**Oxidation-induced electron barrier enhancement at interfaces of Ge-based
semiconductors (Ge, Ge_{1-x}Sn_x, Si_yGe_{1-x-y}Sn_x) with Al₂O₃**

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Highlights:

- Oxidation in O₃ at 300 °C increases electron barrier height at Ge-Al₂O₃ interfaces;
- Variation of Sn content in Ge_{1-x}Sn_x up to 12% has no effect on valence band energy;
- Formation of a germanate interlayer is hypothesized;
- No composition-sensitive interface dipoles are encountered.

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Abstract. Experiments on internal photoemission of electrons at interfaces of $\text{Si}_y\text{Ge}_{1-x-y}\text{Sn}_x$ binary and ternary alloys ($0 \leq x \leq 0.11$; $0 \leq y \leq 0.19$) with amorphous insulating Al_2O_3 reveal that the application of an additional oxidation step (5 min in dry O_3 at 300 °C) after atomic layer deposition of first ≈ 1 nm of alumina results in a significant increase of the electron barrier height (by ≈ 0.4 - 0.5 eV) as compared to the conventionally grown Al_2O_3 layers. Furthermore, this supplemental oxidation step facilitates the removal of Ge sub-oxides from the interface. The observed electron barrier enhancement is suggested to be caused by formation of a wide gap germanate interlayer between the Ge-based semiconductors and alumina.

1. Introduction

It is long known that the unintentional oxidation of a high-mobility semiconductor surface during deposition of oxide insulator in many cases leads to the formation of a narrow bandgap interlayer (IL) [1]. This IL effectively reduces the height of the electron energy barrier at the formed interface [2-4] resulting in low-field charge injection into the insulating layer and causes charge instability of the gate stack associated with it. In particular, oxidation of Ge results in growth of a GeO_x IL with much reduced barrier for electrons [5-7] enabling low-field electron transport across the gate stack and to the oxide traps. Recent attempt to enhance this barrier by supplemental high-pressure oxidation of the Ge/ GeO_2 stack [8] had delivered no measurable improvement. Furthermore, while the thermal budget for this oxidation processing is compatible with pure Ge, it appears to be prohibitively high for $\text{Ge}_{1-x}\text{Sn}_x$ alloys and their derivatives since tin diffusion through the gate stack is observed above 350 °C [9, 10]. In this work we will show that low-temperature (300 °C) oxidation in O_3 of a ≈ 1 -nm thick Al_2O_3 layer deposited on top of Ge-based semiconductor allows for enhancement of the electron barrier by ≈ 0.5 eV as compared to the conventionally grown Al_2O_3 and by nearly 1 eV as compared to the GeO_2 insulation.

2. Experimental

The $\text{Si}_y\text{Ge}_{1-x-y}\text{Sn}_x$ binary and ternary epitaxial layers with different Sn ($0 \leq x \leq 0.11$) and Si contents ($0 \leq y \leq 0.19$) were grown by reduced pressure chemical vapor deposition (RP-CVD) on 200 mm Ge-buffered Si(001) wafers, i.e., Ge-virtual substrates (Ge-VS), and characterized using a variety of physical methods [9, 10]. The subsequent sample fabrication process flow includes HF-HCl-last wet clean, and atomic-layer deposition (ALD) of 5-nm thick amorphous (a-) Al_2O_3 films from $\text{Al}(\text{CH}_3)_3$ and O_3 precursors at 300 °C with interruption after growth of ≈ 1 nm of the oxide for an *in-situ* 5-min anneal in dry O_3 at 300 °C [9]. Next, the samples were split in two batches: The first one was used to fabricate metal-oxide-semiconductor (MOS) capacitors for electrical characterization by Pt deposition as reported elsewhere [9, 10]. In the second batch, MOS capacitors specifically intended for internal photoemission (IPE) experiments [4, 11] were prepared by pulsed laser deposition (PLD) of 20-nm thick a- Al_2O_3 capping layer on unheated substrates followed by thermoresistive evaporation of semitransparent (13-nm thick) Au electrodes and 0.5- μm thick Al backside contact layer. Comparison of capacitance-voltage curves indicates that PLD of Al_2O_3 capping layer causes no significant degradation of the $\text{Si}_y\text{Ge}_{1-x-y}\text{Sn}_x/\text{Al}_2\text{O}_3$ interface properties. The O_3 -annealed oxide stacks were compared to the reference samples with 2-nm thick GeO_2 IL grown in O_2 (1 atm.) at 450 °C and then *in situ* capped by a 6-nm thick a- Al_2O_3 grown by ALD at 300 °C and to the samples with direct PLD of 20 nm Al_2O_3 on the cold substrate immediately after the same HF-HCl wet clean [3, 4]. Table 1 lists the compositions and thicknesses of the studied $\text{Si}_y\text{Ge}_{1-x-y}\text{Sn}_x$ epi-layers and of the insulating stacks. Further, comparison is made to the reported IPE results [7] on $\text{Ge}_{1-x}\text{Sn}_x$ samples with single-layer a- Al_2O_3 insulation deposited in a wide temperature range (-50 to 300 °C) using ALD or molecular-beam deposition [12].

IPE experiments were conducted in the photon energy ($h\nu$) range 1.5–6.5 eV with constant spectral resolution of 2 nm using arrangement illustrated in Fig. 1(b): The MOS capacitor is illuminated by photons of known energy while applying bias voltage V between semitransparent top electrode and semiconductor substrate. Once the energy of photons becomes sufficient to inject electrons from semiconductor over the barrier into the oxide, a photocurrent appears due to electron drift towards positively charged metal electrode. In the case of low or moderately doped semiconductor the spectral threshold of electron photoemission Φ_e corresponds to the energy barrier between the top of semiconductor valence

band (VB) and the bottom of the oxide conduction band (CB) as illustrated in the inset in Fig. 1(b). To determine this spectral threshold, the IPE quantum yield (Y) defined as photocurrent normalized on the incident photon flux is analyzed as a function of photon energy. More details on the IPE technique can be found elsewhere [4, 11].

3. Results

Figure 1 compares semi-logarithmic plots of the IPE yield spectra as measured on differently processed samples under the same bias of +2 Volt applied to the top Au electrode. The spectral curves in panel (a) clearly reveal the major effect: As compared to the reference samples (no *in-situ* O₃ oxidation step), supplemental O₃ oxidation shifts the energy onset of electron IPE to higher photon energies by $\approx 0.4\text{-}0.5$ eV as indicated by the horizontal arrow. This behavior is consistently observed in samples fabricated on various Ge-based substrates: The examples shown in Fig. 1(b) include Si_{0.04}Ge_{0.85}Sn_{0.11} and Ge_{0.97}Sn_{0.03} layers, the Ge-VS, as well as 1.1% tensile strained 50-nm Ge film pseudomorphically grown on top of the relaxed 250-nm thick Ge_{0.9}Sn_{0.1} buffer layer. The reproducible up-shift of the IPE spectral threshold suggests that it is related to the oxide IL in its origin rather than to composition or strain state of the semiconductor. Indeed, the tensile-strained Si_{0.19}Ge_{0.78}Sn_{0.03} layer with 20-nm PLD-grown Al₂O₃ film (without O₃ anneal) exhibits a lower IPE threshold. In its turn, the latter is up-shifted by ≈ 100 meV with respect to the Ge-VS sample with the un-annealed GeO₂/a-Al₂O₃ gate stack which is consistent with the VB top shift found in the Si_yGe_{1-y} alloys with increasing Si content [13]. Interestingly, the low-energy IPE spectral band observed above the threshold at around 2.2-2.3 eV and related to electron IPE into the CB of GeO_x IL [5, 6] is not resolved in the O₃-annealed samples suggesting that the IL is chemically changed during annealing in O₃.

Spectral thresholds corresponding to electron IPE from the VB of semiconductor into the alumina CB [$\Phi_e(\text{Al}_2\text{O}_3)$, cf. the inset in Fig. 1(b)] were determined using linear fitting of the $Y^{1/3}$ - $h\nu$ plots [14] as illustrated in Fig. 2 revealing substantial shift of $\Phi_e(\text{Al}_2\text{O}_3)$ to a higher photon energy. In addition, they also exhibit the deviation of the quantum yield behavior from the ideal model [14] at $h\nu \approx 3.2\text{-}3.3$ eV which can be associated with excitation of direct optical transitions between high-symmetry points near the center of the semiconductor Brillouin zone (E'_0 and $E'_0 + \Delta'_0$ in Ge in notations of Adachi, Ref. 15). Since the final state of electrons excited by these transitions lies energetically well below the bottom edge of the

alumina CB, the rate of the IPE yield increase with photon energy above the onset of the E'_0 and $E'_0 + \Delta'_0$ excitations becomes lower since the latter attenuate the incident light but give no contribution to IPE. The absence of the corresponding yield attenuation feature in the samples with supplemental O_3 anneal indicates that the energy onset of electron IPE in alumina $\Phi_e(Al_2O_3)$ becomes higher than the onset of the E'_0 and $E'_0 + \Delta'_0$ excitations.

Next, to account for the influence of the image-force barrier lowering (the Schottky effect), the inferred IPE threshold energies were plotted as a function of average electric field in the oxide stack (F) using Schottky co-ordinates $\Phi_e - F^{1/2}$ as illustrated in Fig. 3. In samples not subjected to the O_3 -anneal the zero-field barrier height $\Phi_e(0)$ is found in the range 2.85-2.90 eV in good agreement with the previously published results on electron IPE from the GeO_2 -passivated Ge and from $Ge_{1-x}Sn_x$ alloys into the ALD-grown a- Al_2O_3 [4-7]. The lowest IPE threshold $\Phi_e(GeO_x)$ in these samples is between 2.2 and 2.3 eV samples (Φ_2 in Ref. 5) and can be compared to $\Phi_e(0) = 2.4$ eV corresponding to electron IPE from Ge into the high-pressure thermally grown GeO_2 [8]. By contrast, in the O_3 -annealed samples a higher value of $\Phi_e(0) \approx 3.4$ eV is consistently found. This would mean that, thanks to the relatively low-temperature (300 °C) annealing in dry O_3 , electrons encounter a nearly 1-eV higher barrier than at the GeO_2 passivated Ge interfaces. At the same time, physical analysis [9, 10] indicates that no significant diffusion of Sn occurs at this temperature suggesting the formation of a diffusion barrier layer.

4. Discussion

Addressing the possible mechanism of the observed barrier enhancement it is worth of mentioning that capacitance-voltage curves (not shown here, see Refs. 9 and 10) reveal no flatband voltage shifts which might be correlated with the interface barrier changes. Therefore, one may conclude that interface dipole formation is unlikely to be the cause of the observed electron barrier variation. This conclusion is consistent with only marginal sensitivity of the Ge/oxide interface barrier height to the composition of the IL revealed in several earlier studies [2-6, 8].

Rather, the impact of the O_3 oxidation through the 1-nm Al_2O_3 resembles the effect of other group III elements (La, Y, Sc) which consists in elimination of narrow-gap Ge sub-oxides through formation of wide-gap ILs [16-18]. Indeed, the earlier presented structural

characterization results [9,10] indicate significant overlap of elemental profiles of Al and Ge over depth scale comparable to the thickness of the ALD-grown alumina film (5 nm). The thickness of the IL observed in the electron microscopy images is much smaller, typically less than 1 nm [9] after O₃ treatment at 300 °C. This is much reduced as compared to the ~2.6 nm thick IL after O₃ oxidation at 400 °C [19] indicating, at the same time, that a few-nm thick intermixed Al-Ge oxide layer is formed at the interface. Similar effect, including attenuation of the Ge sub-oxide related IPE signal [16], has earlier been reported upon introduction of La to the Ge/oxide interfaces and then associated with La germanate formation [20,21]. Suggesting a similar mechanism, we hypothesize that the O₃ annealing at 300 °C produces a wide-gap Al germanate phase which acts as effective barrier for both electron injection and Sn out-diffusion as well as the electrically passivating layer [9,10,19]. What is remarkable is that the resulting electron barrier height is by almost 0.5 eV higher than that at the Ge/a-Al₂O₃ interface formed without additional oxidation step or at the La-containing Ge/oxide interfaces [16]: It approaches the barrier height which expected on the basis of the band offset transitivity principle for the case of cubic (γ -phase) Al₂O₃ [4, 22].

At the same time, the increase of Sn concentration up to 12% is seen to have only marginal effect on the VB top position in the semiconductor alloy (within the error margin of ± 0.05 eV, cf. Fig. 2 and Fig. 3) as opposed to the case of Si_yGe_{1-y} semiconductors [13]. This suggests that the bandgap narrowing with increasing Sn content in the alloy [cf. Fig. 1(a) in Ref. 10] predominantly occurs on the CB side of the gap.

5. Conclusions

Measurements of Ge/oxide interface barriers using IPE of electrons indicate that relatively low-temperature (300 °C) oxidation of Ge/a-Al₂O₃ stacks leads to a significant increase (by ≈ 0.5 eV) of the electron barrier height. This beneficial effect is observed on a variety of Ge-based semiconductor interfaces ranging from the relaxed and strained elemental Ge to binary Ge_{1-x}Sn_x and ternary Si_yGe_{1-x-y}Sn_x alloys. We suggest that this barrier enhancement is caused by transformation of Ge-oxide IL into a wide bandgap germanate phase upon O₃ oxidizing treatment of the initially deposited ≈ 1 -nm thick Al₂O₃ layer.

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Table 1. Properties of the studied epi-Si_yGe_{1-x-y}Sn_x/Al₂O₃ stacks

Thickness	Si%	Sn%	Strain	Insulator
<i>With O₃ anneal, Al₂O₃ insulator (5 nm ALD+20 nm PLD)</i>				
65 nm	19	3	tensile	Al ₂ O ₃ (25 nm)
45 nm	12	4	relaxed	Al ₂ O ₃ (25 nm)
53 nm	4	11	compressive	Al ₂ O ₃ (25 nm)
50 nm	0	3	compressive	Al ₂ O ₃ (25 nm)
50 nm	0	6	compressive	Al ₂ O ₃ (25 nm)
225 nm	0	10	compressive	Al ₂ O ₃ (25 nm)
30 nm	0	12	compressive	Al ₂ O ₃ (25 nm)
2.8 μm (Ge-VS)	0	0	tensile	Al ₂ O ₃ (25 nm)
50 nm (s-Ge)*	0	0	1.1% tensile	Al ₂ O ₃ (25 nm)
<i>No O₃ anneal (control)</i>				
65 nm	19	3	tensile	Al ₂ O ₃ (PLD 20 nm)
50 nm	0	3	compressive	Al ₂ O ₃ (PLD 20 nm)
2.8 μm (Ge-VS)	0	0	tensile	Al ₂ O ₃ (PLD 20 nm)
2.5 μm (Ge-VS)	0	0	tensile	GeO ₂ (2 nm)/Al ₂ O ₃ (ALD 6 nm)

* – on top of 250 nm relaxed Ge_{0.1}Si_{0.9} layer.

Fig.1. Semi-logarithmic plots of the electron IPE yield spectra measured (a) on the control (no O_3 anneal) and O_3 -annealed samples prepared by deposition of a- Al_2O_3 on the indicated semiconductor and (b) on the samples with O_3 -annealed Al_2O_3 layers grown on different semiconductors. Inset in panel (b) shows schematic of the observed electron transitions.

Fig.2. Determination of IPE spectral thresholds of electron IPE Φ_e using $Y^{1/3}\text{-}h\nu$ plots as measured on the same control (no O_3 anneal) and O_3 -annealed samples as in Fig. 1.

Fig.3. Schottky plots of electron IPE spectral thresholds as measured on the control (no O₃ anneal) and O₃-annealed samples. Thresholds of electron IPE into a-Al₂O₃[$\Phi_e(\text{Al}_2\text{O}_3)$] and into GeO_x[$\Phi_e(\text{GeO}_x)$] found in this work for Sn concentration up to 12 % (circles) are compared to those from Ref. 7 (squares) for Sn concentration up to 8%.