Stability and electronic properties of silicates in the system SiO$_2$–Pr$_2$O$_3$–Si(001)

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Abstract

Pr_2O_3 is one of the most promising hetero-oxides that are the candidates of choice to replace SiO_2 as the gate dielectric material for sub-0.1 μm CMOS technology. In order to enable process integration, however, hetero-oxides require substantial characterization. In particular, the basic interaction mechanisms at the interface to the silicon substrate are the key issues. A solid knowledge of these mechanisms is required to address reliability arguments. The challenges in material science are to understand the chemical bonding of the hetero-oxides and Si on a microscopic scale. We report on the specific variations in the electronic structure which are evident in the valence band features around resonant excitation at the Pr 4d threshold. We also determine the valance band discontinuities at the Pr_2O_3/Si(001) interface and follow the changes in the surface potentials to develop a band scheme, a prerequisite to understanding the properties of charge transport across that interface.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The topic of hetero-oxides has been a major topic in materials science for about a decade. Some of the recent progress has been addressed and reviewed recently both from a technological [1] and from a more fundamental point of view which arises from surface science studies [2]. The interested reader may consider the references within those two reviews for further details. Consequently, the main properties of the candidates to replace SiO_2 will only be briefly stressed here. This paper is not a review but a compilation of some very recent, previously unpublished results of interface studies. The main contribution is the experiments that investigate the interface properties, an issue which is rarely addressed in recent studies.

Pr_2O_3 is a high-k oxide (DK $\approx$ 30) which is considered to be a novel gate oxide in Si-based field effect devices [3, 4] and is known to grow epitaxially on Si(001) [3] via a silicate interface layer [4]. The electronic structure of Pr_2O_3 is well characterized in theoretical studies [5, 6]. We focus on the valence band photoelectron spectra at the Pr 4d resonance around 120 eV,

which involves transitions from the Pr 4d core levels to the empty conduction band states, and study the changes induced by the silicate formation.

We have already assigned the characteristic features in the electronic structure of Pr_2O_3 and reported its very characteristic features of the Pr_2O_3/Si(001) interface as evident in the emission pattern of the Si 2p and O 1s core levels in an earlier study. We have also used resonant photoemission in the valence band regime to characterize the interface states and describe the formation of a new interface transition identified in the Auger electron emission [4].

This paper focuses on the studies of the silicates in the system SiO_2–Pr_2O_3 on Si(001) surfaces which form upon deposition of praseodymium oxide (Pr_2O_3) using *in situ* preparation of ultrathin (<1 nm) epitaxial oxide layers. In our studies we argue that Pr_2O_3 films with thickness larger than 2 nm show bulk properties while the evident differences at lower thicknesses must occur because of modifications in the electronic structure initiated by the interface. Photoelectron spectroscopies (PES) are used for spectroscopic characterization of the interface elements as well as for non-destructive depth profiling. In resonant photoemission studies photoelectron spectroscopy (PES) is done at photon energies that enable the excitation from a deep core hole to the empty conduction band states. At resonant conditions only these states are selectively enhanced which allows optical coupling of the core hole to the empty conduction band states. Information is to be gained from the shape of the particular resonance and by a comparison of the valence band data at excitation energies off and on resonance. Such studies provide information on the electronic structure and, in particular, on how to separate individual contributions in the valence band and conduction band regime. In addition, we report on the valence band and conduction band discontinuities as well as the formation of an interface dipole moment.

2. Experimental details

An analysis of the Pr_2O_3/Si(001) interface based on its electronic structure is given using synchrotron radiation excited photo-electron spectroscopy (SR-PES) at the undulator beam line U49/2-PGM2 [7, 8]. In addition, He I (21.2 eV), He II (40.8 eV) and XPS measurements using Al Kα radiation (1486.6 eV) have been performed using the same HA125 analyser. The synchrotron radiation facilitates the study of the most prominent core levels of semiconductor surfaces with excellent energy resolution. In this paper SR-PES is used with photons in the photon energy range between 100 and 1200 eV originating at a high brilliance undulator beam line at BESSY to study the Pr 3d, Pr 4d, O 1s, Si 2p core levels at the Pr_2O_3/SiO_2 interface. In addition we have recorded the photo-absorption data using photo-emission electron microscopy (PEEM) and have studied the x-ray absorption spectra (XAS) around the Pr 4d, O 1s and Pr 3d absorption edges, respectively.

Pr_2O_3 films were prepared under conditions for which epitaxial layer growth is reported in earlier studies [3, 9]. The clean Si(001)(2 × 1) reconstructed Si substrate surface was prepared by direct heating briefly to 1250 °C, cooling down quickly to about 900 °C and slowly to 600 °C [9]. During the cleaning procedure, the pressure remained in the 10^{-10} mbar range. Pr_2O_3 films were prepared *in situ* by electron beam evaporation of Pr_6O_{11} from a molybdenum crucible with a deposition rate of about 0.5 nm min^{-1}. During deposition, the Si(001) sample was kept at 600 °C to enable the hetero-epitaxial growth of Pr_2O_3 [3, 9]. The oxygen partial pressure was around 10^{-8} mbar.

3. Resonant photoelectron spectroscopy

In figure 1 we have displayed the valence band spectra taken at energies close to and right at the 4d resonance, which is around 125 eV. We have plotted these spectra for a Pr_2O_3 film
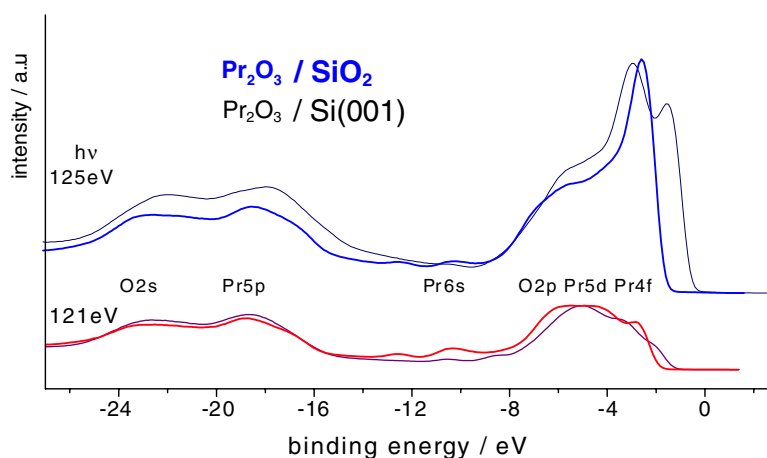
Figure 1. The valence band spectra of Pr_2O_3 in the silicate phase and of pure Pr_2O_3 (bold) taken on ($h\nu = 125$ eV) and off ($h\nu = 121$ eV) the Pr 4d resonance, respectively.

deposited to the native SiO_2 layer (bold curves) to resemble bulk Pr_2O_3 properties. Another sample is characteristic of the silicate phase. It is prepared like an epitaxial oxide layer on Si(001), but with a thickness of about 1 nm (thinner curves). In this comparison the binding energies of the Pr 5p and O 2s levels serve as a reference, while the valence band states show significant variations.

The valence states have a significant contribution from the Pr 5d electrons which shows up in the characteristic behaviour at the Cooper minimum around 240 eV [4]. Here, we focus on the interface properties and notice that there are significant variations occurring for the uppermost valence states close to the valence band maximum (VBM). Obviously, in the interface region the electronic structure is modified and the chemical bonding and valence band occupancy within the topmost states is influenced. The Pr 6s states are shifted upwards while the Pr 5d states move downwards. The Pr 4f electron states can be identified by their enhancement at resonance ($h\nu = 125$ eV). Obviously, the band at -3 eV is a Pr 4f state which also becomes down shifted in the silicate phase. In addition we notice that this emission is split in the interface layer. There a new band appears in the silicate phase at -1.5 eV. It is another Pr 4f state because of its resonant enhancement. At this point, however, it remains open whether this is due to a ground state occupancy or is a consequence of the charge transfer (CT) processes caused by the interaction of the core hole to the Pr 4f levels in the final state [5, 6].

In figure 2 we display XAS spectra recorded at photon energies between 90 and 150 eV. The spectrum of the silicate layer shows an onset at the Si 2p edge near 100 eV. The Pr 4d resonance spectrum starts at 108 eV with a clearly resolved edge. There is some weak fine structure with a characteristic triple peak structure. Next we identify the main Pr 4d resonance which, in the literature, is often assigned as the giant resonance. It is a rather broad resonance which has two peaks at energies around 123 eV and at around 130 eV.

We now compare the silicate phase data to that of bulk Pr_2O_3. The interface data show that the Si 2p edge at around 105 eV, the weak fine structure signals and the first giant resonance at 123 eV are more pronounced. Also, there are shifts towards lower excitation energies at the onset of the Pr 4d edge (1 eV) and in the broad maximum around 130 eV (5 eV). Within the giant resonance there are two final states for the excitation from the Pr 4d levels. These structures are due to unoccupied Pr 4f (123 eV) and Pr 5d (130 eV) states in the empty
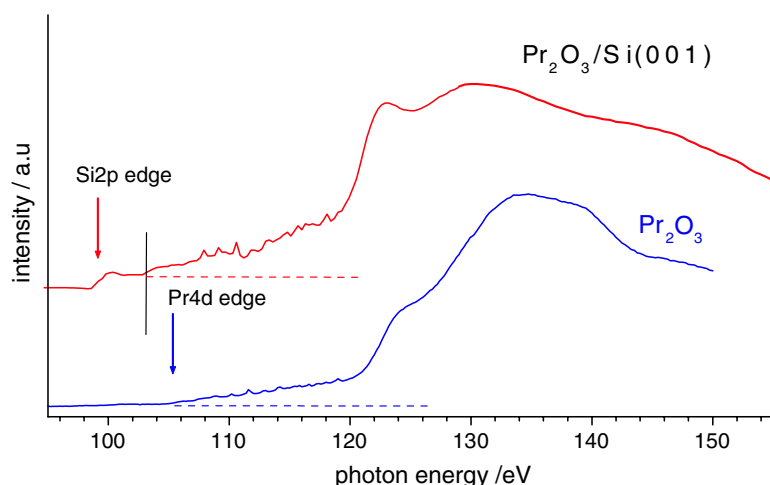
Figure 2. XAS spectra taken at the Pr 4d resonance. The upper curve is that of the silicate phase, the lower curve is the spectrum taken for the pure Pr_2O_3 oxide.

conduction band (CB). This assignment is supported by corresponding constant initial state photoemission experiments in which the first resonance at 123 eV shows a distinct Fano profile, in particular for the Pr 4f initial states [4]. The second resonance at around 130 eV shows no Fano profile and is attributed to the empty covalent bonded Pr 5d, O 2p and Pr 4f states. The intensity gain in the giant resonance at 123 eV indicates a change in the Pr 4f occupancy while the Pr 5d states just exhibit a significant shift and broadening.

The data can be rationalized as in the silicate phase the formation of Si–O–Pr networks causes an increase in the covalent bonding behaviour, i.e. the interaction among the Si 3p, O 2p and Pr 5d/Pr 4f states. The increased covalency changes the b.e. of the contributing states but also enables CT processes in the initial state. An empty Pr 4f level becomes filled by a valence electron leaving a valence hole (L) as well as a more localized Pr 4f ^{2}L state. The higher the covalency the more stable the valence hole will be. This mechanism explains both the new state next to the VBM and the increase of the intensity in the 123 eV resonance. The increase of the intensity in the fine structure close to the Pr 4d edge can also be attributed to the increased covalency. These transitions gain more spectral weight as the selection rules for the individual excitations are less strictly applied.

4. He I and He II data—band matching and dipole formation

We now report on experiments to learn about the band alignment of Pr_2O_3 on Si(001) by taking He I and He II excited photoelectron spectra in the valence band regime.

We start with the bare Si(001) surface and prepare epitaxial layers of Pr_2O_3. We interrupt the film growth after 1 min to record the UPS data. Afterwards the sample is heated to 600 °C again and the film growth is continued. Upon increasing the layer thickness we take the valence band data successively. After the last deposition we measured the thickness of the Pr_2O_3 layer to be around 3 nm. Consequently we have an average increase of the layer thickness of about 0.7 nm/step. The valence band data are compiled in figure 3; the abscissa gives the analyser energy which is the kinetic energy of the emitted photoelectrons without correction for electronic offsets and sample bias. The analyser energy of 46.3 eV corresponds to the
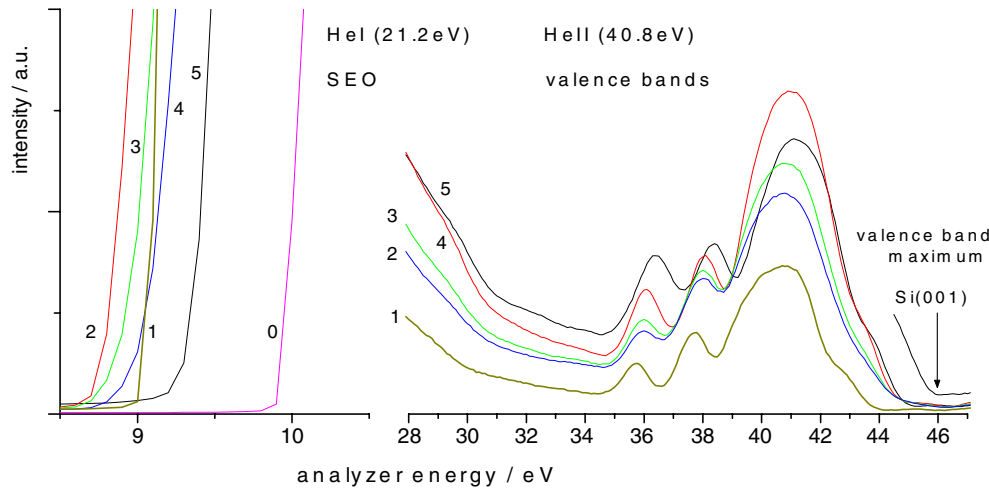
Figure 3. He I and He II data obtained after deposition of Pr$_2$O$_3$ on a Si(001) surface. The left panel shows the thickness dependent changes in the secondary electron onset of the He I spectra. The right panel gives the corresponding He II valence band spectra. As a reference the spectrum around the valence band maximum of the bare Si(001) surface is shown ($\times$10).

Fermi energy of a metallic sample. Consequently, the absolute value of the work function of our bare Si substrate amounts to 4.9 eV. This value is expected for a p-doped Si(001) sample without surface (band bending, surface states, Fermi level pinning, etc).

In figure 3 we show the secondary electron onset of the He I excited spectra (left panel) as well as the valence band features as excited with He II photons (right panel). Step 0 is the unexposed Si(001) surface. The secondary onset indicates that already the first Pr$_2$O$_3$ deposition step causes a shift of about 1.2 eV. Further deposition causes this large change to become reduced until a final value of 0.7 eV is reached. The as determined changes in the SEO and the corresponding position of the VBM are plotted in the diagram shown in figure 2. These data are derived from the series of experiments shown in figure 3 but in addition are confirmed by several independent runs on different substrates.

Such data can be used to determine the total changes in work function which in semiconductors is the sum of changes in the electron affinity X, the band bending potential V_{bb} and the doping potential V_{dop}

$$\Delta\Phi = \Delta\chi + q(\Delta V_{bb} + \Delta V_{dop}), \tag{1}$$

where q is the elementary charge. From the He I spectra the change in $\Delta\chi$ shows up as a shift in the secondary electron onset (SEO) while the changes in the surface potential cause a shift in the position of the valence band maximum (VBM) with respect to the Fermi energy.

From our data we learn that there is an initial dipole moment at the interface which appears only within a layer of around 0.7 nm thickness and amounts to around 1.2 eV. In the same interface region there is a change in the surface potential of the Pr$_2$O$_3$ valence bands which amounts to -2 eV. Both quantities can be derived from our data and in sum reflect the experimentally determined changes in the work function according to equation (1).

Based on the estimation of the conduction band offset and of our thickness dependent valence band data we are able to construct a band scheme of the interface, as depicted in figure 5. Here all values are referred to the Fermi energy; this is an equilibrium constellation. On the left-hand side we have the characteristic data of the Si(001) surface, an electron affinity of 4.08 eV, and the band gap of 1.1 eV with the position of the Fermi energy close to the valence
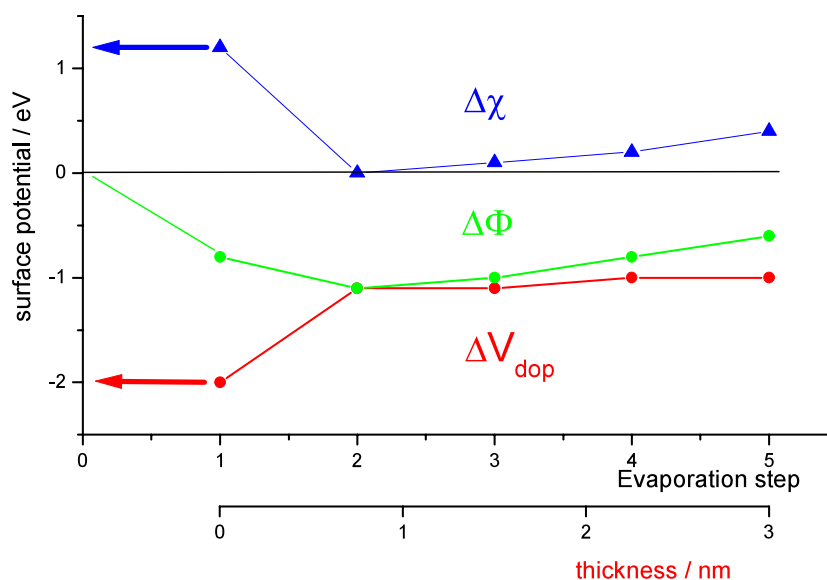
Figure 4. The variations of the electron affinity, the work function and the band bending at the Si(001) surface upon increasing Pr_2O_3 coverage, as derived from the experimental thickness dependent valence band data in figure 1.

band maximum as for a p-type sample. The corresponding data of the Pr_2O_3 are derived from the values obtained in figure 4.

The position of the VBM of Pr_2O_3 is found to appear about 2 eV below that of the bare Si(001) surface. This is the valence band discontinuity which determines the tunnel current of holes. With increasing Pr_2O_3 coverage the position of the VBM rises to reach a value at around 0.7 eV (with respect to the Si VBM) as shown in figure 4. This value is considered to be the position of the VBM of bulk Pr_2O_3. The experimental data indicate that the change in the SEO levels off to reach a value of around 0.6 eV with increasing distance from the interface. This behaviour is in line with the changes in the VBM and reflects the effect of an interface doping within the silicate layer.

At the vacuum level there is a jump of about 1.2 eV. According to equation (1) this is a superposition of the change in the doping potential and the change in the electron affinity levels. Consequently, this value has to be interpreted in terms of a doping potential of about -2 eV which is partially compensated by a change in the electron affinity by 1.2 eV. Steady potentials are reached at a thickness of about 1.5 nm. In order to complete the band scheme we assume the band width of the Pr_2O_3 to be around 5.6 eV [10].

It should be mentioned that band bending in the Si substrate is quite reasonable. However, because of the small separation of E_F and VBM in the p-type material this effect is hardly observable. On the other hand, this should be a more serious problem for n-doped Si wafers.

In the context of our analysis we would like to comment on a recent study of the valence band discontinuity using STM and XPS data of the Pr_2O_3/Si(001) interface [3]. In general the He I, He II determined valence band spectra allow a higher accuracy because of the much better line width of the exciting He I and He II radiation. So our thickness dependent experiment is even more suited to learning about the interfacial region while the XPS data integrate over the total oxide layer thickness. As a consequence the XPS data just determine the difference in the relative energy separation of the valence band (in the present data the values are at elevated
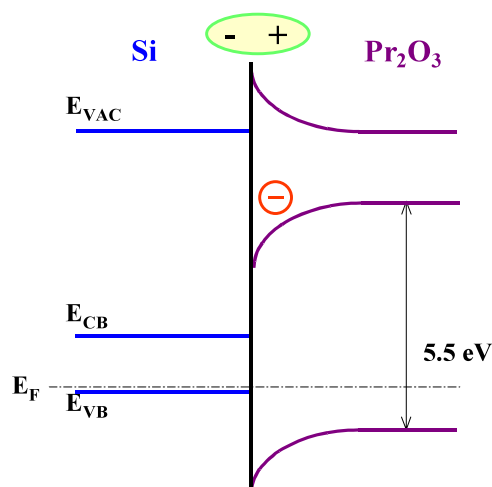
Figure 5. The band scheme of the Si(001)/Pr$_2$O$_3$ interface with the experimental determined discontinuities, interface dipole moment and the band bending in the silicate phase.

thickness). As such, we obtain the same value of about 1 eV, but the accuracy now is ± 0.1 eV and this value does not reflect the discontinuity at the interface as shown in figure 5. To comment on the STM results we would like to ascribe the observed STM signal at a potential of 3.2 eV to a current flow between the Si valence band and the empty Pr-silicate CBM. With this interpretation the result is in agreement with the detailed interface potential diagram shown in figure 5.

The dipole jump indicates an interface dipole moment with its direction towards the oxide. It might be caused by either a structural rearrangement of the Si surface atoms or by negative charges in close contact with the interface. The latter is less likely, as discussed below. We therefore argue that the transition from the more covalent Si–O bonds to the more ionic O–Pr bonds causes an interface dipole moment which is located only at the interface.

The variation in the position of the valence band maximum with increasing coverage indicates that in the interface the oxide is charged within the interface region. There must be an interface agglomeration of negative carriers. We have to rule out that oxygen vacancies V_O^{2+} are responsible, which cause a positive space charge, while excess oxygen would cause the opposite. But more plausible is the existence of metal ion vacancies V_{Si}^- or V_{Pr}^{3-}. It should be mentioned that the construction of such detailed interface potentials is of crucial importance for any modelling of charge transport and carrier dynamics.

At this point it is interesting to note that there is a very small discontinuity at the conduction bands of Si and Pr$_2$O$_3$. For the purpose of a gate insulator this is not a good starting position although the discontinuity of the VBM is excellent. However, this disadvantage is compensated for by the fact that the lowest conduction band states are highly localized and the carriers in these states are therefore expected to have a large effective mass.

5. Conclusions and outlook

The valence band and the conduction band of Pr$_2$O$_3$ are built by covalent Pr 6s, Pr 5d, Pr 4f and O 2p states. There is a significant admixture of Pr 5d states in the valence band. The Pr 4f states are the states next to the VBM/CBM while the Pr 6s states appear at the bottom of the valence band.

In the silicate phase there is an increased covalent bonding in the valence states caused by the Si–O–Pr bonds. Additional, localized Pr 4f states are filled by CT processes. They appear above the covalent bonded valence states right at the VBM and enhance the 4f contribution in the Pr 4d–Pr 4f giant resonance.

The silicate formation goes with an interface dipole moment of about 1 eV. Within that silicate layer we find the initial valence band discontinuity to be about 2.5 eV. In addition, there is an accumulation of positive charges, presumably Pr vacancies. Considering the thickness of the interface, in all of our data we find that stable oxidic properties are obtained for films with a thickness of about 1.5 nm. Consequently, for a total thickness of 3 nm we would achieve an EOT of 0.4 nm. Assuming a reduced DK within the silicate phase this value might go up to 0.6 nm in the worst case. This is an excellent value considering the demand of process engineers which in sub-0.1 μm technologies require an EOT well below 1 nm. At the present state of the film preparation we obtain homogeneous films with thicknesses of around 15 nm corresponding to an EOT of 2 nm.

Acknowledgments

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