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ScienceDirect

Microelectronic Engineerinzg 84 (2007) 2278–2281

MICROELECTRONIC ENGINEERING

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Electronic structure of silicon interfaces with amorphous and epitaxial insulating oxides: Sc_2O_3, Lu_2O_3, $LaLuO_3$

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Abstract

Spectroscopy of internal photoemission, photoconductivity, and optical absorption is used to characterize the differences in the electronic structure of interfaces of silicon with several oxides (Sc_2O_3, Lu_2O_3, $LaLuO_3$) grown as epitaxial layers or as amorphous films. As compared to their crystalline counterparts, the amorphous oxides exhibit significant band-tail states predominantly associated with the smearing-out of the conduction band edge. In Sc_2O_3 a difference in bandgap width between the crystalline and amorphous phases, caused by variation of the energy of the oxide valence band top, is also observed. No structure-sensitive interface dipoles are found to affect the band alignment at the Si/oxide interfaces.

Keywords: epitaxial insulators; internal photoemission; band offsets; bandgap width

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1. Introduction

Epitaxial high-κ insulators have a potential for ultimate gate stack scaling in semiconductor electronic devices because the crystals may offer both a maximal dielectric constant and interlayer-free interfaces. However, still little is known about the impact of crystallinity or disorder on the electronic band structure of high-κ insulating metal oxides and, in particular, on the band alignment at their interfaces with semiconductors. The latter issue is of much physical interest because the ordered atomic structure might give rise to interfacial dipoles. It also remains unclear what components of the electron density of states are most sensitive to crystalline order because the conduction (CB) and valence bands (VB) in the oxides are derived from states of atoms of different types [1,2], which, therefore, overlap differently. Here we report on the first comparison between

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doi:10.1016/j.mee.2007.04.113

electron states in several amorphous and crystalline oxides on Si by using results of internal photoemission (IPE) measurements which enable direct characterization of the cation- and anion-derived electron states by observing electron and hole emission into the CB and VB, respectively [3].

2. Experimental

To reveal general trends when replacing an amorphous insulator by a crystalline one, we compared three different oxide materials: Sc_2O_3, Lu_2O_3, and $LaLuO_3$. *Amorphous* (a-) layers, 20-40 nm thick, were grown on H-terminated (100) Si substrates at room temperature using the molecular-beam effusion (MBE) technique. For the sake of comparison, amorphous $LaLuO_3$ samples were also fabricated by pulsed-laser deposition (PLD) on (100) Si covered with a thin (about 1 nm) chemical oxide layer. To grow *crystalline* (c-) insulators, MBE was performed on H-terminated (111)Si faces in the temperature range 400-700 °C. The 20-40 nm thick oxide layers grown under these conditions are epitaxial, predominantly exhibiting the cubic bixbyite structure as revealed by X-ray diffraction analysis. Next, MOS capacitors were fabricated by evaporation of semitransparent (15-nm thick) Au or Al electrodes. These were used in experiments on IPE and oxide photoconductivity (PC) in the photon energy (hν) range from 2 to 7 eV [3]. In addition, the oxides were characterized optically using visible-UV spectroscopic ellipsometry measurements.

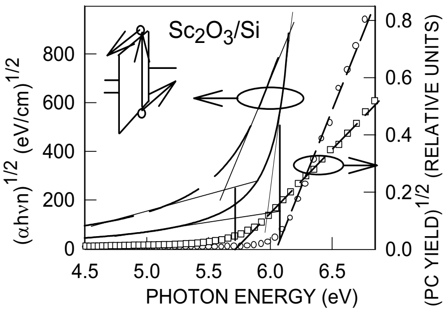

Fig. 1. Photoconductivity spectral curves in samples with epitaxial (○) and amorphous (□) 40-nm thick Sc_2O_3 insulators on p-Si measured with –2 V bias applied to the gold field electrode. The insert shows a schematic of the electron excitations. Solid and dashed curves show the behavour of the normalized optical absorption coefficient (αhνn) in the epitaxial and amorphous oxide, respectively.

3. Results and discussion

Intrinsic PC spectra (Fig. 1) indicate that the bandgap of scandium oxide is sensitive to its structure: Epitaxial c-Sc_2O_3 exhibits a 6.0-6.1 eV wide gap as compared to 5.6-5.7 eV for a-Sc_2O_3. The ellipsometry results also shown in Fig. 1 affirm this effect. They indicate the optical gap width of 6.0 and 5.6 eV in c- and a-Sc_2O_3, respectively. The band gap of Lu_2O_3 and $LaLuO_3$ (both MBE- and PLD-grown) is 5.4±0.1 eV, regardless of the oxide crystallinity (curves not shown). A common feature of all three amorphous insulators studied is a ≈1-eV tail of sub-threshold PC indicative of band tailing into the gap.

When further comparing amorphous and crystalline insulators it was found that the oxide CB edge in the amorphous material is smeared out. This conclusion is inferred from the analysis of the IPE spectra of electrons from the Si VB transitioning into the lowest CB of the oxide [cf. insert in Fig. 2(a)]. As one can see from the $(\text{yield})^{1/3}$–*vs*–hν spectral plots shown for Lu_2O_3 and $LaLuO_3$ in Fig. 2(a) and for Sc_2O_3 in Fig. 2(b), the samples with amorphous oxides exhibit a much enhanced electron injection in the low-photon energy spectral range (hν < 3 eV) as compared to their crystalline counterparts.

The enhanced electron IPE at low photon energy cannot be explained by a simple change of the Si crystal surface orientation because both (100) and (111) faces of Si are known to have close IPE thresholds at interfaces with SiO_2 [3]. Also, the use of MBE to grow both amorphous and epitaxial layers allows one to minimize Si oxidation (to levels below the 0.02 nm [4]), so the presence of a SiO_2 interlayer can firmly be excluded. Therefore, the observed variation in the IPE characteristics of the crystalline oxide as compared to the amorphous one rather refers to differences in the density of electron states distribution near the CB edge. Namely, the oxide CB edge is smeared out in amorphous oxides suggesting a downshift in energy of some CB states. In all three cases, the IPE threshold Φ_e characteristic for crystalline oxides is still observed in the amorphous films at the same energy of $\Phi_e = 3.1 \pm 0.1$ eV. As the same (within the indicated accuracy) barrier values were found when the measurements were repeated under metal bias values ranging from +0.5 to +2 V, we conclude that the image-force barrier lowering is insignificant. This result is consistent with a high dielectric permittivity of the near-interfacial insulator affirming the absence of a SiO_2-like interlayer. The same barrier value indicates the absence of measurable dipole contribution to the barrier height which could have arisen from the ordered atomic structure at the Si/epitaxial oxide interface.

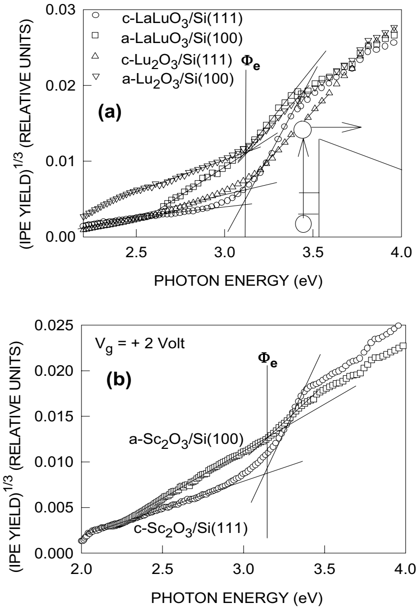

Fig. 2. Quantum yield of electron IPE from the n-type Si valence band into the conduction band of amorphous and epitaxial crystalline Lu_2O_3 and $LaLuO_3$ (a) and Sc_2O_3 (b) layers plotted in $Y^{1/3}$-hν coordinates. All the spectra are measured with +2 V bias applied to the Au electrode on top of a 40-nm thick oxide. The lines illustrate the determination of the spectral threshold Φ_e. The insert in panel (a) presents schematic of the electron photoemission from the VB of Si into the oxide CB.

Hole IPE spectra shown in Fig. 3 for the (111)Si/Sc_2O_3 interface reveal another important result: the threshold Φ_h of hole IPE from Si into the epitaxial oxide is about 0.5 eV higher than that into the amorphous Sc_2O_3 indicating an energy shift of the oxygen-derived states near the top of the oxide VB. The spectra also show a peak in the photocurrent coinciding with the E_2 peak of optical absorption in Si. As this feature is observed both in structures with Al and Au top electrodes, its origin must be related to silicon. The enhancement of this feature in the hole IPE in a-Sc_2O_3 *vis-à-vis* c-Sc_2O_3 samples suggests that the energy of a hole excited in the vicinity of the Σ_4 and X_4 points in the Brillouin zone of Si is sufficient for injection into the valence band of the amorphous oxide. The energy of these points is approximately 2.5-3 eV below the top of the silicon valence band [5]. The valence band offset at the (100)Si/a-Sc_2O_3 interface can be found by subtracting the Si bandgap width (1.12 eV) from $\Phi_h(Si)=3.5$ eV shown in Fig. 3 yielding $\Delta E_V=2.5\pm0.1$ eV. Thus, the injection of holes excited in the Σ_4 or X_4 states becomes possible. By contrast, no hole IPE enhancement can be seen in c-Sc_2O_3 samples. In the latter case the VB offset is close to 3 eV and a hole excited in the Δ_5 or X_4 state in silicon will see nearly no available states to be injected into the oxide VB.

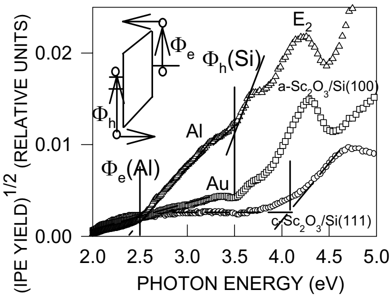

Fig. 3. Quantum yield of electron IPE from metal and hole IPE from p-type Si into amorphous (□,△) and crystalline (○) Sc_2O_3 plotted in $Y^{1/2}$-hν coordinates. All the spectra are measured with -2 V bias applied to the Au (○,□) or Al (△) electrode on top of a 40-nm thick oxide. The lines illustrate the determination of the spectral thresholds Φ_e and Φ_h the meaning of which is illustrated in the insert. The E_2 optical singularity within the Si crystal at hν=4.3 eV is also indicated.

In contrast to Sc_2O_3, no measurable shift of the hole IPE threshold is observed between a- and c-Lu oxides (spectra not shown). This observation is consistent with the marginal influence of the film structure on the bandgap width in these insulators. Also, the observed Lu oxide bandgap width and the interface barrier heights are close to those reported by Seguini et al. for films obtained by atomic layer deposition (ALD) [6]. Therefore, we can correlate the bandgap widening in crystalline Sc_2O_3 as compared to the amorphous film with a downshift in energy of the oxygen-related states near the VB top. In turn, the enhanced band tails seen in all three oxides in the amorphous phase can be ascribed to the tailing of CB states predominantly associated with metal cations.

The latter conclusion is also consistent with the even higher density of band tail states suggested to exist in ALD Lu_2O_3 by the observed considerable difference between the threshold of the PC and that of the optical absorption [6]. Apparently, random variations in the surrounding of Lu^{3+} ions determine the energy spread of the lowest electron states in the oxide conduction band. It is also possible that at certain network sites the Lu^{4+} configuration is favored, leading to a substantially lower energy of the unoccupied d-states and, accordingly, to the down-split states in the oxide conduction band.

It might also be instructive here to compare the revealed trends in the electronic structure of the insulating Sc_2O_3, Lu_2O_3, and $LaLuO_3$ oxides to those observed upon crystallization of ALD alumina layers on silicon [7]. Upon annealing at a temperature exceeding 800 °C amorphous Al_2O_3 characterized by a 6-eV wide bandgap crystallizes to the cubic (γ-alumina) phase with a bandgap width of about 8.8 eV [8]. The upward shift of the oxide CB measured using IPE with respect to the Fermi level of Au appears to be only 0.5 eV. This result leaves the variation in energy of the Al_2O_3 valence band top responsible for most of nearly 3-eV crystallization-induced bandgap widening. This trend appears to be similar to the VB down shift in the crystalline (also cubic) Sc_2O_3 as compared to the amorphous phase observed in the present study. The most significant difference between Al_2O_3 and Sc_2O_3 seems to be the magnitude of the effect, by factor of approximately 5 larger in alumina than in scandia. This difference may be correlated to the significantly smaller 3+ ion radius of Al (0.051 nm) compared to Sc (0.0732 nm) which would mean a much more dense oxide structure of the aluminum oxide. Therefore, we hypothesize that the interaction of lone-pair 2p orbitals of oxygen anions is much enhanced in the dense crystalline Al_2O_3 lattice resulting in energetically deep upper states of the valence band.

4. Conclusions

Comparison between electron state spectra at interfaces of Si with amorphous and epitaxial Sc_2O_3, Lu_2O_3, and $LaLuO_3$ as well as earlier studied Al_2O_3 layers [7] allows us to infer the following trends:

- the band tailing in amorphous oxides is predominantly associated with cation-related states in the oxide CB. This effect can be related to random variation in cation surrounding. The latter may potentially include not only the structural disorder but, also, compositional variations pertinent to the case of complex oxides [9];

- the observed bandgap differences between amorphous and crystalline oxides are mostly related to changes in the energy of oxygen lone-pair electron states which constitute the top of the VB [1]. There seems to be a correlation of this effect with the ionic radius of the metallic cation. The latter would also explain the observation of nearly the same valence band offset of $\Delta E_V = 2.5 \pm 0.1$ eV in a broad variety of oxides (Zr, Hf, Lu, Gd, Dy,…), all ions having a radius close to 0.08 nm;

- at least in three studied Si/oxide systems, no structure-sensitive electrostatic dipole contributions to the barriers are encountered. This might suggest that, in the absence of a considerable density of uncompensated charges, the intrinsic band alignment is determined by the bulk electronic spectrum of the contacting materials rather than by details of atomic bonding at the interface between these materials.

Acknowledgements

The work done at KU Leuven was supported by the Fonds Wetenschappelijk Onderzoek Vlaanderen (FWO) through grant 1.5.057.07. The authors gratefully acknowledge the financial support of the Semiconductor Research Corporation (SRC). L.F.E. gratefully acknowledges an AMD/SRC fellowship

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