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FAST TRACK COMMUNICATION

Electron spin resonance observation of an interfacial Ge P_{b1}-type defect in SiO_2/(100)$Si_{1-x}Ge_x$/SiO_2/Si heterostructures

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Abstract
Using electron spin resonance (ESR), we report on the observation of a first Ge dangling bond (DB)-type interface defect in the SiO_2/(100)Ge_xSi_{1-x}/SiO_2/(100)Si heterostructure manufactured by the condensation technique. The center, exhibiting monoclinic-I (C_{2v}) symmetry with principal g values $g_1 = 2.0338 \pm 0.0003$, $g_2 = 2.0386 \pm 0.0006$, $g_3 = 2.0054$ is observed in maximum densities of $\sim 6.8 \times 10^{12}$ cm^{-2} of the Ge_xSi_{1-x}/SiO_2 interface for $x \sim 0.7$, the signal disappearing for x outside the 0.45–0.93 range. The notable absence of interfering Si P_b-type centers enables unequivocal spectral analysis. Collectively, the combination of all data leads to depicting the defect as a Ge P_{b1}-type center, i.e. not a trigonal basic Ge $P_{b(0)}$-type center ($Ge_3{\equiv}Ge^{\bullet}$). Understanding the modalities of the defect's occurrence may provide an insight into the thus far elusive role of Ge DB defects at Ge/insulator interfaces, and widen our understanding of interfacial DB centers in general.

Enhancement of charge carrier mobility has been advanced as a basic requirement to boost progression in Si-based metal-oxide–semiconductor (MOS) technology [1, 2]. Interesting within this field is the progress made in deposited insulators [3] of high dielectric constant κ with the intent to replace the conventional SiO_2 gate insulator, offering, in parallel, the potential to surmount a key problem with a higher mobility semiconductor such as Ge, i.e. providing an alternative for the less stable $GeO_{2(x)}$ native insulator, thus attaining two goals at once if realized by a high-κ insulator. This has led to a resurgence of interest in the application of Ge where the better bulk electron (3900 versus 1400 cm^2 V^{-1} s^{-1}) and hole (1900 versus 500 cm^2 V^{-1} s^{-1}) mobilities over Si promise higher channel mobility, while the narrower bandgap (0.67 eV at 300 K) enables reduced voltage operation, and hence, less power consumption [4, 5].

A crucial element in successful MOS application is the ultimate quality of the semiconductor/insulator interface, where detrimental interface traps should be reduced to the (sub) 10^{10} cm^{-2} level, still a key issue [6] for Ge MOSFETs. In the case of thermal Si/SiO_2, a dominant role is played by the interfacial Si dangling bond (DB) defects, P_b-type centers [7, 8] as identified by electron spin resonance (ESR), which fortunately can be efficiently passivated [9, 10] by H (standard industrial anneal in forming gas ($\sim$10% H_2 in N_2)). Yet, for Ge, achieving low interface trap density does not appear straightforward: intense research has exposed basic differences [4–6, 11, 12] between the seemingly isomorphic interfaces Si and Ge would form with oxides. ESR has so far failed to resolve interfacial Ge DB type defects [11], which leaves their occurrence and fate indistinct and hence also insight about their potential electrical activity. In a recent work [12], albeit contested in later work [13], it has been concluded from first principles density functional theory on an isolated $Ge_3{\equiv}Ge^{\bullet}$ (the dot symbolizing an unpaired electron) DB in c-Ge that this results from its electronic level being

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situated below the valence band maximum, giving rise in the equilibrium state to merely diamagnetic defects. It would also have an impact on the electrical performance of Ge/insulator entities through the introduction of negative charge.

There have been numerous previous reports on the observation of a Ge DB defect by ESR, albeit merely in less conventional semiconductor(/insulator) entities. This includes a powder of crushed c-Ge [14], a-Ge films [15, 16], and a-$Si_{1-x}Ge_x$:H alloys [17], reporting an isotropic signal of a zero crossing g value g_c in the range 2.0175–2.023 and peak-to-peak derivative width ΔB_{pp} (X-band) ∼39–47 G, depending on manufacturing. Recently, related to work on Ge/insulator heterostructures, the current authors have observed[1] a *structured* powder pattern in c-Ge implanted with Ge^+ ions (120 keV; dose $\sim 1 \times 10^{15}$ cm^{-2}), which could be convincingly fitted by a powder pattern shape with $g_\parallel = 1.9998$ and $g_\perp = 2.0265$ using a Gaussian broadening function of $\Delta B_{pp} = 45$ G. A basic work addressed X-band ESR on *crystalline* SiGe alloys [18], reporting on a first *anisotropic center*, termed SG1, in annealed O-implanted c-$Si_{0.9}Ge_{0.1}$ and c-$Si_{0.6}Ge_{0.4}$ alloys, showing ⟨111⟩ trigonal (C_{3v}) symmetry with $g_\parallel = 1.9998$, $g_\perp = 2.0260$, $\Delta B_{pp\parallel} \sim 13$ G and $g_\parallel = 1.9985$, $g_\perp = 2.031$, $\Delta B_{pp\parallel} \sim 22$ G, respectively. It was ascribed to a three-fold coordinated central Ge atom backbonded to only Si, or a combination of Si and Ge, atoms, situated at the interfaces of SiO_2 precipitates in the SiGe matrix.

In the present work, aimed at clarification, we report on the first ESR observation of a new Ge P_b-type interface defect in (100)$Si_{1-x}Ge_x/SiO_2$ heterostructures, herewith paving the way to assess the role of interfacial Ge DBs in device performance and test predictions.

Samples studied were $SiO_2/Ge_xSi_{1-x}/SiO_2$/(100)Si entities with x in the range $0.45 \leqslant x \leqslant 0.93$, obtained through the condensation technique [19, 20] starting from epitaxially growing a $Si_{0.73}Ge_{0.27}$ layer (104 nm thick) on a Si(22 nm)/SiO_2/(100)Si Si-on-insulator substrate wafer, followed by Si capping. Subsequent subjection to multi-step dry oxidation/inert ambient annealing at different temperatures (900–1150 °C range) results in the formation of high quality $SiO_2/Ge_xSi_{1-x}/SiO_2$ top structures with SiGe layers Ge-enriched to atomic fraction x. Transmission electron microscope observations show a high crystalline quality of the SiGe layer of uniform thickness, with two identical sharp interfaces, and from Raman analysis, uniform SiGe composition [20]. Importantly, the applied thermal budget will leave no GeO_2 present. Conventional first harmonic (K-, and Q-band) ESR observations were carried out at 4.2 K. A co-mounted Si:P marker sample [$g(4.2\text{ K}) = 1.998\,69$] was used for accurate g value and defect density determination purposes; see more detail elsewhere [8, 21].

Figure 1 shows a key set of K-band ESR spectra observed for the applied magnetic field **B** ∥ **n** ([100] interface normal) on samples of different Ge fraction x. For the range $0.54 \leqslant x \leqslant 0.73$, a prominent single signal is observed at $g_c = 2.0140 \pm 0.0003$ of $\Delta B_{pp} \sim 23$ G in increasing intensity, reaching $\sim 6.8 \times 10^{12}$ cm^{-2} of the Si/SiO_2 interface for

[1] Unpublished.

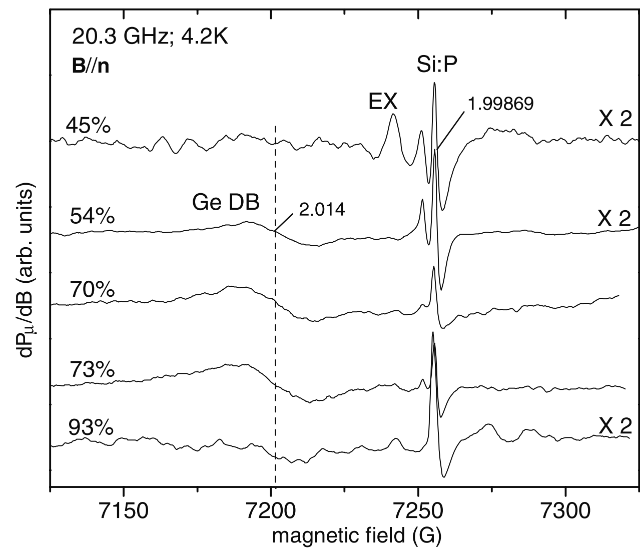

Figure 1. First harmonic K-band spectra observed for **B** ∥ **n** ([100] interface normal) on (100)$Si/SiO_2/Si_{1-x}Ge_x/SiO_2$ entities of different Ge fraction x (%). The signal at $g = 1.998\,69$ stems from a Si:P marker.

$x \sim 0.7$. Notably, apart from a weak isotropic EX center signal (cf figure 1) at $g_c = 2.002\,46$ ($\Delta B_{pp} \sim 3$ G)—an SiO_2 associated defect—no other (interfering) signals, such as Si P_b-type interface centers, are observed, enabling reliable spectral analysis, unbiased by disentanglement issues, unlike in previous work [18]. Angular variation for **B** rotating in the $(0\bar{1}1)$ plane reveals that the signal splits into three branches in a closely 1:2:1 ratio (in order of g_c) intensity ratio. Angular mapping, combining the results of the two ESR frequencies, resulted in a consistent g map, as shown in figure 2. Based on the archival knowledge [22] of encountered point defect symmetries in diamond crystal structures (Si), computer assisted simulation neatly revealed a defect, with C_{2v} (monoclinic-I) symmetry and principal g values $g_1 = 2.003\,38 \pm 0.0003$, $g_2 = 2.0386$, and $g_3 = 2.0054$, with the g_3 (lowest value) axis 31° ± 2° off [100], i.e. 24° ± 2° off a ⟨111⟩ direction towards the [100] interface normal. As apparent from the fitting in figure 2, only three branches out of the seven expected for all equivalent defect orientations in a bulk crystal [22] are observed, indicating the interfacial nature of the defect. Independent direct evidence for the latter was provided through selective etching off the SiO_2 top layer of an $x = 0.73$ sample, resulting in a ∼50% reduction of the ESR signal. In passing, we note that the revealed C_{2v} symmetry and principal g axes orientations are very distinct from the trigonal (C_{3v}) defect previously ascribed to Ge dangling bond type centers in $Si_{1-x}Ge_x$ layers of low x fraction [18]. The latter may concern the $^\bullet Ge\equiv Si_3$ center.

Another noteworthy point, as indicated, is the non-observation by ESR of any Si P_b-type defects for the covered Ge fraction $x \in [0.45, 0.93]$, enabling unobscured interpretation of the Ge defect resonances. With respect to the Ge_xSi_{1-x}/Si interfaces, this may not come as entirely unexpected in the light of previous results [18]. Yet, regardless of the latter interfaces, in particular there is the absence of

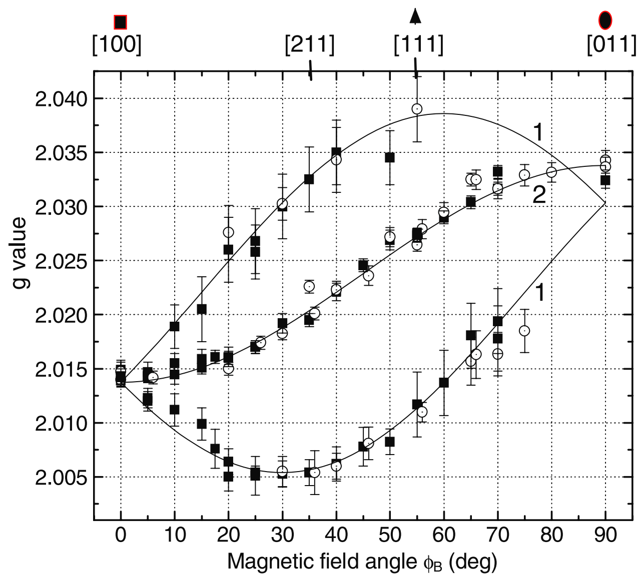

Figure 2. Angular g map of observed GP_{b1} signals at two ESR frequencies [20.3 GHz (■), 34 GHz (○)] on a (100)$Si/SiO_2/Si_{0.27}Ge_{0.73}/SiO_2$ entity for **B** rotating in the $(0\bar{1}1)$ plane. The solid curves represent the fitting result for monoclinic-I point symmetry of a defect in a Si crystal, from where the principal g matrix values $g_1 = 2.0338 \pm 0.0003$, $g_2 = 2.0386 \pm 0.0006$, and $g_3 = 2.0054 \pm 0.0001$ are inferred. The dashed curve branches are not observed experimentally; only the four defect orientations equivalent through the $\bar{4}$-fold symmetry of the (100) face occur clearly exposing the interfacial nature of the originating defect. The added numbers to the branches indicate the relative intensities (area under absorption curves) of the corresponding ESR signals. The g_3 axis is at $31° \pm 2°$ off [100] interface normal.

the stereotypic Si P_b-type signals from the buried SiO_2/Si substrate interface, generally expected regardless of the layers on top. This is not ascribed to limited ESR sensitivity or unusual (different) choice of ESR spectroscopy parameters. Instead, it is seen as the natural result of the sample's thermal history including, among others, an annealing step at 1150 °C. As shown before for thermal (111)Si/SiO_2 [21], such a step may result in drastic elimination of Si P_b-type defects to sub-ESR detectivity levels, due to far advanced relaxation ('viscous flow'), and hence mismatch adaptation, of the (buried) SiO_2 layer in contact with the c-(100)Si substrate.

The basic question then emerges as to the atomic nature of the defect revealed, and its potential electric relevance. Taking the view of an intrinsic DB defect, it could in principle concern an unpaired electron localized in a DB at a Si, Ge, or O atom, where the latter can be credibly excluded on grounds of previous knowledge [23]. Stepping from the known g matrices of the Si $P_{b(0)}$ and P_{b1} interface Si DB defects, closer g value consideration leaves little doubt that the revealed center contains a central Ge DB. Indeed, within a simple molecular orbital consideration for Si or Ge of a DB defect with axial symmetry around the DB direction, simple spin–orbit theory alone predicts $g_\parallel = g_{fe}$ (=2.002 32, the free electron g value) and $g_\perp - g_{fe} = \Delta g_\perp \propto \lambda$, the spin–orbit (SO) coupling constant, where the g properties of the current DB defect are well in line with the ~6.6 times larger λ of Ge than λ_{Si} ($\lambda_{Ge} = 940$ cm^{-1}; $\lambda_{Si} = 142$ cm^{-1}), cf $g_\perp(SiP_b)$ [8] =2.0088 versus $(g_1 + g_2)/2 \sim 2.036$ for the current defect. The conclusion is firmly corroborated by the revealed dominant inhomogeneous line broadening exhibiting a closely linear behavior, amounting to ~1.17 G GHz^{-1} for **B** ∥ [100], resulting from a strain-induced spread σg in g. First order calculation [8] gives $\sigma g_\perp \sim 0.0074$, again ~10 times larger than $\sigma g_\perp (\sim 0.000\,85)$ of Si P_b in thermal [8] Si/SiO_2, as expected on the grounds of λ. The Ge DB g values are affirmed by first principles theory [24]. A striking observation is that the symmetry properties of the currently revealed Ge DB defect are very reminiscent of one of the archetypal P_b-type centers at the Si/SiO_2 interface [25, 26], i.e. P_{b1}, from where we provisionally label the defect as GP_{b1} center.

As known, efficient passivation of the electrically detrimental P_b-type centers at the Si/SiO_2 interface to the (sub)-10^{10} cm^{-2} level is a prerequisite to realize device-grade interfaces, without which there would be no such all-Si dominant semiconductor technology. In this respect, one may wonder about the interaction behavior with hydrogen of the revealed Ge DB interface defect, which is also of potential electrically detrimental character. Such a study may also provide additional insight with regard to the defect's nature. Preliminary studies on thermal treatment in H_2 on an $x = 0.73$ sample indicate that the GP_{b1} defects are, fairly successfully, passivated in H_2 (1 atm, 500 °C, 1 h) by about an order of magnitude. For clarity, such a thermal step would efficiently passivate Si P_b centers in thermal Si/SiO_2 to undetectable sub-10^{10} cm^{-2} levels [10]. The lower efficiency in the current $SiO_2/Ge_xSi_{1-x}/SiO_2$/(100)Si case may have resulted from diffusion limitation on the needed lateral H_2 transport in SiO_2 over ~1 mm in the studied 2 mm-wide slices [27]. Subsequent standard thermal depassivation treatment (vacuum, 605 °C, 40′) fully restored the original GP_{b1} ESR signal, indicating reversal H passivation/depassivation kinetics as well known for Si P_b-type centers [10], attesting to similar chemical reaction schemes.

A basic step on the route to defect identification concerns the atomic backbond arrangement of the central defected Ge atom. Along previous arguments [18], Ge–O bonds are not expected to be part of the defect kernel, while the trigonal basic $^\bullet Ge{\equiv}Ge_3$ and $^\bullet Ge{\equiv}Si_3$ models would simply appear excluded on the grounds of revealed GP_{b1} symmetry. As to the $^\bullet Ge{\equiv}Ge_3$ model, the latter appears corroborated by the results from H passivation studies. Very informative here is the observed defect density dependence on Ge fraction x (cf figure 1). Pertinently, no Ge DB signal is observed for $x \to 100\%$, in agreement with previous work [11]. Collectively, all assembled data, including preliminary explored thermal passivation behavior in H_2, would favor the $^\bullet Ge{\equiv}Ge_2Si$ model, or a variant with some strained central Ge backbond. But obviously, as no observation of resolved ^{73}Ge ($I = 9/2$; 7.8% natural abundance, theoretical atomic hyperfine interactions at ^{73}Ge ~ 2 times smaller than those at ^{29}Si ($I = 1/2$; 4.67% abundant) [23]) hyperfine structure appears feasible by conventional ESR, so final atomic assignment must await comparative first principles theoretical analysis.

The current observation may be put in the context of the thus far elusive role of interfacial Ge DB in Ge/insulator

heterostructures, in particular the theoretical inferences and putative electrical role. As the GP_{b1} defect is unlikely to have concern with the basic trigonal $^{\bullet}$Ge≡Ge$_3$ unit, its observation will not be relevant to theory [12] on the latter, including predicted highly inefficient passivation by hydrogen. Yet, it is felt that the current data may offer a solid test ground, where once correct defect identification is realized, it may open theoretical assessment. Finally, it goes without saying that as an interfacial Ge DB defect detected by ESR, it will potentially operate as a detrimental interface trap, with the degree of threat depending on the particular electron level(s) position in the bandgap—insight into which will require further combined studies of ESR and electrical analysis.

In summary, we have reported on the ESR observation of a first Ge P_{b1}-type defect in a semiconductor/insulator structure, i.e. (100)Si/SiO_2/$Si_{1-x}Ge_x$/SiO_2. It is observed only in the range $0.54 \leqslant x \leqslant 0.73$, in varying intensity and reaching a maximum for $x \sim 0.7$, to become undetectable for $x \leqslant 0.45$ and $x \geqslant 0.93$. With no other overlapping signals present, reliable g mapping together with g value considerations revealed an interfacial Ge DB defect of monoclinic-I (C_{2v}) type symmetry, with presumed DB orbital direction (g_3) 31°±2° off [100] toward [111], unlikely for the trigonal basic Ge P_b center ($^{\bullet}$Ge≡Ge$_3$) or $^{\bullet}$Ge≡Si$_3$. No Si P_b-type centers are observed. The defect symmetry is very reminiscent of the Si P_{b1} center at the thermal (100)Si/SiO_2 interface. Based on the total of the experimental data, interfacial atomic structures $^{\bullet}$Ge≡Ge$_2$Si or ≡Ge–Ge$^{\bullet}$=Ge$_2$ with a strained Ge backbond are provisionally suggested models. No Ge P_b-type defect is observed for $x \to 100\%$, which complies with previous observations and theoretical inference. As before, the observation of the current GP_{b1} defect requires the simultaneous presence of three ingredients at the interface, i.e. Ge, Si, and O, where one role of Si may be the realization of a Ge_xSi_{1-x}/SiO_2 interface with enhanced interfacial strain (mismatch) compared to that of Ge/GeO_x. As the revealed Ge DB defect is not the trigonal Ge P_b ($^{\bullet}$Ge≡Ge$_3$) defect, its observation may not have direct relevance to recent theory; yet the theory might be reiterated for the current GP_{b1} center to potentially account for its disappearance as an ESR-active center for low Si fraction ($x \to 100\%$) with attendant bandgap narrowing.

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