Low-Energy Yield Spectroscopy as a Novel Technique for Determining Band Offsets: Application to the c-Si(100)/a-Si:H Heterostructure

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We present a new experimental method for determining band lineups at the semiconductor heterojunctions and apply it to the c-Si(100)/a-Si:H heterostructure. This method uses a modern version of an old spectroscopy: the photoelectric yield spectroscopy excited with photons in the near UV range. It is shown that both substrate and overlayer valence-band tops can be identified in the yield spectrum due to the high escape depth and the high dynamical range of the technique, thus allowing a direct and precise determination of the band lineup. A value of $\Delta E_V = 0.44 \pm 0.02$ eV was found for the valence band discontinuity.

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The characterization of the heterojunctions represents an important subfield of the physics of semiconductors, due to the key role that the heterostructures play in quantum wells, superlattices, and a number of heterojunction devices. A fundamental property of the heterojunction is the band lineup at the interface, i.e., the relative position of the band edges of the constituent materials. Consequently, a variety of techniques has been applied in order to determine this fundamental parameter [1]. Among such techniques, photoemission spectroscopy is one of the most used and most powerful. The main advantage of photoemission, beside its surface sensitivity, is that it provides a signal which is directly proportional to the density of states and that, therefore, the sought information is obtained with a small amount of assumptions. In all the different versions of this approach the fundamental step consists in determining accurately the band edges and their position relative to the core levels. This procedure has severe limitations, however, which limit its accuracy (see Ref. [2] for a discussion). A fundamental improvement would be the possibility of determining both substrate and overlayer band edges in the same spectrum: "direct technique" [2]. By using ultraviolet photoemission spectroscopy (UPS) this is feasible only when the offset is large.

It is the purpose of this Letter to show that high accuracy and reliability can be obtained by applying a "modern" version of an "old" technique [3–5], i.e., photoelectric yield spectroscopy (YS) excited with low energy photons (visible and near UV range). This technique provides both a high resolution and a high dynamical range (up to 7 orders of magnitude in the signal intensity variation can be followed). Moreover, since the escape depth of electrons increases at low kinetic energies, a thicker near-surface region can be sampled (typically 40–50 Å). As a result, both substrate and overlayer valence band edges can be identified on the same spectrum, thus providing a direct measure of the valence band discontinuity and improving the accuracy of the determination. The method has been applied to the study of hydrogenated amorphous silicon (a-Si:H) grown on crystalline Si(100) surface, a system of great fundamental and technological interest.

The band lineup at the c-Si/a-Si:H interface was investigated in the past with a variety of techniques and conflicting results [6–11]. The reported values for the valence band discontinuity ΔE_V varied from 0 to 0.7 eV. In these studies the amorphous layers were deposited on crystalline substrates whose surfaces where not cleaned in UHV. Therefore, the heterojunctions certainly presented a certain amount of contamination (mostly C atoms) which could severely affect the interface properties and account, at least partially, for the conflicting results.

The heterojunctions of the present work were grown *in situ* by depositing a-Si:H layers by plasma-assisted chemical vapor deposition on p-type ($\rho = 5\ \Omega$ cm) mirror-polished c-Si(100) wafers cleaned in a preparation chamber, connected to the analysis chamber, whose basic pressure was 8×10^{-11} Torr. The cleanness of the resulting c-Si(100) surfaces was monitored by x-ray photoemission spectroscopy and the surface quality by reflection high-energy electron diffraction (RHEED). The contamination was beyond the detection limit and the surfaces showed 2×1 reconstruction. The a-Si:H overlayers were grown from pure SiH_4 at a pressure of 0.3 Torr and at two different temperatures, 70 °C and 250 °C. The growing conditions for the 250 °C samples result in "state of the art" materials characterized by ~1.70 eV optical gap, Urbach tail in the 40–50 meV range, hydrogen content of (10-15)%, density of gap states below 10^{16} states/cm^3 and photo/dark conductivity ratio with AM1 illumination higher than 10^5, as checked extensively on thicker samples by optical and IR absorption, spectral photoconductivity, and photothermal deflection spectroscopy. As expected, the lowering of the deposition temperature to 70 °C brought about an appreciable deterioration of sample characteristics with a marked increase of hydrogen

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content [up to (20-25)%]. The thickness of the overlayers ranged from a few angstroms up to 40-50 Å. We found that the first few monolayers of the overlayer were ordered even though the growing conditions for depositing *a*-Si:H were used. The thickness of the ordered transition layer varied from sample to sample and was much reduced in the low temperature (70 °C) growth. An estimate of the thickness of the amorphous phase in the overlayer was obtained by fitting the Si $2p$ core level line shape [12]. The ordered growth of the first few monolayers is in qualitative agreement with the recent report by Eaglesham, Gossmann, and Cerullo [13], who showed by using the molecular-beam epitaxy (MBE) technique that the epitaxial growth of Si on smooth Si(100) surfaces occurs also at room temperature, albeit with a limiting epitaxial thickness of 10-30 Å only.

In the YS the light of a Xe source was monochromatized by a double grating monochromator in order to reduce the stray light. The exciting photons were in the 3.5-6.5 eV energy range. The photoemitted electrons were analyzed by a double-pass cylindrical mirror analyzer. The YS was operated in the constant final state mode (CFS), i.e., the photoemitted electrons of a chosen kinetic energy were collected as a function of photon energy. The samples were negatively biased in order to reduce the background. In these experimental conditions up to 7 orders of magnitude of signal intensity change as a function of energy could be followed. The system resolution in normal working conditions was 80 meV. The CFS operating mode is at variance with the previous use of the YS technique [3-5], where the total yield mode was employed [14]. The CFS mode is frequently used with high energy photons in the synchrotron radiation spectroscopy, but was only recently employed by our group with low energy photons [15-17].

Typical electron kinetic energies chosen for the CFS-YS were 0.1-0.2 eV above the vacuum level. For such a low kinetic energy the conservation at the free surface of the **k** parallel implies that the electrons which can escape into the vacuum are distributed in a narrow cone around the direction perpendicular to the surface. Hence, the final state for the transitions involved in the CFS-YS is fixed both in energy and in the **k** direction. The interpretation of the signal becomes straightforward, contrary to the total yield case where a variety of functional dependences were found [18], related to the electronic structure in a very indirect way. In the case of transitions in an amorphous material or from localized states and surface states in a crystalline material, it is expected that the transitions are nondirect. With the usual assumption that matrix elements are slowly varying functions of the energy, the CFS-YS spectrum is directly proportional to the density of initial states. In the case of transitions from extended states in a crystalline material, we must distinguish between two possibilities. If the transitions are direct and **k** is conserved in the optical transition, a narrow peak in the CFS spectrum is expected when the photon energy is such that the final state is in the chosen escape cone. The CFS-YS becomes, substantially, an angle-resolved photoemission spectroscopy. Quite to the contrary, if the transitions are indirect and the missing **k** is provided by, e.g., the phonons, the CFS-YS intensity is again proportional to the density of initial states.

We start the presentation of the data by analyzing preliminarily the CFS-YS data taken on the clean surfaces of crystalline and amorphous silicon samples. The spectrum of a hydrogenated *c*-Si(100) surface is shown in Fig. 1(a), where the intensity is displayed on a linear as well as on a logarithmic scale. A hydrogenated surface is considered, since the hydrogenation process is known [19] to remove the "intrinsic" surface-state band, which forms on the clean surface upon reconstruction. Since this surface-state band is located close to the valence-band top E_V in the case of the Si(100) surface, singling out E_V itself is difficult unless hydrogen is used to expose the "bulk" valence band edge. A study of the CFS-YS spectra as a function of hydrogenation and their comparison with the UPS spectra are reported elsewhere [20]. From the spectrum of Fig. 1(a) on the linear scale we see that there is a very sharp rise of emission at 5.3 eV, resulting in a "quasilinear" edge followed by a second structure at ~6.0 eV. Based on the evolution as a function of the final state energy and the analysis of the energy band structure, we attribute the onset at 5.3 eV to indirect transitions from the top of the valence band. The higher energy structure could be due either to direct transitions setting in or to in-

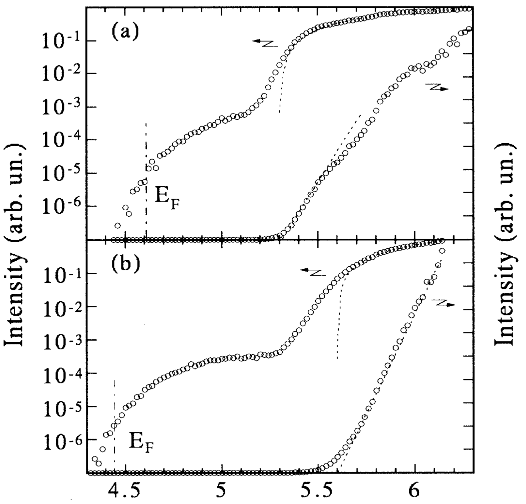

FIG. 1. (a) CFS-YS of a crystalline Si sample with hydrogenated (100) surface. (b) CFS-YS spectrum of a *a*-Si:H sample. The spectra are displayed on a linear scale on the right and on a logarithmic scale on the left. The dotted lines represent the $E - E_V$ dependences.

direct transitions from the $L_{3'}$ critical point in the valence band density of state [20].

The same spectrum reported on a logarithmic scale in Fig. 1(a) allows us to follow the evolution of the states inside the gap, thanks to the high dynamical range of the CFS-YS. For $h\nu < 5.3$ eV there is a steep decrease of emission as expected for transitions originating at the valence-band top. The exponential behavior which extends down to ~5.15 eV results from the broadening due to the experimental resolution. At still lower energies a broad band of deep defects is present, spanning the energy gap with decreasing intensity down to the Fermi level E_F. Based on the close similarity with the yield spectra of *a*-Si:H, we attribute these states to isolated dangling bonds and/or small cluster of dangling bonds due to surface defects, which do not "participate" in the surface reconstruction. These dangling bonds are reduced in number but not completely eliminated by the hydrogen passivation. Similar to the *a*-Si:H case, some of these defect states are also responsible for the pinning of the Fermi level at the surface. The defects which pin the Fermi level most likely are type-*C* defects, reported recently by Hamers and Kohler [21] using scanning tunneling microscopy and local tunneling barrier height measurements. Type-*C* defects consist of two adjacent Si atoms missing along a $\langle 110 \rangle$ direction.

The edge at 5.3 eV is used for defining the top E_V of the valence band. According to the usual procedure followed in the determination of band discontinuities by photoemission spectroscopies, we define E_V from the linear extrapolation to zero as shown schematically in Fig. 1(a). It should be kept in mind, however, that this definition is somewhat arbitrary and, as such, can entail a systematic error in the determination of the valence-band discontinuity at the interface.

In Fig. 1(b) the CFS-YS spectrum of the *a*-Si:H is shown. Considering the linear scale, we see that the edge is now closer to linear behavior and that the falling off of the density of states below $h\nu = 5.6$ eV is less steep than in the *c*-Si case. This slower decay of the intensity can also be appreciated on the logarithmic plot, where it is apparent that the density of states evolves smoothly to an exponential dependence (Urbach tail), whose characteristic energy was found in the range 45-60 meV [15]. At lower photon energies the broad band of dangling bonds is present. This band fills the energy gap with a decreasing state density down to the Fermi level E_F.

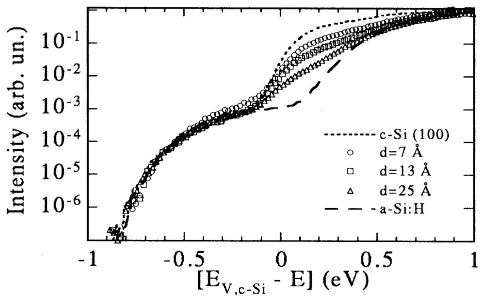

FIG. 2. CFS-YS spectra of a series of hetorojunctions with different overlayer thickness *d* grown at low temperature. Also displayed are the *c*-Si and *a*-Si:H spectra. $E_{V,c\text{-Si}}$ is the crystalline silicon valence band edge. The *a*-Si:H spectrum was shifted according to the measured valence-band discontinuity, as discussed in the text.

In Fig. 2 the evolution of the CFS-YS data is shown for a series of heterojunctions grown at low temperature with increasing *a*-Si:H layer thickness. The progressive reduction of the substrate signal and the concurrent increase of that from the overlayer are clearly visible and it is possible to follow the evolution from the density of states of the clean *c*-Si surface to that of a thick *a*-Si:H sample. At intermediate coverages a double edge corresponding to the emission from substrate and overlayer valence bands is clearly detectable. This situation is shown in more detail in Fig. 3(a) for a heterojunction grown at 250 °C. We identify the edge on the left (whose onset is taken as the zero of the energy scale) with the emission from the crystalline substrate and that at higher binding energy with emission from the amorphous overlayer. Besides the clear evolution seen in Fig. 2, where the relative intensity of the two edges scales according to the overlayer thickness, this

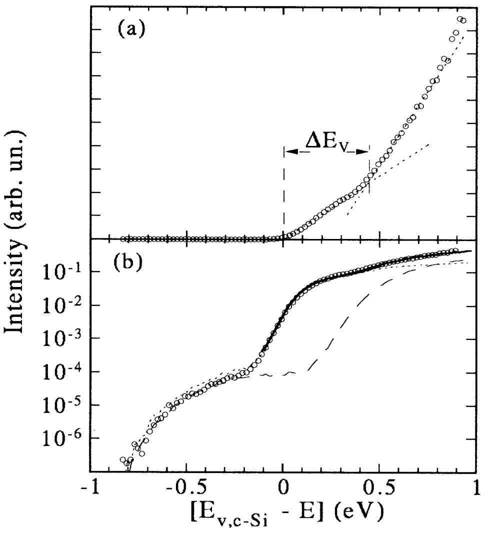

FIG. 3. (a) CFS-YS spectrum of a heterojunction, plotted on a linear scale, showing the double edge structure. The dotted lines represent the linear fit of the two edges. (b) The same spectrum displayed on a logarithmic scale. Dotted and dashed lines are the experimental spectra of *c*-Si(100) and *a*-Si:H samples, respectively, scaled according to the procedure described in the text. The continuous line is their sum. $E_{V,c\text{-Si}}$ is the crystalline silicon valence band edge.

identification is supported by the following experimental features. The energy separation between the onset of the higher binding energy edge and the Fermi level coincides with that measured on thick a-Si:H samples, as it should do since the free surface of the heterojunction is that of the a-Si:H. The identification of the onset of the higher binding energy edge with the a-Si:H valence-band top results in the coincidence between the photothreshold of the heterojunction and that of thick a-Si:H samples.

The simultaneous identification of both substrate and overlayer valence-band maxima on a single spectrum allows a direct and precise determination of the valence band offset ΔE_V at the interface. Two procedures were followed for the determination of ΔE_V. In the first procedure [Fig. 3(a)], the two edges were fitted with linear functions. From the linear fit of the two edges in eight heterojunctions grown at 250 °C and with different overlayer thickness we have obtained an offset of 0.44 eV with a standard deviation of 0.02 eV. The four heterojunctions with low temperature (70 °C) overlayer we have investigated gave the same value for the discontinuity, despite the larger H content. In this case, however, the offset determination was less accurate due to the valence band edge broadening and the higher Urbach tail of the poorer quality overlayers [12].

In the second analysis procedure, described in Fig. 3(b), the heterojunction spectrum was fitted with a linear combination of the experimental c-Si and a-Si:H spectra, by using the relative energy shift and weight of the two spectra as the only fitting parameters, the energy shift giving directly the valence band offset. This analysis procedure represents a more demanding test, since a larger range of intensity variation is taken into account in the fit. Moreover, in this case the offset value is to a large extent independent of the definition of the valence-band top. Inspection of Fig. 3(b) shows that the agreement is very good in the region of emission from the valence band edges. The offset values calculated according to the second procedure coincide with that of the previous analysis.

In conclusion, we have applied low-energy photoelectric yield spectroscopy to the study of the heterojunctions, in the effort of finding a technique which could determine band offsets directly and avoid some of the shortcomings of the photoemission methods. CFS-YS excited with photons in the near UV range exhibits two interesting features, a larger sampling depth of the near surface region and a much higher dynamical range. We have shown that, by taking advantage of these features, it is possible to locate both substrate and overlayer valence-band tops on the same spectrum and obtain a direct determination of the band offset, without most of the shortcomings inherent to the photoemission techniques. Furthermore, the data showed unambiguously that a valence-band discontinuity is present at the c-Si(100)/a-Si:H interface of heterojunctions grown *in situ* in a UHV system by depositing "state of the art" a-Si:H on clean c-Si(100) surfaces. The physical origin of this discontinuity remains to be ascertained. Further work is in progress in order to clarify the last point.

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