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Misfit point defects at the epitaxial Lu_2O_3/(111)Si interface revealed by electron spin resonance

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Electron spin resonance study on heteroepitaxial Si/insulator structures obtained through the growth of epi-Lu_2O_3 films on (111)Si (~4.5 % mismatched) by reactive molecular beam epitaxy indicates the presence in the as-grown state of interfacial P_b defects ($\sim 5\times10^{11}$ cm^{-2}) with an unpaired sp^3 Si dangling bond (DB) along the [111] sample normal, prototypical of the standard thermal (111)Si/SiO_2 interface. The defects, with density remaining unchanged to anneal in vacuum up to temperatures of $T_{an}\sim420$ °C, directly reveal the nonperfect pseudoepitaxial nature of the interface, laid down in electrically detrimental interface traps. These are suggested to be interfacial Si DBs related to Si misfit dislocations. Alarmingly, defect passivation by standard anneal treatments in H_2 fall short. For higher T_{an}, the interface deteriorates to "standard" Si/SiO_2 properties, with an attendant appearance of EX centers indicating SiO_2 growth. Above $T_{an}\sim1000$ °C, the interface disintegrates altogether. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2974793]

Metal oxides of substantially higher dielectric constant κ than SiO_2 ($\kappa\sim3.9$) are introduced to replace the conventional amorphous (a) SiO_2 gate dielectric in Si/SiO_2-based metal-oxide-semiconductor device technology.[1] Inspired by the superb a-SiO_2/Si system, this has commonly focused on amorphous oxides as this state is expected to enable optimal local bonding adjustment to minimize the interface trap density and for other reasons such as ease and low cost in manufacturing and layer uniformity.[2] Among others, of crucial importance is the Si/high-κ insulator interface since its electrical properties should be device grade, close to the Si/SiO_2 standard. Typically, however, the processes used to deposit amorphous metal oxides directly on Si result in the formation of a $SiO_{2(x)}$ interlayer (IL). While amply demonstrated by numerous microstructural imaging techniques, on the atomic scale this has been evidenced by electron spin resonance (ESR) studies[3] through revealing the presence at the Si/high-κ interface of Si dangling-bond-type point defects termed P_b-type centers. In the case of conventional (100)Si/SiO_2, it is known that these trivalent defects are *naturally* incorporated at the interface as a result of the network-lattice mismatch,[4] in areal densities[5] of $\sim1\times10^{12}$ cm^{-2}, for standard oxidation temperatures (800–960 °C). Their presence in Si/high-κ structures would thus demonstrate the presence of a SiO_x-type IL. Despite the superb electronic quality of the Si/SiO_2 interface thus potentially realized, the presence of a SiO_x IL in Si/high-κ structures conflicts with the requirement of minimizing the net equivalent Si oxide thickness. The $P_{b(0)}$ defects (trivalent interfacial Si dangling bonds) have been evidenced as the dominant malignant fast interface trap system.

By contrast, less effort has been devoted to the "opposite" solution, i.e., the use of epitaxial oxides with the potential of ultimate gate stack scaling able to provide atomically truly abrupt IL-free interfaces with Si, maximum κ values, and to offer opportunities to eliminate interface states through interface engineering.[6,7] Here, as to the interface, one may aim for atomic insight: While the atomic nature of occurring *inherent* interface traps (point defects) in the archetype Si/SiO_2 structure has been convincingly uncovered by the unique ESR technique in conjunction with an electrical study,[4] with several definitely identified (P_b,P_{b0},P_{b1},E'), that quest stays for the epi-insulator/Si interface—*a fortiori*, what defects would remain at all. This is the subject of the current work providing a first ESR study on the atomic nature of inherently occurring (interfacial) point defects in an epidielectric/Si structure, i.e., epi-Lu_2O_3/(111)Si. The layered structure evolution under postgrowth annealing (PGA) is studied as well.

Among the rare earth oxides, Lu_2O_3 is an interesting alternative gate material to study the nature of the epitaxial dielectric/Si interface. Previously, both amorphous and crystalline films have been prepared on (100)Si by various techniques,[8–10] exhibiting similar interesting properties, i.e., dielectric constants of ~12–13, optical band gap of ~5.6 eV, a suitable approximately symmetric band alignment with Si, with both the conduction band and valence band offsets >2 eV, and amenable thermodynamic stability in contact with Si.[8,9] Yet, ultrathin (2–5 nm) a-Lu_2O_3 layers on (100)Si fabricated using atomic layer deposition (ALD) were recently found[9] unstable against silicate formation under vacuum annealing at $T\geq900$ °C.

Epitaxial Lu_2O_3 films (~35 nm thick) were grown by reactive molecular beam epitaxy on p-type 3 in. (111)Si wafers held at 700 °C using an elemental Lu source in a partial O_2 pressure of 2×10^{-6} Torr. Four-circle x-ray diffraction studies showed that this resulted in high quality films with a cubic bixbyite structure with the [111] axis along the [111]Si substrate normal and with the films predominantly (99.8%) grown in the orientation relationship of $(111)[\bar{1}10]Lu_2O_3\|(111)[\bar{1}01]$Si (denoted as B-type). A rocking curve analysis indicated a high degree of structural perfection of the Lu_2O_3 film. Scanning transmission electron

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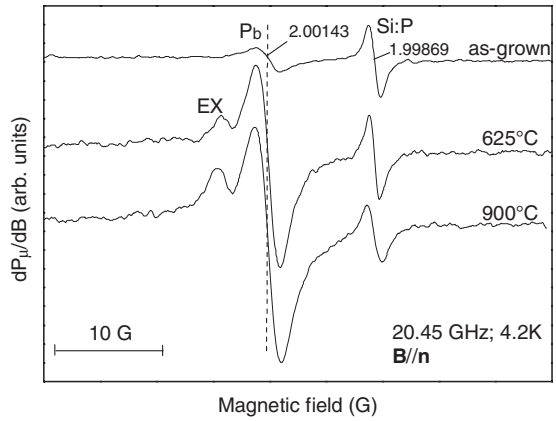

FIG. 1. First-derivative *K*-band ESR spectra observed at 4.2 K on (111)Si/Lu_2O_3 in the as-grown state after annealing in vacuum at 625 and 900 °C. The signal at $g=1.998\ 69$ stems from a Si:P marker sample.

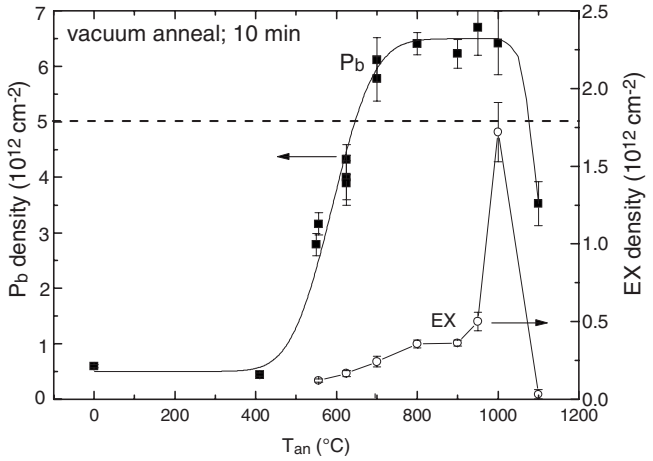

FIG. 2. Evolution of P_b (■) and EX (o) densities as a function of isochronal PGA in vacuum. The solid curve is merely meant to guide the eye in exposing the leveling in defect generation and the lagging behind (~100 °C) of the EX production vis à vis P_{b0}. The dashed curve indicates the inherent P_b density typical of standard thermal (111)Si/SiO_2 (Ref. 11).

microscopy (STEM) demonstrated a high quality epitaxial growth, free of any detectable IL. Despite a lattice mismatch of ~4.5% between Lu_2O_3 and Si, calculated using $f=(a_{Lu_2O_3}-2a_{Si})/a_{Lu_2O_3}$, where a is the lattice parameter, no misfit dislocations (MDs) could be detected in cross-sectional views. The layered structure thermal stability was analyzed by subjecting samples to isochronal (~10 min) PGA at temperatures in the range of $T_{an}=400-1100$ °C in vacuum ($<4\times10^{-6}$ Torr). Separate sets of samples were used for the various thermal steps. As an additional test related to potential ESR activation/maximization of paramagnetic defects, some samples were vacuum ultraviolet (VUV) irradiated ($h\nu=10$ eV) in room ambient. Details about the ESR practice can be found elsewhere.[5,11]

Figure 1 illustrates observed ESR spectra, while Fig. 2 shows the evolution of the density of observed point defects by ESR as a function of T_{an}, revealing several notable aspects: In the as-grown state, the epi-Lu_2O_3/(111)Si structure appears not to be defect free: A single anisotropic resonance signal is observed, where g mapping via magnetic field (**B**) angular dependent measurements (**B** rotating in the $(\bar{1}10)$ plane) gave the principal values $g_\parallel=2.001\ 43\pm0.000\ 03$ and $g_\perp\sim2.008\ 74\pm0.000\ 03$. This reliably allows identification of the signal as originating from the axial symmetric P_b interface defect, typically observed at the thermal (111)Si/SiO_2 interface, characterized by[12] $g_\parallel=2.0014$ and $g_\perp\sim2.0088$. Pertinently, the ESR parameters match well. The inferred defect density ($[P_b]\sim5.9\times10^{11}$ cm^{-2}) corresponds to one-tenth of the value ($\sim5\times10^{12}$ cm^{-2}) inherent to[11,13] standard thermal (111)Si/SiO_2. This provides, on atomic scale, direct evidence of nonperfect pseudoepitaxy, although the interface thus still appears about ten times better than standard thermal (111)Si/SiO_2. It leaves the basic quest as to the origin of these defects. No defects from the Lu_2O_3 layer could be observed. Supplementary VUV irradiation did not reveal any Lu_2O_3-associated or additional P_b-type defects; i.e., no H passivation was involved.

However, upon annealing from $T_{an}\sim500$ °C onward, the structure becomes thermally unstable, as indicated by the steeply growing P_b density up to $T_{an}=700$ °C to reach $[P_b]\sim6.3\times10^{12}$ cm^{-2}, a density comparable to the natural occurring density in (111)Si/SiO_2. It would indicate that the epi-Lu_2O_3/(111)Si interface has transformed into a truly Si/$SiO_{2(x)}$-type, evidencing a formation of a SiO_x-type IL. This formation of a Si/SiO_x-type IL may be put in the light of such IL formation linked with the previously observed transformation of the $LaAlO_3$ network on (100)Si from the amorphous to the polycrystalline state.[14] For further annealing at higher T_{an} up to ~1000 °C, that situation does not change as $[P_b]$ remains constant. Here, it may be added that $SiO_{2(x)}$-type IL formation after PGA at 400 °C (1 Torr O_2) in the case of a-Lu_2O_3/(100)Si entities has been concluded from x-ray electron spectroscopy.[10]

The gradual growth from $T_{an}\sim420$ °C of a Si/SiO_2-type interface is independently affirmed (see Fig. 1) by the observation, after VUV irradiation, of the EX defect, a SiO_2-associated center.[15] It starts to be observed at $T_{an}\sim550$ °C and increases to the density of $\sim4\times10^{11}$ cm^{-2} at 800 °C; like P_b, its areal density remains rather unchanged up to $T_{an}=950$ °C. The growth temperature profile of EX appears upward shifted (retarded over ~100 °C) compared to P_b, indicating an additional growth (or modification) of the IL (Fig. 2). For still higher T_{an} (>1000 °C), both defect densities in tandem drop drastically, indicating the Si/SiO_2-type interface to collapse, i.e., elimination of the "pure" SiO_x component. This disruption of the interface, i.e., the breaking up of the SiO_x-IL, is possibly linked to the previously observed[9] decomposition (metallic Lu formation) of the Lu_2O_3 layer for ALD a-Lu_2O_3 (2–5 nm)/Si structures.

Touching the basics of heteroepitaxy, the fundamental quest arises as to the origin and incorporation of the revealed P_b centers at the epi-Lu_20_3/(111)Si interface, bearing testimony to nonperfect epigrowth, in fact, inherent relicts of such growth. Generally, the latter may perhaps not come as a surprise given the rather substantial mismatch in lattice parameters between the matching epifaces of the Lu_2O_3 and Si crystals. We may envision several possibilities.

First, it would seem natural to start from the involved mismatch of ~4.5% between Lu_2O_3 and Si in this heteroepitaxial growth. As is known, when the pseudomorphic film thickness exceeds a critical thickness d_c, the film will plastically deform (relax) through the formation of a MD network. The value of d_c may be obtained from the equation $d_c\approx b/(6f)$, a rough approximation of the transcendent theoret-

ical result,[16] where **b** is the dislocation Burger vector. For the current case, with $f \sim 4.5\%$ and using $b = 0.38$ nm typical for Si, we obtain an upper limit $d_c \sim 1.4$ nm $\ll d_{Lu_2O_3} = 35$ nm of the grown Lu_2O_3 epifilm. Thus a MD network should have formed, although no such MD network could be directly demonstrated in cross-sectional STEM views; it might indicate that the film was not totally relaxed. Should no reconstruction occur in the MD core, given the positive lattice mismatch, this in fact would constitute row of ordered Si DBs at the (111)Si/dielectric interface all potentially appearing as P_b-like centers. Indeed, paramagnetic Si DB-type defects related to deformation induced dislocations in bulk Si have been reported by ESR observations, referred to as Si-*R* or *D* centers observed at $g = 2.005$ after annealing at $T \geq 800$ °C.[17] Now for $f \sim 4.5\%$, and assuming a fully relaxed Lu_2O_3 epifilm (untrue pseudomorphic), this would result in a MD network involving $\sim 3.5 \times 10^{13}$ cm^{-2} defected interfacial Si atoms, that is, the same number of Si DBs if no core reconstruction would occur, ~60 times larger than the detected P_b's on the as-grown sample. So, on this account the observed P_b's could well be related with MDs; yet in line with ESR observations for bulk dislocations[17,18] on Si, distinct bond reconstruction would have occurred. The latter is corroborated by ESR spectral properties, i.e., the absence of an explicit dipolar fine structure or excessive dipolar line broadening.[19] So, within the scope of available data, the relationship of P_b's with MDs is feasible. Importantly, in this view and assuming a truly abrupt interface, it would indicate that the P_b defect can occur at a Si/insulator interface in no strict Si/SiO_2-type environment.

A second view might envision failing epitaxy where some small irregular patches of SiO_2 IL have formed. However, this possibility is excluded since based on P_b properties in standard thermal $(111)Si/SiO_2$, the Si/SiO_2 patch area would amount to ~12% of the total Si/dielectric interface area—probably unacceptably unrealistic for a successful pseudomorphic epigrowth. It is further countered by failing passivation heat treatments in H_2. Here it was observed that passivation treatment in H_2 (1 atm, 1 h, 405 °C) left $[P_b]$ unaltered with experimental accuracy. It indicates that the P_b defect system cannot be inactivated below the initial density, whose behavior would be rather unexpected for conventional $(111)Si/SiO_2$ areas where P_b's can be readily passivated by such treatment to well below the ESR detection limit (a few times 10^{10} cm^{-2}).

The third possible cause for the occurrence of point defects could be antiphase boundaries (APBs) and related threading dislocations (TDs) at APB triple junctions. As stated, such APBs are believed to be a common feature of the epitaxy of bixbyite structure films on Si, formed when growing film islands coalesce.[6] However, as far as these APBs and related TDs are predominantly a matter of imperfection within the epitaxial bixbyite Lu_2O_3 film, these are unlikely to be the source of the observed P_b interface defect system.

Finally, assuming a high quality pseudoepitaxial growth, a fourth possibility could suggest the incorporated P_b defect system to stem from unavoidable steps at the pristine initial Si surface impairing perfect epitaxial interface registry *per se*. However, in a straightforward (ball-and-stick) picture, arguably, such step edges (one to three atom steps) at the (111)Si surface would naturally lead to 19°-type P_b variants rather than the observed regular 90° P_b centers. So, this possibility seems countered on the ESR basis. Taken together, the above considerations lead us to the suggestion that the observed P_b's in as-grown epi-Lu_2O_3/(111)Si entities are related to MDs, considered as unavoidably incorporated to account for the 4.5% lattice mismatch.

In summary, an ESR analysis of inherently occurring point defects in an epitaxially grown high-κ/Si structure (epi-Lu_2O_3/Si) has been presented, particularly in the interfacial region. A main finding is that the epigrowth is imperfect, as revealed by the observation of P_b defects typical of the $(111)Si/SiO_2$ interface. A key point of interest concerns the precise origin and locality of these electrically detrimental centers, where it is concluded that these are most likely to be related to Si DBs at Si MDs introduced as a result of the ~4.5% lattice mismatch. Alarmingly, standard passivation annealing in H_2 fails, which, given the technological significance, will necessitate a more in depth investigation. The epi-Lu_2O_3/(111)Si entity appears only marginally stable, only up to $T_{an} \sim 420$ °C, and its interface is seen to evolve to a fully Si/SiO_2-type at $T_{an} \sim 700$ °C, as heralded by the observed $(111)Si/SiO_2$ natural P_b defect density. For $T_{an} > 1000$ °C, the Si/SiO_2 nature of the IL starts to collapse, possibly linked to the disintegration of the Lu_2O_3 film altogether.

The application of ESR appears adequate to monitor the thermal (interface) evolution of layered structures, able to reveal atomic imperfections linked to heteroepitaxial growth on the very atomic scale.

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