Structure and electrodynamics at a crystalline oxide-semiconductor heterojunction: dipole charges and the "Coulomb Buffer" in the Si(001):SrSi$_2$:SrO interface

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Using a combination of theoretical and experimental techniques, we have shown that the barrier height for electron exchange at a dielectric/semiconductor interface is set by dipole formation in a distinct interface phase that acts as a "Coulomb Buffer". This Coulomb buffer is tunable, offsets the relative electrostatic potential on either side of the interface, and functionalizes the barrier height concept itself.

Key words: crystalline oxides, silicon, heteroepitaxy, interface structure

1. INTRODUCTION

As the real feature size of metal-oxide semiconductor systems approaches the nanoscale (dimensions<100 nm), the oxide-equivalent thickness for gate dielectrics should reach ~2 nm and at this size, SiO$_2$ direct tunneling becomes an important off-state leakage mechanism that increases exponentially with decreasing thickness. A considerable amount of resources are being spent on amorphous oxides in an attempt to extend the SiO$_2$/Si concept at such small scale. Although the SiO$_2$/Si concept is an attractive approach, steric hindrance and the statistical nature of defect formation with directional bonding are intrinsic to the amorphous/crystalline interface [1,2] leading to discontinuity in the dielectric displacement. This situation can be completely avoided with a crystalline oxide/semiconductor (COS) interface that, by virtue of the high dielectric constant in the oxide, could fundamentally change the scaling laws for silicon based transistor technology.

Despite the great scientific and technological interest in COS materials, there are still a number of fundamental questions regarding the physics and behavior of these systems. Of crucial importance is the lack of understanding of the interplay between interface geometry, electronic structure, functionality, and performance. The key issue to be addressed is the accurate determination of the electronic structure of the heterojunction and its connection with the interface geometry. What makes this both a challenging and scientifically interesting problem is that the COS interface is a complex heterostructure that contains an intermediate layer that acts as a bridge between the semiconductor and alkali-earth oxide leading to a nearly perfect commensurate structure.

Mckee et al. [3,4] have demonstrated that a high dielectric constant alkaline earth oxide can be grown in perfect registry with silicon

through a layer sequencing technique that allows for the systematic manipulation of the interface band structure and interface charge. A perfectly commensurate COS interface allows for the direct manipulation of dielectric displacement and inversion charge at the dielectric/semiconductor interface. This concept has unprecedented implications for new physics and device functionality that cannot be considered for SiO_2 on silicon. COS offers a new physical platform for growing a variety of thin film and nanostructured oxide materials including ferroelectric, piezoelectric, and quantum dots.

The characterization of COS materials was performed by McKee, et al. [3] using reflection high-energy electron diffraction, X-ray photoelectron spectroscopy, and Z-contrast imaging. At 1/4 of a monolayer (ML) coverage they found that a highly commensurate c(4x2) structure was formed and that this structure is not an adsorbed structure but is rather a c(4x2) silicide in which the alkaline earth metal has replaced or displaced silicon atoms in the top surface.

Unlike the incommensurate orthorhombic silicide that forms if the surface exposure is continued past 1 ML, this silicide structure is commensurate and thermodynamically stable and remains at the interface. In addition, from thermodynamic data, the phase equilibra for a three component, alkali-earth metal-Si-O system are known to form silicides and, based on the configuration of the stable tie lines between the three components, they are metal oxide dominant as well.[5] The particular interface structure is clearly the key to understanding the physics and device functionality of these systems.

Experimentally, the determination of the interface geometry is done through HREED experiments that provide information on the periodicity of the system; XPS, that provides electronic information but no direct structural information and Z-contrast imaging data, that provide atomic scale resolution within a small region of the sample. Using these techniques in combination with first principles calculations has enabled us to clarify the fundamental interplay between structure and function in this particular heterojunctions, with particular emphasis on the possibility of tuning the electronic properties of the system

through manipulation of the interface geometry.[6]

2. METHODS

We have performed first principles self-consistent total energy calculations within standard Density Functional Theory (DFT) in the Local Density Approximation (LDA) [7]
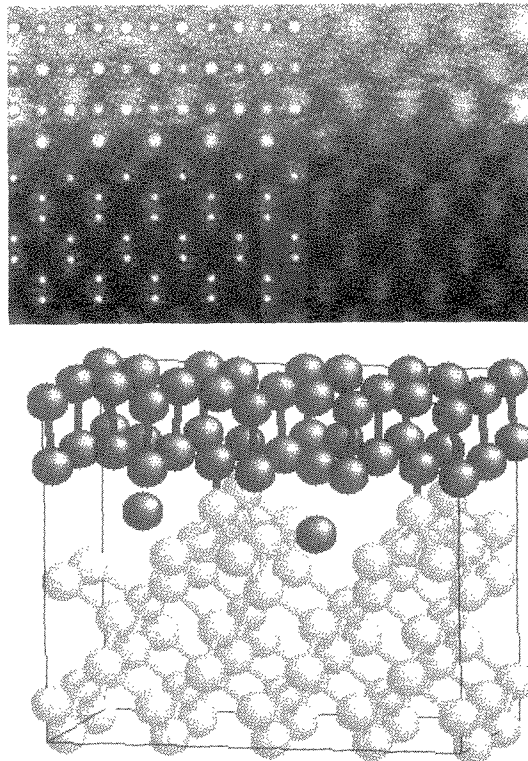

Figure 1. Upper panel. Z-contrast image of the Si:SrSi₂:SrO interface. On the left side the position of the individual atoms has been highlighted. Lower panel. Theoretical equilibrium geometry of the interface, as obtained in our first principle calculations. Brown atoms: Si, red: O, pink: Sr.

using the Perdew-Zunger parameterization of the Ceperley-Alder form of the exchange-correlation energy.[8] Nonlocal, norm-conserving ultrasoft pseudopotentials based on the Vanderbilt scheme [9] have been employed and we have explicitly included as valence states the semicore Sr *4s4p* states. A single k-point in the irreducible wedge of the surface Brillouin zone and a 30 Ry cut-off energy are found to be sufficient for accurately describing the energetics of surface reconstruction and interface formation. The initial stage of interface formation between Si and SrO have been simulated using large supercells containing up to 118 atoms in a

c(2x4) geometry and a wide vacuum region. The different configurations are built on a Si slab with one surface terminated by H atoms and up to 8 bulk atomic layers. Finally, our geometry assumes the theoretical in-plane lattice parameter of the Si substrate lattice, 5.398 Å.

Experimentally, the system has been characterized using X-ray photoelectron spectroscopy (XPS) data,[4] HREED and Z-contrast imaging. The XPS data are developed in a sequenced fashion, starting with clean, reconstructed silicon, followed by growth interruptions and characterization at monolayer additions up to the 6 monolayer, 16.3Å BaSrO film; the X-ray excitation of the underlying core level of silicon is continually observed as reference. At this total thickness, the valence band spectra from the oxide overlayer is fully developed as the O,2-p state (panel A, Figure 1). The valence band edge is obtained from the linear fit and extrapolation to be 1.91 eV below the Fermi level of the system.[4] The band diagram is then deduced as illustrated (panel B, Figure 1); band bending is measured, and the bulk Fermi level of the system is fixed based on $1 \times 10^{15}/cm^3$, p-type silicon doping.

3. RESULTS

We have calculated the relaxed coordinates and electronic structure of the SrO/Si system by starting from the model deduced from Z-contrast imaging of the interface (Figure 1, upper panel). The relaxed interfacial geometry, reported in Figure 1, lower panel, is characterized by the peculiar arrangements of the Si and Sr atoms in the interface region with a silicide ($SrSi_2$) stochiometry. The Si atoms of the interfacial layer are five-fold coordinated, as they are bonded with the four Si atoms of the underlining Si bulk, and make an additional bonding with the O atom of the first oxide monolayer (in the calculations that follow we have restricted ourselves to SrO). The Si-O bond-length is 1.75 Å, close to the Si-O distance in SiO_2, while the Sr-O distance is 2.46 Å. The Sr ions in the silicide monolayer sit in the troughs between the Si-O bonds, and prefer an alternate rather than parallel geometry. However, the energy difference between the two is extremely small

(0.06 eV/Sr atom), so that a combination of the two geometries is to be expected in actual samples. The interface is semiconducting, with an interface state associated to the Si-O bond.[5] Our analysis of the electronic properties of the interface shows that 3 ML of oxide are sufficient to ensure a bulk-like electronic behavior.

The distinct structural arrangement of Sr and Si in this interface phase is not intuitive. However, what is obvious from examining the interface structure (Figure 1), is that it supports the symmetry and coordination of the bulk (001)SrO plane, thus minimizing its electrostatic energy. Moreover, it facilitates the heteroepitaxy to homoepitaxy transition for growth of subsequent oxide overlayers in the flat fcc structure as observed by both RHEED and XPS in the growth sequence.[10] The interface phase has both a density (1/2 that of (001) Si) and site occupation of silicon atoms that promotes the charge transfer. The Si-O bonds between the silicon atoms in the interface phase and the oxygen in the SrO overlayer ensure the heteroepitaxial structure of the oxide overlayer with minimal interfacial strain. The Sr ion in the $SrSi_2$ interface phase is atop a surface "valley" site of the underlying bulk terminated silicon and acts as an electrostatic (Coulomb) buffer that guarantees the correctness of the interface stochiometry.

Besides having an important structural role, the interface phase is the region where the electrons will redistribute to equilibrate the electrical charge at the junction (in other words, this is the region where the *Schottky barrier* will be established). On the other hand, in this same region, the alkali metal in the
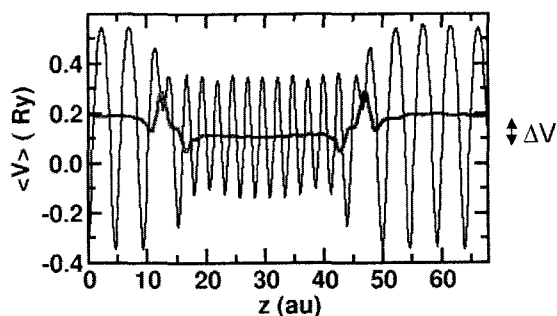
Figure 2. Profile of the electrostatic potential and its planar average for a Si:SrSi₂:SrO interface. The region for 15<z<45 au corresponds to bulk Si.

interface phase and the oxygen in the oxide will establish strong ionic bonds that will contribute to the chemical stability of the interface and to the electronic properties of the system. In fact, the primary consequence of the equilibrium between these two factors, electronic redistribution and ionic bonding, is the very functionalization of the concept of electronic potential barrier at the interface, or the possibility to tune the potential profile acting on a single atomic plane. This functionalization happens in what we have named *Coulomb Buffer*, that for the particular case of the Si/SrO interface can be identified with the silicide region at the interface, but, in reality, is a general concept of broad implications that can be adapted to a wide variety of structures. In the following we will discuss a particular application of the above concept, namely the role of the Coulomb Buffer in fixing and tuning the valence band offset of the heterostructure.

In principle, the valence band offset between two materials is simply understood; primarily there are two distinct contributions: the first, ΔE_v, is a band structure part, purely the bulk termination, $E_{v,ox} - E_{v,si}$, and the second, ΔV, contains all of the interface physics. ΔE_v is the difference between the energies of the valence band edges when the average electrostatic potentials of the bulk terminated oxide and semiconductor structures are aligned, and ΔV is the difference in the values of the average electrostatic potentials of the two sides of the interface. [11,12] Arguably the valence band energy levels, E_v, are trivially understood for the bulk materials, but the way in which the electrostatic potentials align at the interface is certainly not.

Unlike the classical, continuum view of the junction electrostatics, where the structure of the junction is ignored, a heteroepitaxial, layer-sequenced structure presents an electrostatic potential that contains strong oscillations due to the positions of the atoms. These oscillations (see Figure 2, black curve) must be carefully considered if an accurate picture is to be obtained of how the anisotropy of chemical bonding and charge transfer influence the potential line-up. We follow a

planar averaging method that has been developed earlier [11] for treating such oscillations by defining a planar average of the potential for the atoms in each plane parallel to the interface, indicated by the red curve in Figure 2. This then gives us a one-dimensional (normal to the interface) macroscopic average of these oscillations that rigorously accounts for atomic structure at the junction interface and hence, unequivocally a way of defining the electrostatic potential for the system.

The discontinuity of this one-dimensional potential (the missing part of the barrier height problem) at the junction is then a direct measure of a macroscopic dipole moment that contains the essential physics that we require for our unifying picture of the band offset. We thus define ΔV as the dipole shift of the relative electrostatic potentials:

$$\Delta V = \frac{e^2}{4\pi} \int (\bar{\bar{n}}(z) - n_0)z\,dz,$$

where n_0 is the average electronic density of the two bulks (8 electrons per unit cell in both Si and BaSrO), and $\bar{\bar{n}}(z)$ is the macroscopic average of the electronic density across the interface (11).

It is important to note that, within our pseudopotential approach, the absolute value of the dipole shift, output of our calculation, is not a unique measure of the physical ("mesurable") interfacial dipole.[12] However, its variation with respect to some physical quantity is indeed measurable, and in the particular case we will discuss in the following, amounts to the variation of the valence band offset.

The Coulomb Buffer acts on the electrodynamical properties of the junction

	VBO (eV)	d_{M-O} (Å)
Si/BeSi₂/SrO	-2.44	1.44
Si:MgSi₂:SrO	-2.02	2.11
Si:CaSi₂/SrO	-1.91	2.33
Si:SrSi₂:SrO	-1.91	2.46
Si:BaSi₂:SrO	-1.87	2.57

Table I. Valence band offset for different silicide variants of the Si/SrO junction.

through a series of microscopic dipoles whose distribution can substantially modify the potential profile. These dipoles are localized in the silicide regions, and come from the specific structure of the chemical bonding at the interface. There are "electronic" dipoles, due to the particular electronic charge distribution in the region of the bonding between silicon and oxygen atoms, and "ionic" dipoles, coming from the ionic bonds between the strontium of the silicide and the oxygen of the oxide.

In our study we have demonstrated, that the Coulomb Buffer allows us to modify the electronic potential profile at the junction, through the manipulation of the ionic dipoles localized on the single atomic plane of the interface phase.[5]

In Table I and figure 3 we summarize the results that we have obtained for the valence band offset variation induced by a change in the ionic dipole at the interface. This change has been initially confirmed by a simple *gedanken* experiment. If these interface dipoles do indeed play a role in tuning the electron energy alignment at the interface, an artificial variation of the Sr-O distance in the silicide layer should affect the relative macroscopic dipole potential. The results of this test are summarized in Figure 3, black solid line, where the displacement of the Sr test charge does modify the macroscopic dipole. The generalization of this result to a more physical case is reported in Table I and Figure 3, color symbols, with a compilation of values calculated with variations in interface compositions that take advantage of solubility and solution chemistry in the Group IIA alkaline earth silicides and oxides; the cation size changes, so tuning the relative metal-oxygen distance, but charge does not. The striking result within these numbers is found in the variation of the VBO (SrO as the

constant dielectric) as we move with increasing atomic number down the Group II alkaline earth metal column for the metal in
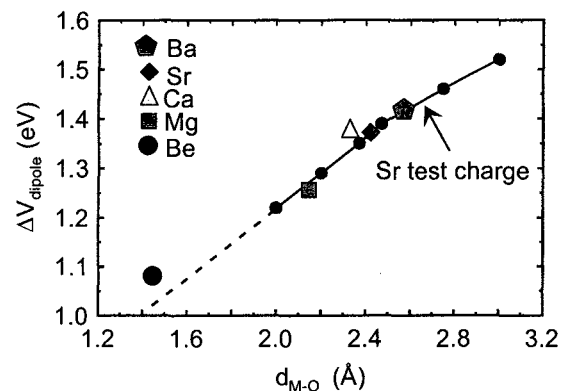

Figure 3. Variation of the macroscopic dipole potential at the interface induced by changing the alkali metal ion in the silicide layer. Although the absolute value of ΔV does not have a true physical meaning, its variation reflects the variation in the valence band offset reported in Table I.

the interface phase (Table I). Our calculations show that this effect correlates with the displacement of the alkaline earth ion in the silicide relative to the oxygen ion site in the overlayer oxide.

Charge transfer and chemical bonding between the silicide and the alkaline earth oxide fix the boundary conditions and the junction electrostatics. The relative electrostatic potentials of the bulk terminations (silicon and the cubic oxide) are thus shifted substantially, and ΔV, as the extra contribution to the junction barrier height, has arisen as a dipole contribution from both ion and electron displacement processes in an interface phase.

These theoretical results correlate well with experimental measurements of valence band offsets, both in the magnitude (exp. VBO = -1.3 eV vs. theo. VBO = -1.46 eV for $SrSi_2$:SrO) and in the variation from Sr to Be at the interface. This last results is best illustrated in Figure 4, where we show the core-level shift of the Ba-4d peak for the silicide variants $SrSi_2$ and $BeSi_2$.
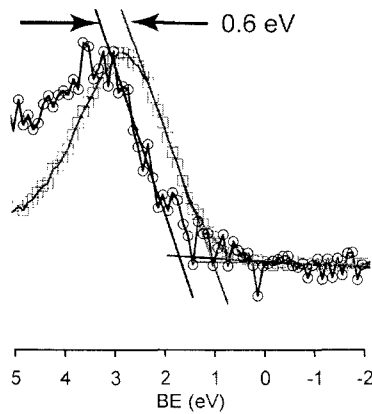
Figure 4. Core-level shift of the Ba-4d peak for the silicide variants: $SrSi_2$ (red) and $BeSi_2$ (black). The dielectric in this case is an alloy of SrBaO.

4. CONCLUSIONS

In this work we have introduced the notion of an interface specific region and shown that this region should be interpreted as a fundamental component of a dielectric junction. This interface phase not only determines the equilibrium geometrical structure of the junction, allowing clean heteroepitaxy of the oxide on Si, but also controls the overall junction electrostatics via what we have called a Coulomb Buffer. This Coulomb Buffer is fundamentally distinct from wave function decay of interface states that comes from the classical bulk termination view of the barrier height problem. The effect of the Coulomb Buffer is to place and displace the interface atoms, uniquely "fixing" the electrostatic boundary conditions for a stable semiconductor/oxide structure. Both theoretical and experimental work are proceeding to further clarify this new effect and its potential as input for designing nanoscale materials systems, but this experiment/theory synergism has already provided the first demonstration of how structure-specific chemical bonding in a sub-monolayer phase can be fundamental to balancing the relative electrostatic potential at dielectric/ semiconductor interfaces.

Finally, this electrodynamic representation provides a unifying concept for understanding and designing barrier height function that relies on the general barrier offset problem in semiconductor physics.

6. REFERENCES

[1] G. Lucowsky, Y. Wu, H. Miimi, V. Misra, and J.C. Phillips, Appl. Phys. Lett. 74, 2005 (1999).

[2] G. Lukowsky and J.C. Phillips, Appl. Sur. Sci. 166, 497 (2000).

[3] R.A. McKee, F.J. Walker and M.F. Chisholm, Phys. Rev. Lett. 81, 3014 (1998).

[4] R.A. McKee, F.J. Walker and M.F. Chisholm, Science, 293, 468 (2001).

[5] I. Barin and O. Knacke, "Thermodynamic Properties of Inorganic Substances", (Springer, Berlin, 1973).

[6] R.A. McKee, F.J. Walkerm M. Buongiorno Nardelli, W.A. Shelton and G.M. Stocks, Science, 300, 1726 (2003).

[7] Calculations in this work have been done using the PWscf package (S. Baroni, A. Dal Corso, S. De Gironcoli and P. Giannozzi, http://www.pwscf.org) and the Vienna Ab initio Simulation Package (VASP).

[8] J. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981); D. Ceperley and B. Alder, Phys. Rev. Lett. 45, 566 (1980).

[9] D. Vanderbilt, Phys. Rev. B, 41, 7892 (1990).

[10] R.T.Tung, Phys. Rev. B **20**, 205310(2001).

[11] A. Baldereschi, S. Baroni and R. Resta, Phys. Rev. Lett. 61, 734(1988).

[12] M. Peressi, S. Baroni, R. Resta and A. Baldereschi, Phys. Rev. B43, 7347(1991).