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Band offsets between Si and epitaxial rare earth sesquioxides (RE$_2$O$_3$, RE=La, Nd, Gd, Lu): Effect of 4f-shell occupancy

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Internal photoemission of electrons and holes into cubic Nd$_2$O$_3$ epitaxially grown on (100)Si reveals a significant contribution of Nd 4f states to the spectrum of the oxide gap states. In contrast to oxides of other rare earth (RE) elements (Gd, Lu) epitaxially grown in the same cubic polymorph, to hexagonal LaLuO$_3$, and to polycrystalline HfO$_2$, the occupied Nd 4f states produce an additional filled band 0.8 eV above the O 2p derived valence band. The unoccupied portion of the Nd 4f shell leads to empty electron states in the energy range of 1 eV below the RE 5d derived conduction band. The exposed Nd 4f states suggest the possibility to use this metal and, possibly, other REs with low f-shell occupancy to control the interface band offsets by selective interface doping. © 2008 American Institute of Physics. [DOI: 10.1063/1.3003872]

Insulating oxides of rare earths (REs), particularly the sesquioxides RE$_2$O$_3$, are attracting attention as dielectric materials suitable for replacing SiO$_2$ in microelectronic devices because they combine the best features of candidate insulators including high dielectric permittivity ($\varepsilon$), wide bandgap, and thermodynamic stability. 1 In addition, thanks to significant molar volume, their lattice parameter can be selected to enable epitaxial growth on surfaces of crystalline semiconductors. What still remains unclear is the role of the partially occupied 4f states of the RE cations in determining the barriers for electrons and holes. It was found for thin layers of amorphous or polycrystalline heavy RE sesquioxides (Gd, Dy, and Lu), several RE scandates (LaSc$_2$O$_5$, DySc$_2$O$_5$, and GdSc$_2$O$_5$), LaAlO$_3$, and LaLuO$_3$ that the occupancy of the 4f shell has only a marginal influence on the band alignment with Si or Ge. 4–10 The conduction band (CB) and valence band (VB) offsets at these interfaces appear to be close to those at the interfaces of the same semiconductors with HfO$_2$ in which the 4f shell is filled. 11 In the case of low f-shell occupancy, however, the splitting between occupied and empty f-states is expected to decrease 12 causing the sesquioxide gap narrowing. 3,13,14 Optical measurements indicate significant gap narrowing in light RE sesquioxides (Pr, Nd, Sm, and Eu), which is ascribed to the occupied 4f states lying energetically above the O 2p states in the oxide VB. 15 By contrast, the presence of unoccupied f-states in the upper portion of the gap was suggested to narrow the gap in Nd$_2$O$_3$. 16 The important factor affecting the energy position of RE 4f states is known to be the crystal field splitting, 17 making this portion of the electron spectrum sensitive to the oxide crystal phase. Oxides of light REs (La, Pr, and Nd) usually crystallize in the hexagonal phase, while heavy RE sesquioxide crystals have the cubic Mn$_2$O$_3$ (bixbyite) structure, 18,19 making meaningful comparison between bulk the phase(s) of different RE sesquioxides difficult. In the present work, this problem is resolved by growing cubic (bixbyite) RE oxides epitaxially on atomically clean Si crystal surfaces. While not observed for Gd$_2$O$_3$, Lu$_2$O$_3$, Lu$_2$O$_3$, and HfO$_2$, we reveal the f-shell contribution to the density of states (DOS) in Nd$_2$O$_3$ by analysing the oxide CB and VB edges separately using internal photoemission (IPE) of electrons and holes from Si.

Two Si surface orientations were used to enable the epitaxial growth: (100) for Nd$_2$O$_3$ and Gd$_2$O$_3$ and (111) for Gd$_2$O$_3$ and Lu$_2$O$_3$. The growth was performed at 650–700 °C by evaporating the source material under a low background pressure of oxygen resulting in abrupt Si/RE oxide interfaces. 20,21 Earlier comparison of Gd$_2$O$_3$ epitlayers on (100) and (111)Si faces indicated the same band alignment between Si and the oxide, 10 thus allowing a direct comparison among the studied sample series. To investigate the possible effect of unoccupied states of La on the oxide and interface DOS, epitaxial LaLuO$_3$ films were grown on (111)Si. This composition allowed us to reduce the chemical interaction of La with ambient moisture known to occur at room temperature. 22 The resulting epitaxial LaLuO$_3$/[111]Si films are found to crystallize as a hexagonal La$_2$O$_3$–Lu$_2$O$_3$ solid solution structure rather than the perovskite structure. Nevertheless, the band offsets at the interface between hexagonal LaLuO$_3$ and Si appear to be the same as in the amorphous LaLuO$_3$/[100]Si studied earlier, 9,11 suggesting only a weak sensitivity of the O 2p–RE 5d gap to the structure of the oxide. For the sake of comparison to the case of a filled 4f shell, polycrystalline HfO$_2$ layers containing tetragonal and monoclinic phases were deposited at 485 °C from metallo-organic precursor on (100)Si.

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substrates covered with a 0.8-nm-thick chemical oxide. The thickness of the oxide layers was in the range between 4 and 40 nm as determined using x-ray reflectivity and spectroscopic ellipsometry (SE) measurements. Capacitor structures were fabricated by thermoresistive evaporation of 0.5 mm² semitransparent (15-nm-thick) Au or Al electrodes onto the oxide. These were used in IPE and photoconductivity (PC) room temperature experiments. The quantum yield \( \gamma \) was defined as the photocurrent normalized to the incident phonon flux and analyzed in the photon energy \( (h\nu) \) range of 2–6.5 eV with constant spectral resolution of 2 nm. By considering the IPE of electrons and holes from Si into different insulators, the initial energy distribution of photoexcited charge carriers in Si is the same for all samples. Therefore, the observed differences in the IPE spectra will reflect the different energy distribution of the DOS over the insulating collector layers studied.

Panels (a) and (b) in Fig. 1 exemplify the spectral dependences of the normalized optical absorption coefficient \( (\alpha) \) determined by fitting the SE data and of the PC yield, respectively, for the insulating layers studied in the photon energy range close to the onset of intrinsic absorption. Compared to other oxides, Nd\(_2\)O\(_3\) shows significantly enhanced absorption consistent with the smaller gap width observed in bulk crystals \( (E_g \approx 4.7 \text{ eV}) \) as measured at 300 K (Ref. 15) and 78 K. Using a linear fit of the \((ah\nu)^{1/2}\)-\(h\nu \) plot (\( n \) is the refractive index), indicated in Fig. 1(a) by lines, we obtain a similar bandgap \( E_g \approx 4.8 \pm 0.1 \text{ eV} \) for the bixbyite Nd\(_2\)O\(_3\) film. Although the same threshold can also be inferred from the PC spectral curves shown in panel (b), the PC quantum yield in Nd\(_2\)O\(_3\) appears to be disproportionally low as compared to the strong optical absorption evident in (a). This observation indicates that most of the optical transitions involved in the optical absorption produce no free charge carrier, i.e., they are either of excitonic nature as occurs, for instance, in Y\(_2\)O\(_3\) or the electrons and holes are generated in strongly localized states facilitating efficient geminate recombination. To resolve this dilemma we performed IPE measurements which exclude the excitonic effects.

Logarithmic plots of electron and hole IPE yield as a function of \( h\nu \) are shown in Fig. 2 (positive bias) and Fig. 3 (negative bias), respectively, with the bottom right inserts illustrating the determination of electron and hole IPE thresholds using \( Y^{1/3,h\nu} \) (Ref. 25) or \( Y^{1/2,h\nu} \) (Ref. 26) plots, respectively. As revealed by the electron IPE spectra presented in Fig. 2, (100)Si/Nd\(_2\)O\(_3\) shows greatly enhanced emission in the low \((h\nu<3 \text{ eV}) \) energy range. As the density of interface traps derived from CV curves in the Nd\(_2\)O\(_3\) samples is found to be in the same range as in Gd\(_2\)O\(_3\) or Lu\(_2\)O\(_3\) samples (of the order of \( 10^{12} \text{ cm}^{-2} \)), involvement of defect-assisted “pseudo-IPE” (Ref. 23) is unlikely to explain this enhancement of electron current. This conclusion is supported by the observation of the \( E_1 \) optical singularity at \( h\nu=3.4 \text{ eV} \) related to \( \Lambda_3-\Lambda_1 \) excitation in silicon in all samples, pointing to the Si substrate as the source of the photoelectrons. Therefore, the cause of the IPE enhancement is associated with a downshift of the Nd\(_2\)O\(_3\) CB bottom by approximately 1 eV. A second important observation is the smearing out of the IPE threshold associated with electron.

FIG. 1. (a) Square root of the optical absorption coefficient \( \alpha \) (normalized to the photon energy \( h\nu \) and refractive index \( n \)) as a function of photon energy derived from SE data for the RE oxides and HfO\(_2\) studied. Lines indicate linear fits to extract the bandgap \( E_g \) of Nd\(_2\)O\(_3\). (b) Square root of the PC quantum yield as a function of photon energy measured on different oxides under an externally applied electric field \( F \) of \(-1 \text{ MV/cm} \) (cf. the band diagram in the inset). Lines indicate linear fits to determine the bandgap \( E_g \) of Nd\(_2\)O\(_3\).

FIG. 2. Logarithmic spectral plots of the electron IPE quantum yield from Si into the CB of different RE oxides and HfO\(_2\) measured under an externally applied electric field \( F \) of \(+1 \text{ MV/cm} \). The inset shows \( Y^{1/2,h\nu} \) plots used to determine the threshold \( E_1 \) of electron IPE from the Si VB to the oxide CB. Arrow \( E_1 \) shows the energy of the \( \Lambda_3-\Lambda_1 \) excitation in the Si crystal.
increasing negative bias voltage, however, the Nd$_2$O$_3$ sample

electric fields the threshold of the hole IPE from the Si CB to the oxide VB.
The lines in the insert illustrate the determination of the IPE spectral thresholds. Arrows
occupied states lying approximately 0.8 eV above the O 2p states. Thus, hybridization of these states is unlikely.

The energy band diagram at the Si/Nd$_2$O$_3$ interface can now be compiled, as shown in the top left insert in Fig. 3 with contributions of Nd 4f states indicated by dashed regions. The latter allow one to reduce both the CB and VB offsets by nearly 1 eV, thus offering a method of interface barrier control by the introduction of a controlled amount of Nd into other RE sesquioxides. An obvious advantage inherent to this approach is that Nd is incorporated into the oxide structure as an isovalent substitution without necessarily forming dangling bonds or any other coordination defects.

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IPE into the unoccupied RE 5d states in the (100)Si/Nd$_2$O$_3$ structure, which constitute the lowest portion of CB in the other four oxides. This IPE threshold (indicated as $\Phi_e$ in the insert in Fig. 2) is found around 3.1–3.2 eV at the interfaces of Gd$_2$O$_3$, Lu$_2$O$_3$, LaLuO$_3$, and Ho$_2$O$_3$ with Si, but becomes less pronounced in Nd$_2$O$_3$ which might suggest hybridization of the Nd 5d and 4f states in its CB.

Hole IPE spectra, such as shown in Fig. 3 for different voltages applied to the Au electrode of (100)Si/Nd$_2$O$_3$(19 nm)/Au capacitors, indicate that in low electric fields the threshold of the hole IPE $\Phi_h$ is 3.7 ± 0.1 eV, which is close to that for the Gd$_2$O$_3$ case. With increasing negative bias voltage, however, the Nd$_2$O$_3$ sample develops a low-energy IPE tail stretching down to 2.9 ± 0.2 eV. The clear observation of the abovementioned $E_1$ optical singularity, marked by arrows in Fig. 3, suggests again Si as the source of the photoemitted holes. Apparently, the IPE tail corresponds to hole injection into a band of occupied states lying approximately 0.8 eV above the O 2p derived VB top. As such an effect is not observed in any of the other RE sesquioxides studied or in Ho$_2$O$_3$, it is likely associated with occupied Nd 4f states which would also be in agreement with results obtained from photoelectron spectroscopy experiments.27 According to the observed hole IPE thresholds are identified in Fig. 3 as $\Phi_e(0\ 2p)$ and $\Phi_h(\text{Nd } 4f)$. The former threshold is seen at nearly the same energy in Nd$_2$O$_3$ as in Gd$_2$O$_3$, Lu$_2$O$_3$, or Ho$_2$O$_3$, suggesting

that the energy of the O 2p states is insensitive to the energy of the Nd 4f states. Thus, hybridization of these states is unlikely.

Figure 3. Logarithmic spectral plots of the hole IPE quantum yield from (100)Si into the VB of Nd$_2$O$_3$ (19 nm) measured under different negative biases applied to the Au electrode. For comparison, the yield is also shown (scaled down by factor of 10) for the (100)Si/Gd$_2$O$_3$ (11.2 nm)/Au structure. The bottom right inset shows $Y(1-\ h\ p)$ plots used to determine the threshold $\Phi_e$ of hole IPE from the Si CB to the oxide VB. The lines in the insert illustrate the determination of the IPE spectral thresholds. Arrows $E_1$ and $E_2$ mark the energy of $\Delta \gamma - \Delta \lambda$ and $\gamma - \lambda / \Sigma_\gamma - \Sigma_\lambda$ excitations within the Si crystal, respectively. The top left insert shows schematic energy band diagram at the Si/Nd$_2$O$_3$ interface inferred from the PC and IPE results. The energy scale is in measured with respect to the top of the Si VB. Shadowed areas indicate the DOS components derived from the Nd 4f states.