distribution is observed. Note however that due to the limited energy resolution of the electron energy analyser, the electrons are detected inside an energy window of breadth ΔE_R centred on E_R. Care must therefore be taken to exclude the possibility that this energy E_R corresponds to transitions to regions of the conduction band in which the energy distribution of the electronic states can have a very strong energy dependence within a range comparable to ΔE_R. Such dependence would produce a spectrum in which the convolution of the density of valence and conduction electronic states (rather than only the density of the electronic valence states) would be taken in account.

The following interesting feature of the vacuum level E_{VL} may also be relevant to the determination of E_R. As the radiation used to generate the photoelectrons has a Gaussian distribution even after being monochromated, the photoelectron kinetic energy distribution will have the same Gaussian distribution. If the kinetic energy of the photoelectrons that is used is very low, then the Gaussian kinetic energy distribution may overlap the vacuum level. In this case, those photoelectrons whose energies lie below E_{VL} will not be emitted. If the energy window of the analyser associated with E_R also straddles E_{VL}, then again only those photoelectrons that are actually emitted (in the portion of the Gaussian that lies above E_{VL}) will be detected. The effect of this is equivalent to using a more highly monochromatic incident beam. Typical analysis energies chosen were 0.05–0.2 eV above the vacuum level.

3. Results and discussion

The hypothesis for overcoming the problem discussed in the introduction, i.e., the determination of the valence band discontinuity at interfaces with non-homogeneous over-

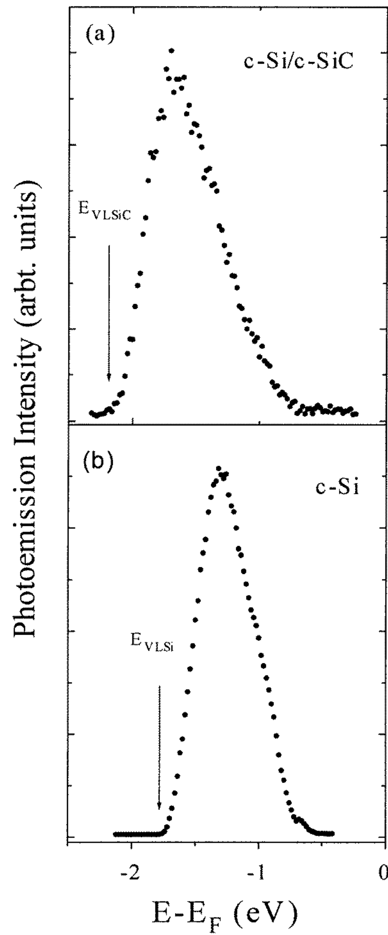

Figure 1. Photoemission spectra recorded using a photon energy of 6.02 eV: (a) for the c-Si/c-SiC heterojunction; (b) for the clean c-Si substrate.

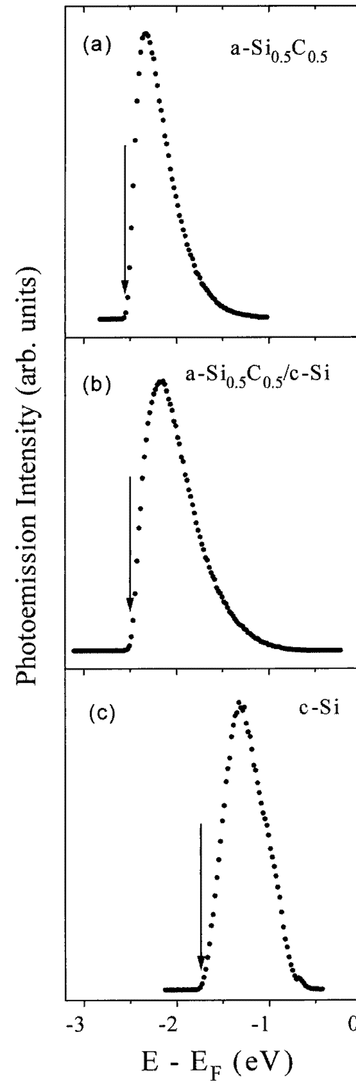

Figure 2. Photoemission spectra recorded using a photon energy of 6.02 eV: (a) for the a-$Si_{0.5}C_{0.5}$ sample; (b) for the c-Si/a-$Si_{0.5}C_{0.5}$ heterojunction; (c) for the clean c-Si.

layers, is based on its principal feature: the difference between ϕ on the covered and non-covered regions. In LEYS–CFS, only electrons having a specific kinetic energy E_R are recorded, so the contribution to the interface spectrum of the photoelectron excited in the uncovered substrate can be suppressed if the work function of the overlayer is lower than that of the substrate. In this case there will be some energy for which only the photoelectrons created under the overlayer will be able to traverse the surface. Taking advantage of this feature, it is possible to select an analysis energy E_R for which the photoelectrons excited in the uncovered substrate regions are not collected, thus suppressing their unwanted contribution to the interface spectrum, and eliminating the ambiguity in the determination of the position of E_V.

The c-Si/c-SiC heterojunction is a suitable system on which to test the hypothesis, since the overlayer has three-dimensional growth and its work function is smaller than that of the silicon substrate. Figure 1 shows the photoemission spectra recorded using $h\nu = 6.02$ eV for both the heterojunction (a) and the substrate (b); these were used to determine the vacuum level energies of the overlayer E_{VLO} and substrate E_{VLS}, shown in the figure by arrows. The Fermi level energy position E_F was located on the spectra by performing a measurement for a freshly evaporated gold layer. E_{VLS} is straightforward to obtain from the spectrum; conversely, to determine E_{VL} for the interface, it must be assumed that the overlayer generates the observed cut-off. To verify this assumption a photoemission spectrum of a SiC overlayer with no contribution from electrons generated below the interface (i.e., one that completely covers the substrate and is thick) must be analysed. Unfortunately in this situation the SiC overlayer presented charging effects, which made the determination of E_{VL} ambiguous. To overcome this problem, an amorphous thick a-$Si_{0.5}C_{0.5}$ layer and an a-$Si_{0.5}C_{0.5}$/c-Si interface were analysed. As the a-$Si_{0.5}C_{0.5}$ overlayer shows FV growth, it will cover the substrate from the early growth stages, and due to its characteristics [9] a rather thick film will not present charging effect problems. The photoemission spectra recorded from a thick a-$Si_{0.5}C_{0.5}$ overlayer and from a-$Si_{0.5}C_{0.5}$/c-Si interface are shown in figure 2. For comparison, the spectrum for bare silicon has been added to the figure. It can be seen, as pointed out by arrows, that the thick overlayer (figure 2(a)) and the interface (figure 2(b)) have the same cut-off energy. This result was expected: the cut-off energy is a surface parameter.

Using $\phi = h\nu - (E_F - E_{VL})$, the measured vacuum level and Fermi level energy, the work functions were calculated; there were $\phi = 3.9$ eV for the c-SiC and $\phi = 4.3$ eV for the silicon substrate. Choosing an analysis energy E_R within this range of energy, the electrons generated in the silicon substrate under the c-SiC will contribute to the LEYS–CFS c-SiC/c-Si spectrum, but the ones that traverse the surface through the uncovered substrate surface region will be suppressed from the spectrum.

Figure 3 shows the LEYS–CFS spectra recorded for the silicon substrate (figure 3(c)) and for the interface at two different analysis energies: below the substrate vacuum level, E_{Rb} (figure 3(a)) and above it, E_{Ra} (figure 3(b)). The LEYS–CFS spectra are recorded as a function of photon energy; the conversion to binding energy is performed using the equation $E_B - E_F = h\nu - E_R - E_{VL}$. A linear plot of the silicon substrate LEYS–CFS spectrum (figure 3(c)) shows a very sharp rise of emission at 0.69 eV, resulting in a 'quasilinear' edge; this onset was attributed to indirect transitions from the top of the valence band [2]. The spectrum of the interface recorded with E_R above E_{VLS} (figure 3(b)) has a similar shape to the bare Si one; the most marked structure of the Si spectrum at 1.5 eV can still be seen in it. In contrast, for the spectrum recorded with E_R below E_{VLS} (figure 3(a)), no similarity with that for the bare Si substrate can be observed and it is possible to identify two edges: one near the Fermi level and the other at higher energy. These edges are respectively identified with the emission from the Si below the SiC islands and the emission from the SiC islands. Since the LEYS–CFS interface spectrum is formed from photoelectrons generated in the substrate plus those generated in the overlayer, the following procedure was used to support this identification: the heterojunction spectrum was fitted with a linear combination of the experimental c-Si and c-SiC spectra [11]. As shown in figure 4, the agreement is very good in the region of emission from the valence band edges. However, 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 between the defect density in the heterojunction and that in the thick films. Similar discrepancies are found for other heterojunctions [4]. The valence band discontinuity can be determined from the relative shift of these two experimental spectra or directly in the interface spectrum from the relative shift of the two identified edges [2]. The value found from the linear fit of the

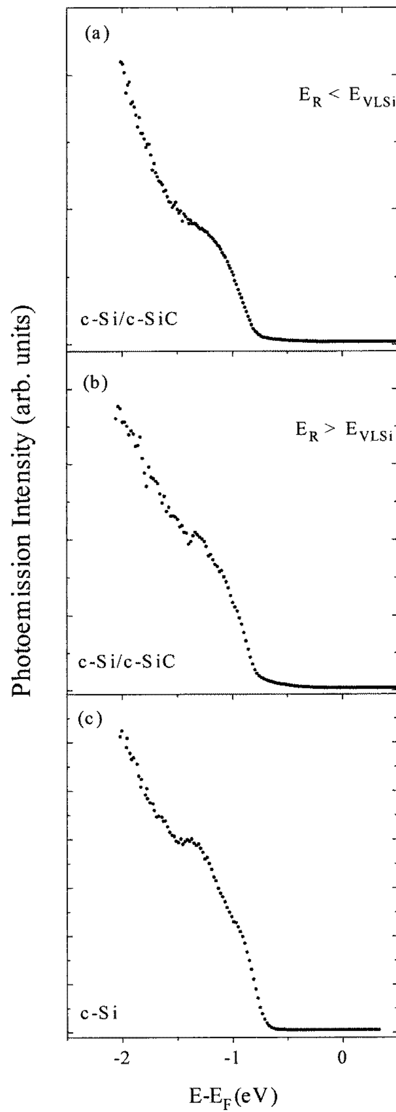

Figure 3. LEYS–CFS spectra: (a) c-Si/c-SiC recorded with the analysis energy below the substrate vacuum level; (b) the same with the energy above the substrate vacuum level; (c) for the c-Si substrate.

edges for five heterojunctions was $\Delta E_V = 0.78$ eV with a standard deviation of 0.06 eV. This value of ΔE_V is in accordance with the one calculated by Robertson [12]. He evaluated the valence band discontinuity (ΔE_V) for the c-Si/c-SiC interface using *linear models* [13] (in which ΔE_V is given as a difference between two bulk energy levels referred to a common reference level) and *interface dipole models* [14] (where charge transfer, polarization, and screening at the interface are explicitly included), obtaining 2.65 eV and 0.85 eV respectively. Comparing these theoretical values with the measured one, it is evident that ΔE_V evaluated using the dipole model is in accordance with the measured result. This agreement indicates that the effect of the interface dipoles needs to be considered in order to account for the measured discontinuity.

As regards the experimental values reported ($\sim$1.05 eV), the value obtained here is in a range that is in accordance with them [15–18]. The small variation in these values is probably

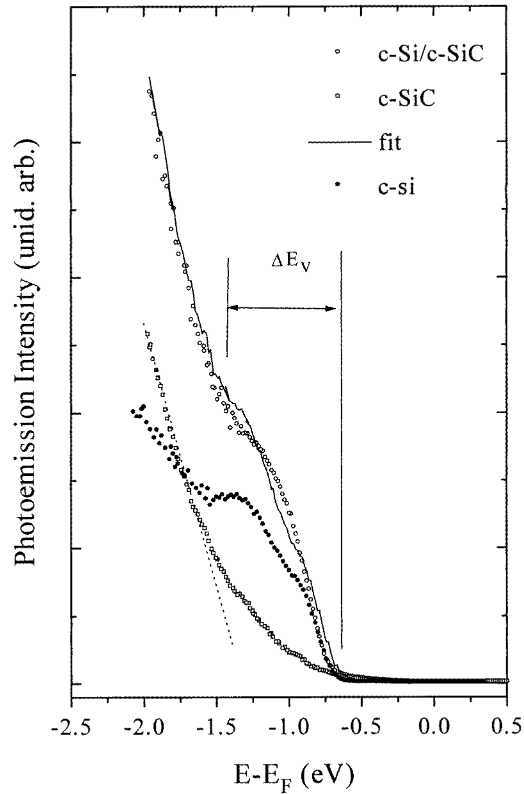

Figure 4. The LEYS–CFS spectrum of the c-Si/c-SiC interface. The spectra of a clean c-Si and SiC samples are also shown. The fit using the linear combination of the experimental c-Si and c-SiC spectra is represented by the continuous curve.

due to a difference in the density of the interface defects, which has an effect on the interface dipole and so on the band line-up.

4. Conclusions

It is possible to record a LEYS–CFS spectrum for a heterojunction exhibiting three-dimensional growth, in which the contribution to the spectrum from the photoelectrons excited in uncovered substrate regions is suppressed by appropriate tuning of the analysis energy, provided that the ϕ-value of the overlayers is less than that of the substrate. Further work is in progress in order to arrive at a procedure to be used in the case where ϕ for the overlayer is higher than that for the substrate.

Using the new interpretation of LEYS–CFS it was possible to determine the valence band discontinuity at the c-Si/c-SiC heterojunction; the value obtained, 0.78 ± 0.06 eV, in is in accordance with earlier reports [12, 15–18].

Acknowledgments

The author is grateful to Professor Florestano Evangelisti, Dr M De Seta and Dr S M Driver for helpful discussions.

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