

Amorphous Si/Ge heterojunctions: Band discontinuities and local order studied by photoemission spectroscopy

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We present a study of the heterojunctions formed when Ge is deposited onto a variety of atomically clean Si-based amorphous substrates. With the use of synchrotron-radiation photoemission spectroscopy we are able to measure the valence-band discontinuities and also probe the local order at the interface. We find that linear theories of band discontinuities are valid to an accuracy of 0.2 eV for these materials.

I. INTRODUCTION

The physics of amorphous and hydrogenated amorphous semiconductors has recently attracted much interest,¹ which is motivated both by fundamental and applicative reasons. On one hand, one can study the effect of loss of long-range order on structural and electronic properties of these materials, while on the other hand applicative interest is warranted by the development of devices (e.g., solar cells) based on hydrogenated amorphous semiconductors.

The study of interfaces involving amorphous semiconductors is still in its infancy.²⁻⁵ Among the issues of interest here is how disorder (and also hydrogenation) affects relevant interface parameters such as valence- and conduction-band discontinuities or the Schottky barrier height; a relevant issue is also that of morphology.⁶ Previous work² has shown, for example, how the lack of valence-band discontinuities at the $a\text{-Si}_x\text{C}_{1-x}:\text{H}/a\text{-Si}:\text{H}$ interface plays an important role in the behavior of high-efficiency solar cells which use such heterostructures.

The most important parameters characterizing a heterojunction are the valence- and conduction-band discontinuities. Much theoretical and experimental effort⁷⁻¹⁴ has been recently dedicated to the problem of band discontinuities, the goal being to acquire predictive capability. If this is achieved it might be possible to design heterojunction devices based on a band-discontinuity theory. However, the theoretical situation is far from clear, and the electron affinity rule (the oldest and possibly most used theory) only recently has been shown experimentally to be wrong.¹⁴

In this paper we present a study of the heterojunction formed when Ge is deposited in ultrahigh vacuum on a number of Si-based substrates prepared under varying conditions. Preliminary results on the $a\text{-Si}:\text{H}/a\text{-Ge}:\text{H}$

heterojunction, in which both components are grown *in situ* by glow discharge (GD), are also reported. We will also compare our results to those obtained on a crystalline Si (*c*-Si) substrate. By measuring band edges and core-level binding energies with photoemission spectroscopy, we are able to determine valence-band discontinuities and by following variations in the width of relevant core levels probe the local atomic order at the interface. Our results are discussed in the light of recent theories⁷⁻¹² and show that the band discontinuity between *a*-Ge and a variety of Si-based substrates is negligible.

II. EXPERIMENT

Photoemission experiments were performed at the synchrotron radiation facility in Frascati, Italy, using two beamlines, one equipped with a Seya-Namioka and the other with a "Grasshopper" monochromator. In both cases experiments were conducted in ultrahigh-vacuum (UHV) conditions (operating pressure 1×10^{-10} Torr) and photoelectrons were analyzed with a PHI double-pass cylindrical-mirror analyzer operating under computer control.

We present results for four different Si-based amorphous substrates which we used in order to assess the effect of disorder, hydrogenation, and preparation technique on the measured valence-band discontinuity ΔE_v .

(a) $a\text{-Si}:\text{H}(\text{GD})$ was grown by rf glow discharge in a capacitive reactor attached to the experimental chamber and subsequently transferred under UHV conditions in the measurement chamber. Atomic cleanliness was checked by Auger spectroscopy. The discharge was done in pure silane (SiH_4) with a pressure of $p = 0.6$ Torr and a flux of $\phi = 10$ sccm (standard cubic centimeters per minute). The rf power was held below 5 W and the substrate was kept at 250°C. These growing condi-

tions typically produce films with a hydrogen content of ~ 10 – 15 at. %.

(b) *a*-Si:H(SP) was produced by glow discharge as described above but was then exposed to air and cleaned in the measurement chamber by Ar sputtering.³

(c) *a*-Si was evaporated directly in the measurement chamber with an electron-gun evaporator;³ the evaporation rate was 1 – 2 Å/min. During evaporation the pressure in the chamber never exceeded 10×10^{-10} Torr and a room-temperature substrate was used.

(d) *a*-Si:H(EV) was also prepared in the experimental chamber with electron-gun evaporation on a room-temperature substrate, but in this case the sample was also bombarded with hydrogen by means of an ion gun during Si evaporation. Hydrogen pressure was 5×10^{-6} Torr and the ion-gun accelerating potential was 200 eV; samples grown in these conditions are amorphous and incorporate hydrogen as detected, for example, in photoemission valence-band spectra.^{15,16}

Germanium was evaporated from a degassed W coil placed in the experimental chamber. Evaporated thicknesses were measured with a quartz thickness monitor; the evaporations were done at pressures lower than 1×10^{-9} Torr and at a rate of 1 – 2 Å/min. Ge deposited on an amorphous substrate in this manner is known to be amorphous (see also Ref. 17). We also report preliminary results on the *a*-Si:H(GD)/*a*-Ge:H(GD) interface. This heterostructure was grown by sequential depositions of *a*-Ge:H on *a*-Si:H(GD); the *a*-Ge:H overlayers were grown by rf glow discharge of germane (GeH_4) in the same reactor used for the *a*-Si:H substrate and in similar conditions.

Valence-band discontinuities ΔE_v can be determined in a photoemission experiment by following the energy position of the valence-band maximum E_v . If ΔE_v is large it can be measured directly on a valence-band energy distribution curve (EDC); if, on the other hand, ΔE_v is small, it is necessary to account for possible band bending changes by following the energy position of substrate and overlayer core levels. While in principle this procedure can be complicated by core-level line-shape changes due to interface chemical shifts, the alloying between Si and Ge produces no shift in the position of Ge 3*d* or Si 2*p* core levels, only a line broadening; this fact has been experimentally confirmed both in amorphous Si-Ge alloys (*a*-Si_{*x*}Ge_{*1-x*}) and in hydrogenated amorphous alloys¹⁸ (*a*-Si_{*x*}Ge_{*1-x*}:H) and is also expected on the basis of the small electronegativity difference between Si and Ge.⁸ We conclude that the position of the Si 2*p* and Ge 3*d* core levels is an accurate measure of band bending changes.

The estimated overall uncertainty in the determination of ΔE_v is ~ 0.1 eV and is mostly due to the determination of the valence-band maximum in the experimental energy distribution curves. This is done by a linear extrapolation to zero of the leading spectral edge, a procedure currently followed in similar experiments on crystalline heterojunctions. In the case of amorphous semiconductors a further source of ambiguity results from the continuum of localized states tailing towards the Fermi level which blur the top of the valence band.

However, by combining the estimate of the density of states and of noise under normal experimental conditions, it can be estimated³ that E_v , as determined above locates the energy where the density of states decreases below $\sim 10^{21}$ cm⁻³ eV⁻¹; such a density of states is thought to correspond¹⁹ to the transition between extended and localized states in amorphous Si and therefore we can argue that E_v , as defined above locates the mobility edge within 0.1–0.2 eV.

III. RESULTS

In Fig. 1 we show the typical evolution of valence band EDC's for *a*-Si:H(GD)/*a*-Ge as a function of Ge coverage. While the details may change, this evolution is typical of all the amorphous Si/Ge heterojunctions we have studied. The spectrum for the clean surface is dominated by the hydrogen-induced peak at 6.5-eV binding energy; emission closer to the Fermi level is due to Si 3*p* valence states. As Ge is evaporated onto the substrate the valence band EDC gradually changes to that typical of *a*-Ge (70 Å of Ge); the main feature in the *a*-Ge spectrum is the broad peak near E_F due to Ge-4*p*

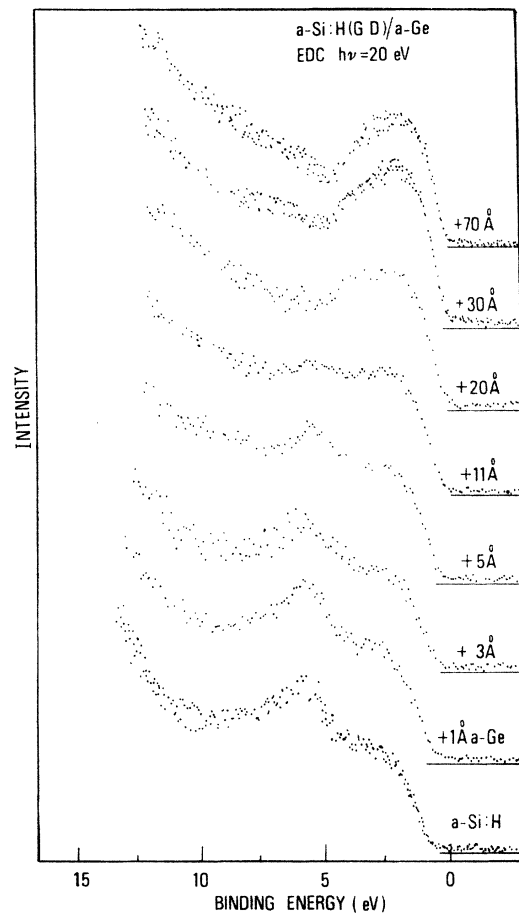


FIG. 1. Evolution of valence-band EDC's for *a*-Si:H(GD)/*a*-Ge. There is a gradual evolution of spectral features from those typical of *a*-Si:H to the spectrum of *a*-Ge (70 Å of Ge).

valence states. Structural disorder is responsible for loss of structure in the spectral features and movement of the center of mass of the $4p$ states toward E_F with respect to the crystalline case. It is tempting to interpret intermediate coverage spectra simply as a linear superposition of the two extremes; this interpretation is valid only if interdiffusion can be ruled out. Analysis of core-level intensities indicates that this is in fact the case:³ the ratio of the integrated intensities of the Ge $3d$ to Si $2p$ EDC's is seen to increase consistently with a layer-by-layer growth mode. A similar conclusion was reached by Abeles *et al.* for $a\text{-SiN}_x\text{:H}/a\text{-Si:H}$ and $a\text{-Si:H}/a\text{-SiO}_x$ interfaces.⁴ As can be seen in Fig. 1 (and in Fig. 2), E_v , as defined above, slowly moves towards lower binding energies as Ge is evaporated.

In order to judge how much of the movement of E_v is due to a real band discontinuity and how much is due to band bending induced by Ge adsorption, we have recorded EDC's from the Ge- $3d$ and Si- $2p$ core levels.

As an example, in Figs. 2 and 3 we show the energy position of E_v , of the Ge $3d_{5/2}$ and, for Fig. 3, also of the Si $2p_{3/2}$ core levels as a function of Ge thickness for Ge evaporated onto $a\text{-Si:H(GD)}$ and $a\text{-Si:H(EV)}$. Similar data for the other two substrates have been presented in Ref. 3. The positions of the spin-orbit components of the core levels were obtained from a fitting procedure as described below. For the clean surface of $a\text{-Si:H(GD)}$, the Fermi level E_F is initially at midgap, as expected for a hydrogenated amorphous material and in agreement with previous results;¹⁶ this feature is not always present for evaporated or sputtered material and can be used to judge the quality of the surface, as discussed below. As Ge is evaporated both E_v and the core-level positions move to lower binding energy by ~ 0.7 eV. We conclude that the valence-band discontinuity for these heterojunctions is 0 within experimental error and that shifts in E_v are totally due to a 0.7-eV band bending

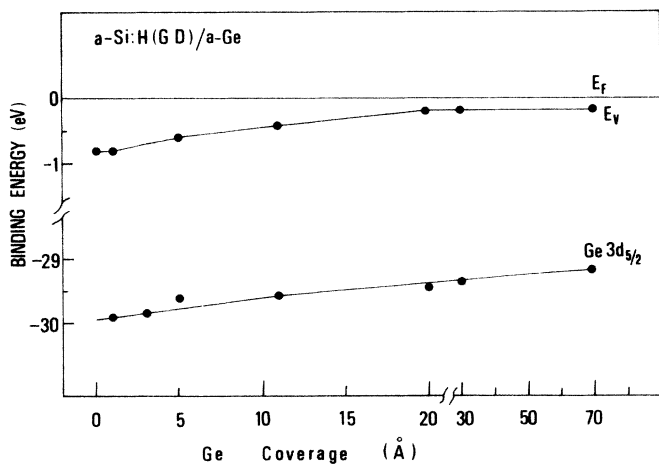


FIG. 2. Position of the valence-band maximum (E_v) and of the Ge $3d_{5/2}$ core level with respect to the Fermi level (E_F), as a function of Ge overlayer coverage for $a\text{-Si:H(GD)}/a\text{-Ge}$. Changes in the position of E_v are compensated exactly by changes in core-level position, so the resulting valence-band discontinuity is zero.

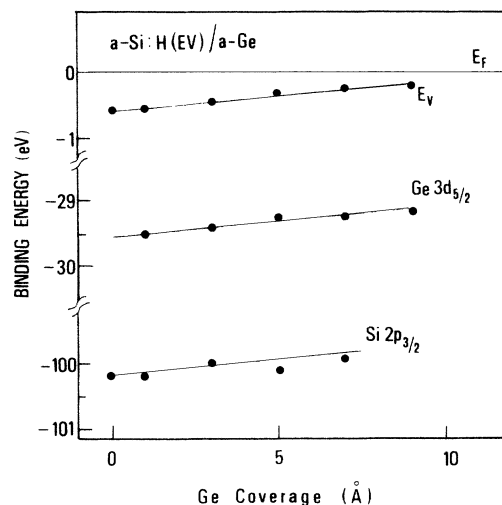


FIG. 3. Same as Fig. 2, but for $a\text{-Si:H(EV)}/a\text{-Ge}$; the position of the Si $2p_{3/2}$ is also reported.

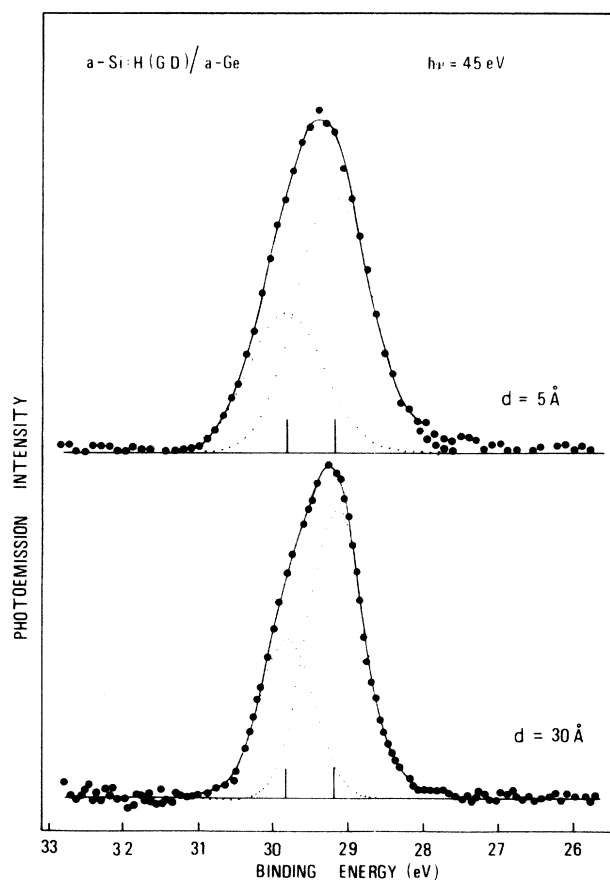


FIG. 4. Example of core-level EDC's from Ge $3d$ core levels and fits to the data. The EDC's are shown after subtraction of a quadratic background and the two spin-orbit split components are shown. As the Ge overlayer thickness d is increased from 5 to 30 Å, the full width at half maximum of each component changes from 1.21 to 0.83 eV. Binding energies refer to the valence-band maximum.

TABLE I. Values of optical gaps of substrate and overlayer, valence- and conduction-band discontinuities, valence-band position relative to the Fermi level, and Ge $3d_{5/2}$ core-level variance for different heterojunctions.

Heterojunction	E_g (substrate) (eV)	E_g (overlayer) (eV)	ΔE_v (eV)	ΔE_c^a (eV)	$ E_v - E_F $ (eV)	$\sigma_{d=1}$ (eV)
<i>c</i> -Si/ <i>a</i> -Ge ^b	1.15	0.7	0.17	0.28		
<i>c</i> -Si/ <i>a</i> -Si ^c	1.15	1.26	0.1	0.21		
<i>a</i> -Si/ <i>a</i> -Ge ^d	1.26	0.7	0	0.56	0.2	0.41
<i>a</i> -Si:H(GD)/ <i>a</i> -Ge	1.7	0.7	0	1.0	0.8	0.40
<i>a</i> -Si:H(EV)/ <i>a</i> -Ge	1.7	0.7	0	1.0	0.6	0.43
<i>a</i> -Si:H(SP)/ <i>a</i> -Ge	1.7	0.7	0.2	0.8	0.4	0.49
<i>a</i> -Si:H(GD)/ <i>a</i> -Ge:H(GD)	1.7	0.9	0.05	0.75		

^aInferred from columns 1, 2, and 3.

^bReference 21.

^cReference 20.

^dReference 3.

which occurs within the first ~ 20 Å of Ge deposition.

In Table I we list values for experimental band discontinuities. For the purpose of comparison and discussion we include data for *c*-Si/*a*-Si (Ref. 20), *c*-Si/*a*-Ge (Ref. 21), and preliminary data for *a*-Si:H(GD)/*a*-Ge:H(GD). The apparent contradiction between values of ΔE_v obtained on *a*-Si:H(SP), on one hand, and *a*-Si:H(EV) and *a*-Si:H(GD) on the other hand point to the importance of sample preparation, as will be discussed below.

The width and position of the Ge $3d$ and Si $2p$ core levels have been shown to carry structural information.^{22,23} In order to investigate local ordering at the interface we have therefore performed fits of the Ge $3d$ core levels.

Each Ge $3d$ core level was fit with two Gaussians representing the two spin-orbit-split components with $j=5/2$ and $3/2$. We used a fixed experimental branching ratio $R=0.55$, a fixed spin-orbit splitting of 0.6 eV, and an equal width for the two components;²³ the fitting

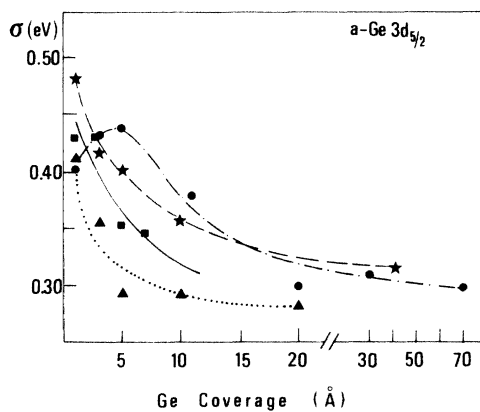


FIG. 5. Gaussian width of Ge $3d_{5/2}$ core level as a function of Ge overlayer thickness for four different interfaces. The values have been corrected for experimental resolution. The symbols are \blacktriangle , *a*-Si/*a*-Ge; \bullet , *a*-Si:H(GD)/*a*-Ge; \star , *a*-Si:H(SP)/*a*-Ge; \blacksquare , *a*-Si:H(EV)/*a*-Ge.

parameters were the position of the doublet and the common variance σ of the Gaussians. In Fig. 4 we show, as an example, typical experimental EDC's and corresponding fits for two overlayer coverages of Ge on *a*-Si:H(GD).

We found that the binding energy of the Ge $3d$ doublet remains constant within experimental error as a function of Ge overlayer thickness d for all the heterostructures we studied. This is not surprising given the small difference in electronegativity between Si and Ge; in fact, Harrison⁸ has calculated that charge transfer at the Si/Ge interface is only $0.001e$. However, we find that there are significant changes in the width of these core levels as a function of d . From the experimental σ_{expt} and the calculated resolution of monochromator and electron analyzer, represented by a Gaussian variance σ_{res} , we calculate $\sigma = (\sigma_{\text{expt}}^2 - \sigma_{\text{res}}^2)^{1/2}$.

The magnitude of σ is due to the core-hole lifetime and, if present, to broadening due to inequivalent emission sites. We assume that Ge- $3d$ core-hole lifetime is independent of overlayer thickness and will discuss variations of σ in terms of variations in the environment of the emitting Ge atoms. In Fig. 5 we plot values of σ as a function of Ge overlayer thickness for three different *a*-Si:H substrates and for the *a*-Si substrate. As can be clearly seen there is a general tendency for σ to decrease with d .

IV. DISCUSSION

The results of our measurement are summed up in Table I. We will now discuss these results in the light of recent theories on valence-band discontinuities, discuss disorder-induced charge fluctuations at amorphous Si/Ge interfaces, and discuss if and how much differences in local order affect the value of ΔE_v .

Much theoretical work has been dedicated recently to the problem of valence-band discontinuities.⁷⁻¹² Most theories are of the "linear" kind, i.e., the band discontinuity between two semiconductors is estimated as the difference between some property of two materials; by analyzing experimental data Katnani and Margariton-

do¹³ found that the lower limit to the accuracy of such theories is 0.15 eV. Notice that such an accuracy limit, while approximately equal to experimental error in photoemission experiments, is insufficient for applications. Some theorists, on the other hand, use an inherently nonlinear approach by performing calculations for one particular interface with given boundary conditions (see, for example, Van de Walle and Martin¹⁰). Unfortunately there exists no theory which takes into account the effect of amorphicity or hydrogen incorporation on the value of ΔE_v . We can therefore compare our results only with theories on crystalline heterojunctions. Before discussing the values we obtain for ΔE_v , we will analyze the changes in width of the Ge 3d core level during interface formation which yield information on local order at the interfaces we studied.

The values of σ plotted in Fig. 5 are the variance of a Gaussian which represents core-level photoemission width corrected for the magnitude of experimental resolution. As already mentioned we do not observe shifts in the binding energy of the Ge 3d levels as a function of overlayer thickness; because of this, consistent with the calculated very small charge transfer at the Si/Ge interface, and to the lack of shift in binding energy of the Ge 3d levels in $a\text{-Ge}_x\text{Si}_{1-x}$ and $a\text{-Ge}_x\text{Si}_{1-x}\cdot\text{H}$,¹⁸ we do not expect that the consistently higher values of σ observed at the interface are due to unresolved satellites originating from Si—Ge bonds. Rather we interpret changes in σ as due to structure-induced local charge fluctuations²⁴ (SILCT) reflecting changes in local order, i.e., bond-length and bond-angle variations. Fluctuations of the net atomic charge of about 0.2 e.u. rms have been found in computer-generated continuous-random-network models of $a\text{-Si}$ by Guttman *et al.*²⁵ Such SILCT have been invoked, for example, to justify the broadening of the Si 2p level in $a\text{-Si}$ compared to $c\text{-Si}$.²² In fact, we expect that Ge atoms initially chemisorbed on the clean $a\text{-Si}$ surface will be in a more structurally disordered environment than those in bulk $a\text{-Ge}$. Significantly, the highest σ value for $d = 1 \text{ \AA}$ is found for sputtered $a\text{-Si:H}$ whose surface is most likely the most disordered due to the presence of sputtering-induced defects. In this interparticle variations of σ between that at $d = 1$ and the subsequent values reflect varying degrees of ordering. For all interfaces, σ tends to decrease and differences in the four curves plotted in Fig. 5 depend on details of interface disorder. The values of σ must be compared to the equivalent value obtained for thick samples of $a\text{-Ge}$ (Ref. 23), $\sigma_a = 0.23 \pm 0.02 \text{ eV}$. We may thus calculate the disorder-induced interface broadening $\sigma_{dis} = (\sigma_{d=1}^2 - \sigma_a^2)^{1/2}$; if we use an average $\sigma_{d=1} = 0.44 \text{ eV}$ for $a\text{-Si:H/a-Ge}$ we obtain $\sigma_{dis} = 0.38 \text{ eV}$. Given a proportionality constant $k = 3.3 \text{ eV/unit charge}$ ²⁶ between chemical shift and unit-charge transfer, we may calculate an average static charge fluctuation at $a\text{-Si:H/a-Ge}$ interfaces, $\Delta q = 0.12 |e|$. Differences in the initial values of $\sigma_{d=1}$ correspond to significant differences in local ordering at the interface, the increasing order being $a\text{-Si:H(SP)}$, $a\text{-Si:H(EV)}$, $a\text{-Si:H(GD)}$. The anomalous behavior of $\sigma(d)$ for $a\text{-Si:H(GD)/Ge}$ for $d \leq 5 \text{ \AA}$ is highly surprising and remains unexplained.

We conclude that significant variations of local order are present at amorphous Si/Ge interfaces; the present data set, together with data for $c\text{-Si/a-Ge}$ and $a\text{-Si/a-Ge}$, allows us to address the issue of band discontinuity and local order for this system.

The experimental value for ΔE_v for the $c\text{-Si/a-Ge}$ heterojunction is 0.17 eV.²¹ By considering the role of interface dipoles, Tersoff⁷ calculated $\Delta E_v = 0.18 \text{ eV}$, while inclusion of such effects in a tight-binding scheme led Harrison and Tersoff⁹ to calculate $\Delta E_v = 0.29 \text{ eV}$; such values, given the experimental and theoretical accuracies, should be considered in good agreement with experiments.

We find that the amorphicity of the substrate causes this discontinuity to disappear at the $a\text{-Si/a-Ge}$ heterojunction. This effect can be due to a smearing of the valence-band maximum due to disorder-induced localized states; in the framework of linear theories, which imply the property of transitivity, it is also compatible with the observed^{3,20} 0.1-eV upward shift of E_v in going from $c\text{-Si}$ to $a\text{-Si}$. The incorporation of hydrogen in the $a\text{-Si}$ substrate, in growth conditions which usually incorporate 10–15 at. % of H, does not affect the value of ΔE_v , except for the case of $a\text{-Si:H(SP)}$, in which case $\Delta E_v = 0.2 \text{ eV}$ was found.

We must compare the values obtained for the $a\text{-Si:H/a-Ge}$ heterojunction with that predicted by using a transitivity rule. In fact it has been found²⁰ that $\Delta E_v = 0$ for $a\text{-Si:H/a-Si}$ and would therefore predict valence-band alignment for $a\text{-Si:H/a-Ge}$.

We have already remarked that the three different $a\text{-Si:H}$ substrates exhibit different degrees of ordering, as shown for example by analysis of the width of Ge 3d core levels at the interface. Another feature which distinguishes the three $a\text{-Si:H}$ substrates is the initial position of E_v with respect to the Fermi level E_F . Significantly, E_F is at midgap only for $a\text{-Si:H(GD)}$, the technological material, as expected for a hydrogenated amorphous semiconductor which has a continuum of filled gap states up to E_F and surface dangling bonds saturated by hydrogen;^{16,27} deviations from this behavior are most probably due to surface defects. In fact, Wagner *et al.*²⁸ have found that sputtered $a\text{-Si:H}$ has a low but non-negligible density of surface states; our data agree with this conclusion but are not compatible with their placement of E_F at midgap for intrinsic sputtered samples. The values for $|E_v - E_F|$ at the surface are 0.6 and 0.4 eV for $a\text{-Si:H(EV)}$ and $a\text{-Si:H(SP)}$, respectively, and we point out that the quantity $|E_v - E_F|$ is seen to correlate with interface disorder as judged from $\sigma_{d=1}$, as discussed above.

By their very nature linear theories do not take into account details of interface morphology and/or ordering and the issue of how much these factors affect the value ΔE_v is therefore relevant (see, for example, Van de Walle and Martin¹⁰). We find that for $a\text{-Si:H/a-Ge}$ these differences, due to very different sample preparation methods and borne out by different values of $|E_v - E_F|$ at the surface and $\sigma_{d=1}$, do not affect the value of ΔE_v more than 0.2 eV. Such an accuracy limit is close to

that expected in general for linear theories.¹³

In conclusion, we have presented a study of the heterojunction formed when Ge is deposited on a number of *a*-Si-based substrates. We find that different preparation conditions lead to different degrees of interface order and that the value of ΔE_v is not affected more than 0.2 eV by these differences in morphology. We conclude that linear theories are valid for these materials within a 0.2-eV accuracy limit.

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