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Electronic states and band lineups in c-Si(100)/a-Si$_{1-x}$C$_x$:H heterojunctions

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Heterostructures formed by depositing *in situ* amorphous hydrogenated silicon-carbon alloys on Si(100) substrates were characterized by photoelectric-yield spectroscopy, UPS, and XPS. It is shown that both substrate and overlayer valence-band tops can be identified on the photoelectric-yield spectrum, thus allowing a direct and precise determination of the band lineup. We find a valence-band discontinuity varying from 0.44 eV to 1.00 eV for carbon content ranging from 0 to 50%. The present data can be used as a test for the lineup theories and strongly support the *interface dipole* models. [S0163-1829(97)02312-6]

I. INTRODUCTION

The characterization of the heterojunctions realized by depositing hydrogenated amorphous silicon (a-Si:H) or amorphous silicon-carbon alloys (a-Si$_{1-x}$C$_x$:H) on crystalline silicon (c-Si) is a subject of increasing interest, because these kinds of heterojunctions are employed in a variety of devices. Furthermore, these heterostructures provide an interesting way of monitoring the evolution of the band lineup as a function of the carbon content in the overlayer and can be used to test chemical trends in the lineup theories without the presence of strain effects, since in the amorphous state silicon and carbon can be mixed at all compositions and there is not a need for lattice-matching at the interface. The way silicon-carbon starts its growth on the c-Si surface is also of interest since its understanding can be useful in the widespread effort to obtain good quality c-SiC and diamond films on crystalline silicon surfaces.

Among many interesting properties of semiconductor heterojunctions, a fundamental one is the band lineup at the interface, i.e., the energy difference between the band edges on either side of the junction. The problem of band lineups in the heterojunctions has been greatly debated theoretically as well as extensively investigated experimentally. However, experimental investigations of amorphous-amorphous and crystalline-amorphous heterojunctions are scanty. In particular, to our knowledge, only three papers dealt with the c-Si/a-Si$_{1-x}$C$_x$:H system[1–3] reporting conflicting results. Cuniot and Lequeux[1] inferred the band lineup from current-voltage and photocurrent-voltage characteristics and found a valence-band discontinuity $\Delta E_v \sim 0.27$ eV for an a-Si$_{1-x}$C$_x$:H overlayer having an optical gap of 1.9 eV. Larger valence-band discontinuities were found by Essick *et al.*[2] by capacitance techniques on a series of heterostructures with a-Si$_{1-x}$C$_x$:H overlayer optical gaps ranging from 1.75 to 2.1 eV. ΔE_v increased from 0.65 to 0.83 eV in the alloy range investigated. A valence-band offset equal to 0.35 eV was determined by Magafas *et al.*[3] from current-voltage and capacitance-voltage measurements. However, the heterojunctions investigated by them had a not-hydrogenated a-SiC overlayer, whose carbon content was not specified by the authors. The gap they quote (i.e., 1.35 eV) is much smaller than that of any hydrogenated amorphous alloy, so that it is not possible to compare their result with the previous ones.

In the present paper we report on the investigation of a-Si$_{1-x}$C$_x$:H alloys and c-Si(100)/a-Si$_{1-x}$C$_x$:H heterojunctions as a function of carbon content. The heterojunctions were deposited on clean and well characterized Si(100) substrates in ultrahigh-vacuum conditions. The samples were concurrently characterized by UPS, XPS, and photoelectric yield spectroscopy. The results of the three different spectroscopies were compared in order to obtain a better understanding of the systems investigated. Moreover, as shown in a previous paper[4] on the characterization of the c-Si/a-Si:H heterojunction, high accuracy and reliability can be obtained by applying the photoelectric yield spectroscopy excited with low energy photons (visible and near-UV range) and operated in the constant final state mode. This technique is characterized by a high resolution and a high dynamical range. Furthermore, since the escape depth of electrons increases at low kinetic energies, a thick near-surface region can be sampled (typically 40-50 Å), allowing a wider thickness range for the heterojunction overlayers that can be analyzed. Both substrate and overlayer valence-band edges can be identified on the same spectrum, thus providing a direct measure of the valence-band discontinuity.

II. EXPERIMENT

The a-Si$_{1-x}$C$_x$:H alloys were grown by plasma-assisted chemical vapor deposition at low RF power from SiH$_4$+CH$_4$ mixtures at a deposition temperature of 270 °C and a pressure in the 0.3–0.5 Torr range. The heterojunctions were prepared *in situ* by depositing thin alloy layers on crystalline silicon substrates. The substrates, mirror-polished p-type ($\rho = 5\ \Omega$ cm) wafers, were previously cleaned via a $T = 1100$°C thermal annealing in a UHV preparation chamber in which the basic pressure was better than 2×10^{-10} Torr . Substrate contamination was beyond the XPS detection limit. The cleaning, deposition, and analysis chambers were all connected and the samples could be transferred under UHV conditions avoiding surface contamination. The analysis chamber was equipped with RHEED, UPS, XPS, and yield spectroscopy.

Concerning the yield spectroscopy (YS), the light from a

Xe source was monochromatized by a double grating monochromator in order to reduce stray light. The exciting photons were in the 3.5–6.5 eV energy range. The photon flux was measured before the experiments by positioning a photomultiplier in front of the entrance window of the analysis chamber. Corrections for the reflection at the sample surface were also taken into account. The photoemitted electrons were analyzed by a double-pass cylindrical mirror analyzer (CMA PHI model 15-255 G). The YS was operated in the constant final state (CFS) mode, i.e., the photoemitted electrons of a chosen kinetic energy were collected as a function of the photon energy. The samples were negatively biased in order to reduce the background. In these experimental conditions up to seven 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, as checked on the Fermi function cutoff of gold.

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 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 and the interpretation of the signal becomes straightforward. 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 bulk 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.

UPS spectra were recorded with the same double pass cylindrical mirror analyzer. Two photon sources were used, namely the He I radiation ($h\nu = 21.2$ eV) and the Xe lamp monochromatized with a double grating monochromator. The system resolution was 70 meV for the spectra excited with He lamp and 100 meV for the spectra excited with 6.02 eV photons from the Xe lamp. The resolution was checked on the Fermi function cutoff of gold.

XPS measurements were performed with a monochromatized ESCA system (PHI model 3057) equipped with a hemispherical electron-energy analyzer. The photon source was the Al $K\alpha$ line ($h\omega = 1486.6$ eV). The resolution of the system (source + analyzer) was 0.35 eV, as checked on the Si $2p$ core level.

The overlayer thickness was determined from the relative intensities of the Si $2p$ and C $1s$ core levels assuming an exponential attenuation of the signal with an electron escape depth $\lambda = 18$ Å (Ref. 5) and assuming that the carbon concentration in the heterojunction overlayer was equal to that of the corresponding thick amorphous films grown in identical conditions. The estimated thicknesses are reported in Table II. Typical growth rates were 2 Å/s.

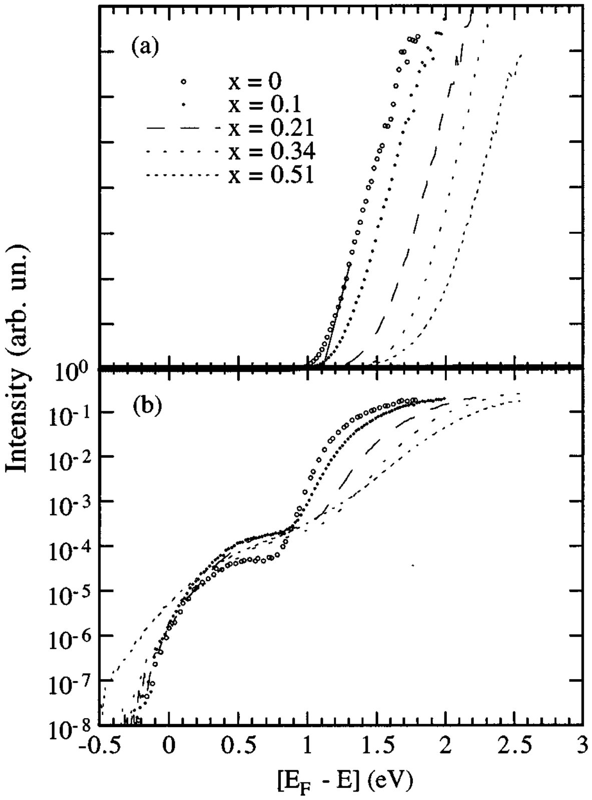

FIG. 1. (a) CFS-YS spectra of the a-Si$_{1-x}$C$_x$:H alloys displayed on a linear scale. (b) Same spectra displayed on a logaritimic scale.

III. a-Si$_{1-x}$C$_x$:H ALLOYS

The CFS-YS spectra of a series of alloys with increasing carbon concentration are shown in Fig. 1. The zero of the energy was taken at the Fermi level, whose energy position E_F on the CFS-YS spectra was determined in two ways. In the first procedure, the cutoff due to the occupation probability of the lowest binding-energy states was fitted with the Fermi function. Since the density of gap states is high enough this procedure is usually a reliable one. In the second procedure, the Fermi level was first located on the UPS spectra excited with $h\nu$ = 6.02 eV photons by measuring a freshly evaporated gold layer. Then E_F was positioned on the corresponding yield spectra by bringing to coincidence the signals from the valence-band edge in the two spectroscopies.

Considering first the a-Si:H sample, we see on the linear scale that an edge very close to a linear behavior is present in the spectra which can be used for defining the top E_v of the valence band from its linear extrapolation to zero as shown schematically by the continuous line, according to the usual procedure followed in the determination of band discontinuities by photoemission spectroscopies. On the logarithmic plot it is apparent that at lower energies the density of states (DOS) evolves smoothly to the exponential dependence

TABLE I. Physical parameters of the a-Si$_{1-x}$C$_x$:H alloys investigated as a function of carbon concentration. E_v is the energy separation of the valence-band top from the Fermi level; E_g is the optical gap; E_0 is the Urbach's characteristic energy; ϕ and χ are the work function and the photothreshold, respectively.

x	E_v	E_g	E_0	ϕ (eV)	χ (eV)
0	1.1	1.7	54	4.22	5.32
0.1	1.22	1.8	75	4.19	5.41
0.25	1.47	1.9	96	3.85	5.32
0.35	1.65	2.1	126	3.87	5.52
0.5	1.81	2.3	179	3.49	5.30

TABLE II. Valence-band discontinuities of the investigated c-Si/a-Si$_{1-x}$C$_x$:H heterojunctions. (1), (2), and (3) refer to different determinations as explained in the text. d is the overlayer thickness. ΔE_v for the c-Si/a-Si:H case ($x=0$) is 0.44 eV as determined in Ref. 4.

x	d (Å)	(1) ΔE_v	(2) ΔE_v	(3) ΔE_v
0.10	11	0.56	0.56	0.48
0.25	9	0.73	0.72	0.66
0.35	8	0.78	0.75	0.83
0.50	7	0.97	1.00	0.92

characteristic of the Urbach tail. Urbach's characteristic energy E_0, as measured on a variety of samples grown in the same conditions, was found[6] to vary in the range 45–60 meV. At still lower binding energies the broadband of the dangling bonds is present, spanning the energy gap with decreasing intensity up to the Fermi level E_F.

As expected, alloying with carbon causes a shift of the edge toward higher binding energies as a result of the opening of the gap caused by the replacement of Si-Si bonds by the stronger Si-C ones.[7] Concomitantly, there is an appreciable broadening of the exponential region and the top of the valence band becomes less defined due to a higher degree of disorder. The corresponding Urbach's characteristic energies E_0 are reported in Table I. The density of the deep defect states increases moderately. In order to have for the alloys too a reference level, we define the top of the valence band as the extrapolation to zero of the linear part of the edge as done before. It should be kept in mind, however, that the exact meaning of this level in relation to the valence band becomes less clear with increasing carbon content, as can be appreciated upon inspection of Fig. 1. The values obtained for E_v are reported in Table I. Also reported are the optical gaps as measured on samples grown by employing deposition parameters similar to ours.[8] We see that the increase of the energy separation between E_F and E_v roughly follows the opening of a gap.

From the yield spectra as a function of the photon energy we have also determined the work function ϕ and the photothreshold χ. The values are reported in Table I. It is interesting to note that the photothreshold remains constant upon alloying and that, consequently, the introduction of carbon in the network and the concomitant opening of the gap bring about a reduction of the electron affinity.

IV. HETEROJUNCTIONS

The CFS-YS spectra of the c-Si/a-Si$_{1-x}$C$_x$:H heterojunctions are shown in Fig. 2. The overlayer thicknesses are reported in Table II. Two valence-band edges can clearly be seen on the linear-scale graphs, the edge closer to the Fermi level corresponding to emission from the crystalline substrate and that at higher energies corresponding to emission from the overlayer valence band. These identifications are supported by the following arguments. First of all, as will be discussed in detail later on, the c-Si $2p$ core level in the heterojunction was measured and the known energy separation from the c-Si valence-band top was used to check the energy position of the top itself on the yield spectra. A second consistency check is represented by the fact that the overlayer photothreshold resulting from the identification of the second edge agrees with that of bulk a-Si$_{1-x}$C$_x$:H alloys. 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 at the interface. Two analysis procedures were adopted in order to extract the offset value ΔE_v from the data. In the first procedure the substrate and overlayer edges were fitted with a linear function, as shown in Fig. 2 on the linear graphs. The values obtained for the offsets are reported in column (1) ΔE_v of Table II.

The second analysis procedure can be outlined with the help of the logarithmic graphs of Fig. 2. In this method the heterojunction spectrum was fitted with a linear combination of the experimental c-Si and a-Si$_{1-x}$C$_x$:H spectra obtained from thick samples, 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. The fits agree very well with the experimental data in the region of the two valence-band edges so that the band offsets can be easily extracted. These values, reported in column (2) ΔE_v of Table II, are in very good agreement with those of the previous analysis. It is interesting to note that in some cases, as in the $x=0.25$ and $x=0.35$ samples of Fig. 2, a discrepancy between fit and data was found in the defect-state region, the defect density in the heterojunction overlayer being usually smaller than that measured in the corresponding thick amorphous layer. It seems, therefore, that the growth on a clean and ordered substrate results in a less defective initial layer.

The valence-band lineups were also determined by the conventional procedure which combines UPS and XPS measurements to infer the offset value. The UPS spectra were used to determine the energy position of the valence-band top of the a-Si$_{1-x}$C$_x$:H overlayers relative to the Fermi level. This was possible because our heterojunctions had a rather thick overlayer compared with the escape depth of the UPS photoelectrons, and, therefore, the $h\nu = 21.2$ eV photoemission spectra measured the overlayer valence band only, as can be seen in Fig. 3, where the heterojunction spectrum is compared with that of the corresponding thick alloy sample. Then, the energy position of the c-Si substrate valence-band top was determined by adding to the Si $2p_{3/2}$ core level energy the value $\Delta E_{c,v}$ of the energy separation

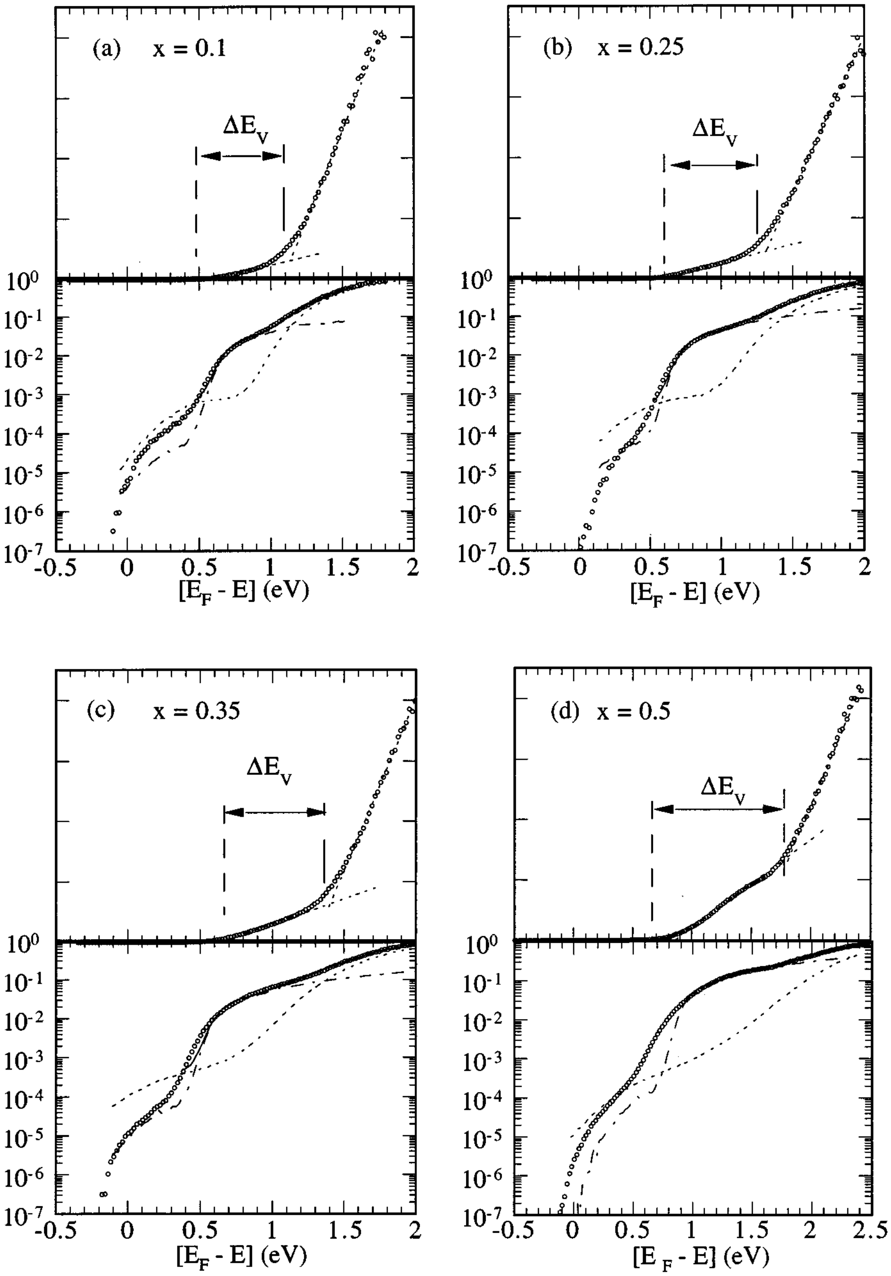

FIG. 2. (Upper panels) CFS-YS spectra of the c-Si/a-Si$_{1-x}$C$_x$:H heterojunctions, plotted on a linear scale, showing the double edge structures. The dashed lines are the linear fit to the substrate and the overlayer valence-band edges. ΔE_v is the valence-band discontinuity. (Lower panels) The same spectra displayed on a logarithmic scale. Dash-dotted and dashed lines are the experimental spectra of c-Si (100) and thick alloys, respectively, scaled according to the procedure described in the text. The continuous lines are their sum.

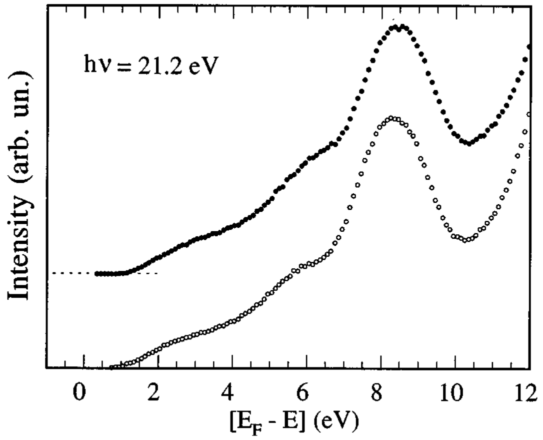

FIG. 3. UPS spectra of a heterojunction (empty circles) and of the corresponding thick alloy film ($x=0.25$) (filled circles).

between the core level and the valence-band top, as measured on a clean c-Si(100) surface. $\Delta E_{c,v}$ was found to be 98.66 eV. The value for the discontinuities obtained with this procedure are reported in column (3) ΔE_v of Table II. The agreement with the other determinations is satisfactory. It should be kept in mind, however, that this kind of determination of the band discontinuity, being an *indirect* technique, is intrinsically less accurate than the *direct* technique we have employed above.[4]

V. DISCUSSION

We have found that the valence-band discontinuity ΔE_v increases monotonically from the value 0.44 eV for the pure hydrogenated amorphous silicon overlayer to 1.00 eV for the $x=0.5$ case. Making use of the data reported in Table I for the band gaps, the diagram in Fig. 4 can be plotted. We see

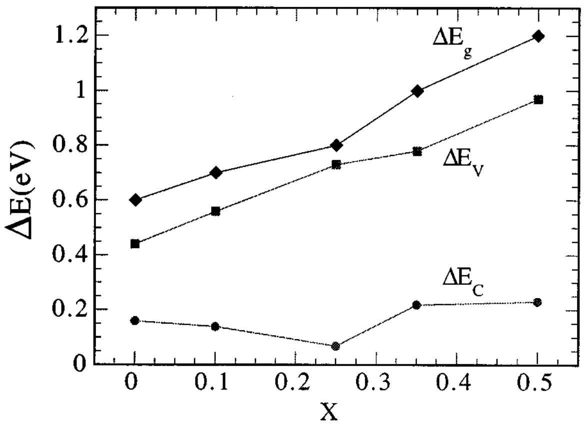

FIG. 4. Conduction ΔE_c and valence ΔE_v band discontinuities as a function of carbon content. ΔE_g is the increase of the optical gap over that of *c*-Si.

that the band-gap difference tends to distribute itself more on the valence-band side than on the conduction side. On the average we have $\Delta E_v / \Delta E_g \cong 0.8$ (ΔE_g being the increase of the optical gap over that of the *c*-Si), while the conduction-band discontinuity remains essentially constant. We have to point out, however, that the valence-band edge as extracted from the photoelectric yield spectra could not coincide with the edges of the optical gap. Nevertheless the information on the trends should be significant and, in particular, the fact that the gap and ΔE_v increase at the same rate with carbon concentration remains true.

Due to its difficulty, the problem of the band offset at the interface between crystalline and amorphous semiconductors was treated theoretically by few authors.[9,10] In particular, to our knowledge, no calculations exist for the *c*-Si/*a*-$\mathrm{Si}_{1-x}\mathrm{C}_x$:H system. Therefore, we firstly consider the existing estimations for the heterojunction of *c*-Si with crystalline silicon carbide and then we analyze the possible modifications due to disorder and hydrogen.

The *c*-Si/*c*-SiC heterojunction is a rather interesting one as a test of the existing two general classes of models developed for the understanding of the band lineup, i.e., *linear* models, where the band offset is given as the difference between two bulk energy levels referred to a common reference level, and *interface dipole* models, where charge transfer, polarization, and screening at the interface is explicity considered.[11–13] Since there is a large difference in electronegativity between *c*-Si and *c*-SiC the predictions for the offset in the two schemes differ drastically and are beyond the experimental uncertainty. *Linear* model theories predict a very large value for the offset: $\Delta E_v = 2.65$ eV was evaluated by Robertson[9] by using the tight-binding approach introduced by Harrison,[14] which uses the atomic energy levels for establishing the band lineup. Since the gap of SiC is 2.35 eV, this estimate places the SiC conduction-band minimum below the crystalline silicon valence-band top.

Taking into account the interface dipoles, as suggested by the second class of models, reduces drastically the predicted offset. A value of $\Delta E_v = 0.85$ eV for the *c*-Si/*c*-SiC heterojunction was estimated by Robertson[9] in the *screened* (or pinned) limit by using Tersoff's[11] model.

Band lineups mostly depend on the chemical species and bonding of the semiconductors so theoretical estimates for the crystalline junctions should be valid to a large extent for the amorphous counterparts also. However, corrections due to the different kinds of disorder and the presence of hydrogen need to be discussed. As for disorder, we have to take into account the effect of the topological disorder and to consider the possibility that compositional disorder also could be present in the amorphous overlayers.

An order-of-magnitude estimate of the effect of topological disorder on the valence-band offset can be obtained from the analysis of the *c*-Si/*a*-Si interface that was investigated experimentally[15] and theoretically.[10] Experimentally it was found that the valence-band top of *a*-Si is 0.1 eV higher in energy than the valence top of *c*-Si. This alignment was interpreted as the consequence of the spreading of the valence band due to topological disorder that introduces localized states above the demarcation level.[16] A recent theoretical calculation by Van de Walle and Yang[10] finds the same kind of alignment, i.e., that the valence-band top of *a*-Si is higher than that of *c*-Si. However, the offset they evaluate is 0.25 eV. Due to the sensitivity of the lineup to the amount of disorder and the sample density and taking also into account the experimental error (± 0.1 eV) intrinsic to the technique used in Ref. 15, the agreement between experiment and theory should be considered satisfactory. We conclude, therefore, that the effect of topological disorder on the lineup is of the order of a few tenths of eV and is proportional to the extention of the localized states brought about by disorder above the valence-band mobility edge. We notice, furthermore, that in the case of the silicon-carbon overlayer the topological disorder would act to reduce the valence-band discontinuity.

The presence of compositional disorder (i.e., the presence of homonuclear C-C and/or Si-Si bonds beyond the number required to satisfy the stoichiometry) could affect strongly the measured valence-band discontinuity. Indeed, in the case of *a*-Si/*a*-$\mathrm{Si}_{1-x}\mathrm{C}_x$:H heterojunctions it was found that the presence of a large number of Si-Si bonds results in a tail of Si 3*p* states that move the valence-band top to higher energy and give a negligibly small discontinuity.[17] It is important, therefore, to establish the amount of compositional disorder in the present alloys for x close to 0.5. As shown in Ref. 7, compositional disorder should be small in our samples and consequently the top of valence band should result primarily from Si-C bonds.

An estimate of the magnitude of the hydrogen effect can be obtained from the comparison of the offsets in the *c*-Si/*a*-Si and *c*-Si/*a*-Si:H heterojunctions. From the theoretical point of view the *c*-Si/*a*-Si:H heterojunction was investigated by Van de Walle and Yang.[10] They found that the *c*-Si valence-band top is higher in energy than the *a*-Si:H one and that $\Delta E_v = 0.2$ eV for an overlayer containing ~11% of hydrogen. Therefore, the effect of hydrogen is strong, lowering the amorphous band edge relative to that of the crystal by ~0.04 eV for each atomic percent in the system. As shown in Fig. 4, we found experimentally[4] a valence-band discontinuity of 0.44 eV in heterostructures whose amorphous overlayer typically contained 15–20 % of hydrogen . The agreement between experiment and theory on the hydrogen effect is good and we can consider the trend established on a rather firm ground. In conclusion, while the topological disorder tends to decrease the band discontinuity, the presence of hydrogen tends to increase it. As a consequence, the two effects tend to compensate themselves, at least for not too high H content.

From the above analysis we conclude that the present data can be used confidently as a test for the lineup theories and that they strongly support the *interface dipole* models. Indeed, the evaluation of the discontinuity taking into account the chemical trends only gives a very large offset, which is more than a factor of 2 larger than the experimental value. This large discrepancy cannot be accounted for by the presence of the various kinds of disorder in the overlayer nor by the hydrogen effects. Quite to the contrary, an offset value close to the experimental one can be obtained by taking into account polarization effects at the interface and the resulting interface dipoles as done by the *interface dipole* models.

VI. CONCLUSIONS

We have investigated c-Si(100)/a-Si$_{1-x}$C$_x$:H heterojunctions by using photoelectric-yield spectroscopy operated in the constant-final-state mode, a technique characterized by a high dynamical range, a good resolution, and a relatively large escape depth. We were able to determine with good precision the valence-band discontinuity in a direct way, i.e., by locating both valence-band tops on the same spectrum. For comparison sake the lineup was also determined by the conventional procedure which combines UPS and XPS measurements to infer the offset value. The valence-band discontinuity ΔE_v was found to increase monotonically from the value 0.44 eV found in the case of a-Si:H overlayer to $\sim$1.0 eV in the $x=0.5$ case. Finally, it was shown that the effect of interface dipoles needs to be considered in order to account for the measured discontinuities.

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