Dipole-Induced Changes of the Band Discontinuities at the SiO_2-Si Interface

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We prove experimentally that the band lineup at the SiO_2-Si interface can be modified by means of an intralayer. Hydrogen and cesium intralayers produce modifications of 0.5 and 0.25 eV in opposite directions. Possible explanations of these dramatic changes are discussed.

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The application of photoemission techniques has produced substantial progress in understanding the nature of important semiconductor interface parameters.[1] The band discontinuities which accommodate the difference between the two forbidden gaps are the most important parameters of semiconductor (insulator)-semiconductor heterojunctions. Since the beginning of the research on heterojunctions, tailoring of these quantities with a controlled process has been the most ambitious goal. The achievement of such a goal would open the way for substantial improvement in the ultimate performance of all kinds of heterojunction devices, and for the development of entirely new devices.[2]

Our present results show that ultrathin Cs or H intralayers at the interface between SiO_2 and Si produce giant changes in the band lineup. Changes of the same magnitude have been independently observed in Si-SiO_2 interfaces by Grunthaner *et al.*[3] These results demonstrate the feasibility of changing band lineups by intervention in the local chemistry of the interface. Furthermore, their analysis helps clarify the nature of the observed intralayer effects for these and other interfaces.

Several previous studies[4–8] explored the effects on the band lineup of interface properties such as the overlayer morphology, the crystallographic orientation, and the growth sequence. Most of these investigations, however, revealed only small or negligible effects. In particular, no band-offset changes were detected from changes in the overlayer morphology in the ZnSe-Ge[4] and GaP-Si[5] heterojunctions, nor from changes in the stoichiometry and structure of the GaAs(100)-Ge interface,[6] in particular by addition of an Al intralayer.

Recently, experiments on Cd-Si, ZnSe-Ge, and SiO_x-Si interfaces suggested that the valence-band discontinuity can be changed by ultrathin intralayers of Al or H.[9,10] These results generated some controversy, since the observed changes were quite close to the experimental uncertainty in measurement of the band lineup. The experiments described in this article revealed changes beyond any conceivable experimental uncertainty, definitely demonstrating that the band lineup between two given materials can be significantly modified by ultrathin intralayers. Furthermore, they suggest that the interface dipole contribution to the band lineup can be as large as 0.5 eV or more. This conclusion is of fundamental relevance to the current controversy among different theoretical models for heterojunction band discontinuities.

At present, most theoretical approaches belong to two general categories: models based on the concept of midgap energy[11,12] and models related to the electron-affinity rule.[13–18] In the first case, the band discontinuities are determined by the alignment of the midgap energies of the two semiconductors. The midgap energy of each semiconductor is the level separating the valencelike and conductionlike interface gap states. This approach implies an important role of the interface dipoles in determining the band lineup.

The controversy among different kinds of band-lineup models is mostly related to the magnitude of the interface dipole contributions and to their nature. These questions also have a practical aspect, since interface dipoles provide, at least in principle, flexibility in modifying the band lineups. Our present work shows that the influence of the interface dipoles on the

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band lineup is relevant for the SiO_2-Si interface, and also that such dipoles can be changed in a controlled way.

Specifically, we found that the band discontinuities are dramatically changed by ultrathin interface intralayers. We used intralayers of two different materials with very different electronegativity, cesium and hydrogen. These materials produced giant changes of the valence-band discontinuity, ΔE_v, in opposite directions. ΔE_v increased by 0.25 eV with Cs, and decreased by 0.5 eV with hydrogen.

The experiments were performed with synchrotron radiation photoemission at the storage ring ADONE of the Frascati National Laboratory. For SiO_2-Si, photoemission is a straightforward probe of the valence-band discontinuity. In fact, for reasonable overlayer thicknesses, the substrate emission is still visible, and both valence-band edges appear in the spectra. The edge positions can be estimated by linear extrapolation. The accuracy of this method, although limited, is sufficient to detect the giant intralayer effects described here. Figure 1 shows the photoemission spectra in the region near the top of the valence bands, for intralayer-free SiO_2-Si and for SiO_2-Si with cesium (nominal thickness -0.5 Å) and hydrogen intralayers.

SiO_2 substrates were obtained by electron-bombardment deposition *in situ* of 50 Å of silicon on cleaved Si(111) in an oxygen atmosphere ($\sim 5\times 10^{-5}$ mbar).

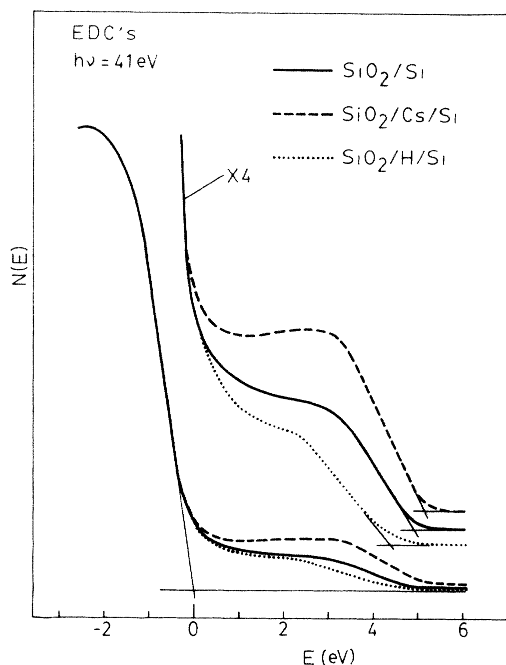

FIG. 1. Photoemission spectra taken in the region of the valence-band edges reveal the valence-band discontinuity at the SiO_2-Si interface. The spectral changes reveal the modifications of the valence-band discontinuities by cesium or hydrogen intralayers.

The cleaved Si substrate was kept at 250 °C and a 200-eV ion gun was used to bombard the system with oxygen ions during the SiO_2 growth. The good quality of the SiO_2 substrates obtained in this way was demonstrated by the valence-band photoemission spectra taken after growth. Subsequently, SiO_2-Si interfaces were obtained by electron-bombardment deposition of Si. Typical thicknesses of 10 Å were found ideal to observe both band edges with a well-developed overlayer valence band.

Cesium intralayers were obtained by *in situ* thermal evaporation. After depositing 0.5 Å of Cs, we observed no change in the line shape of the SiO_2 substrate photoemission spectrum. Hydrogen intralayers were obtained by exposure of the SiO_2 substrates for 2 min to a hydrogen atmosphere ($\sim 5\times 10^{-4}$ mbar) in the presence of an incandescent filament. As in the case of cesium deposition, the line shape of the SiO_2 spectrum was not modified by the exposure to hydrogen.

We also obtained the same hydrogen-induced change revealed by Fig. 1 with two alternative procedures. Both procedures consisted of exposure of the SiO_2-Si interface to hydrogen, after deposition of the Si overlayer. In the first procedure the Si overlayer thickness was kept below 5 Å. In the second procedure the overlayer thickness was of the order of 10 Å, and the exposure to hydrogen was accompanied by hydrogen-ion bombardment with a 100-eV gun. The equivalency of ΔE_v changes obtained by the three above approaches indicates that hydrogen atoms located at the interface are always responsible for them. This is reasonable, since the SiO_2-Si interface has a large density of unsaturated Si bonds which can capture the H atoms.

The intralayer-induced modifications in the band lineup are evident in Fig. 1. Specifically, ΔE_v changed from 4.9 eV for the intralayer-free interface to 5.15 eV for the Cs intralayer and to 4.4 eV for the hydrogen intralayer. In the case of hydrogen, the question may arise of a possible simulation of the above effect by a regression of the silicon overlayer valence band due to hydrogenation. To rule out this possibility, we performed a similar photoemission study of the interface between amorphous silicon and hydrogenated amorphous silicon. We did not observe any measurable discontinuity at this interface, confirming earlier indications that the valence-band edges of *a*-Si and *a*-Si:H are aligned with respect to each other.[16]

The observed intralayer-induced changes in ΔE_v are due to modifications of the interface dipoles, and this demonstrates that such dipoles do play a major role in the band lineup. Several kinds of interface dipole terms can be affected by the intralayers: dipoles due to the formations of different kinds of interface bonds, dipoles due to the presence of dangling bonds, and di-

poles due to diffusion of charged impurities. The interplay between different terms changes from interface to interface—for example, hydrogen intralayers produce opposite changes of ΔE_v in our interfaces and in those of Ref. 3, which were prepared with a completely different procedure. Thus, a complete theoretical treatment of these phenomena requires a complete description of all dipole terms.

Such description is a formidable theoretical task. We did, however, attempt to model the intralayer effects on one class of dipoles, i.e., those due to charge transfer upon formation of interface bonds. The amorphous character of our SiO_2-Si interface makes it impossible to use electronegativity approaches applicable to crystalline interfaces.[17] The approach we used bypasses this difficulty.

The model simulates the SiO_2-Si interface with two planes of spheres with densities equal to the surface density of crystalline Si, 1.36×10^{19} atoms/m^2, and to the average surface density of SiO_2, $\sim8.4\times10^{18}$ molecules/m^2. The distance between the two planes is taken equal to the sum of the covalent radius of Si, $R_{Si}\sim1.1$ Å, and an "equivalent radius" of the SiO_2 molecule, derived from the average SiO_2 bulk density, $R_{SiO_2}\sim(2.4\times10^{-2})^{-1/3}/2\sim1.7$ Å.

The electronegativity difference between the two species causes a charge transfer across the interface, and therefore an interface dipole. Also, the different surface densities of the Si and SiO_2 planes leaves unsaturated Si bonds at the interface. These unsaturated bonds provide natural bonding sites for the intralayer atoms. From the surface densities of Si and SiO_2, we estimate the density of Si dangling bonds to be of the order of 5×10^{18} m^{-2}.

The charge transfer can be estimated by the Sanderson criterion,[19–21] i.e., equal electronegativity value is reached when two or more species of different initial electronegativity react to form a stable chemical compound. For a molecule, this electronegativity, S_m, is given by

$$S_m=\left(\prod_{i=1}^{N}S_i\right)^{1/n}, \tag{1}$$

where S_i is the electronegativity of the ith among the N atoms forming the molecule. The charge transfer (in electronic charges) affecting the ith atom is given by

$$\rho_i=(S_m-S_i)/\Delta S_i, \tag{2}$$

where $\Delta S_i=2.08S_i^{1/2}$ is a normalization factor. The values of S_i and of ΔS_i are tabulated in Ref. 18, and in Table I we show those relevant to this work.

In the first approximation, Eq. (2) can be used to calculate the charge transfer between adjacent Si and SiO_2 spheres in the two planes of atoms at the interface, neglecting the two bulks beyond it. This gives a charge transfer of $\rho_0=0.18$ electrons. A more realistic picture is obtained by inclusion of the charge transfers affecting the spheres in the planes beyond those at the interface. We accomplish this by modeling the bulk beyond each of the two interface planes with a series of equally spaced planes of spheres. The magnitude of the charge transfer for spheres in the nth plane from the interface is assumed to decrease exponentially with n:

TABLE I. Parameters used for the Sanderson electronegativity model (from Ref. 18).

Species	S (eV)	ΔS (eV)
H	3.55	3.92
O	5.21	4.75
Si	2.84	3.51
Cs	0.28	1.1
SiO_2	4.25	4.29

$$\rho_n=A\exp(\alpha n). \tag{3}$$

The constants A and α (which is negative) are determined by the following conditions: (1) The charge transfer for $n=1$ is obtained from Sanderson's rule. For the silicon side, this corresponds to Sanderson's estimate for the central atom in a hypothetic Si-Si-SiO_2 molecule. Equations (1) and (2) give $\rho_1=0.12$ electrons. (2) The total charge transfer across the interface is equal in magnitude to that calculated for two isolated planes, ρ_0. These conditions give $\alpha=\ln(\rho_1/A)$ and $A=r_1\rho_0/(\rho_0-\rho_1)$.

The estimated ρ_n's, combined with the average surface density of SiO_2, give the surface charge density for each plane of spheres. The corresponding dipole voltage drop is calculated with use of the appropriate interplanar distances, derived from the radii of the spheres, and the average of the Si and SiO_2 dielectric constants. The resulting total dipole voltage drop is 2.8 eV.

Let us now consider the effect of a hydrogen intralayer. We assume that the hydrogen atoms saturate the dangling silicon bonds at the interface, i.e., that their density is of the order of 5×10^{18} m^{-2}. This results in an additional interface dipole, due to transfer of charge from silicon to hydrogen. Such change, δV_H, can be estimated with a procedure similar to that used for the Si-SiO_2 interface dipole. The distance between the hydrogen and silicon planes is taken equal to the sum of the covalent radii of silicon and hydrogen, $1.1+0.32=1.42$ Å, and the dielectric constant is taken equal to that of amorphous Si, ~10. The result is $\delta V_H\simeq0.3$ eV. This corresponds to a *decrease* of ΔE_v of the same magnitude.

A similar approach can be used to estimate the effects of the Cs intralayer. The relevant differences

between this case and hydrogen are that the density of intralayer atoms is given by the equivalent thickness of the intralayer, and that the charge transfer is from Cs to Si. We estimate an additional dipole which reduces the total interface dipole by $\delta V_{Cs} \simeq 0.2$ V, thereby increasing ΔE_v.

The above model, although very simple, gives surprisingly good results. We emphasize, however, that the model has severe limitations and is not intended to provide a detailed description of the interface structure. In particular, it takes into account only one class of interface dipole terms, and treats the charge transfers in a very approximate way. The differences between our results and those of Ref. 3 suggest that a more advanced description should take into account the presence of different interface oxides and perhaps microdiffusion processes. Furthermore, charges and defects at the Si-SiO_2 interface can be introduced by threefold coordinated Si atoms, strained Si—Si bonds, and valence-alternation pairs.[22,23] Impurities such as hydrogen and alkali metals interact with these factors. For example, Ngai and White[22] discussed the possible breakage of "weak" Si—O bonds by Na atoms, directly relevant to our Cs-intralayer results.

Clearly, our model does not account for all these potential contributions to the interface charges and dipoles. A realistic treatment requires additional information on the nature of the interface defects, which can be obtained with a coordinated use of photoemission and other transport and optical probes.[24] Our model, however, does show that at least one kind of possible interface-dipole changes produces effects of the same magnitude as those we observe. Thus, our conclusion, that the modulation of ΔE_v is due to changes in the interface dipoles, is reasonable.

Our results are very encouraging about the possibility of modulating the heterojunction band discontinuities by means of controlled interface doping. Together with the recent achievements of Capasso *et al.*,[25] these findings could deeply affect the technology of heterojunction devices. In particular, the current methods of producing interfaces between SiO_2 and hydrogenated amorphous silicon are likely to give discontinuities which are strongly affected by the mechanism we discovered.

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