Excellent surface passivation of germanium by a-Si:H/Al2O3 stacks

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ABSTRACT
Surface passivation of germanium is vital for optimal performance of Ge based optoelectronic devices especially considering their rapidly increasing surface-to-volume ratios. In this work, we have investigated the surface passivation of Ge by a stack consisting of a thin layer of hydrogenated amorphous silicon (a-Si:H) and an aluminum oxide (Al$_2$O$_3$) capping layer. Plasma-enhanced chemical vapor deposition was used to deposit the a-Si:H (0–10 nm), while thermal and plasma-enhanced atomic layer deposition (ALD) were employed for the Al$_2$O$_3$ films (0–22 nm). Transient photoconductance decay measurements revealed a recombination velocity as low as 2.7 cm s$^{-1}$ for an a-Si:H layer as thin as 1.8 nm and an Al$_2$O$_3$ film of only $\sim$6 nm. In this state-of-the-art passivation scheme, the plasma-enhanced ALD process for the Al$_2$O$_3$ capping layer proved superior to the thermal ALD process since it resulted in an exceptionally high negative fixed charge density ($Q_f \sim 10^{13}$ cm$^{-2}$), which proved a key factor for the low surface recombination velocity. Transmission electron microscopy and energy x-ray dispersion revealed that a thin SiO$_x$ layer ($\sim$1.4 nm) forms between a-Si:H and Al$_2$O$_3$ during the ALD process, which is thought to be the origin of this high negative fixed charge density. This passivation stack is regarded as highly interesting for applications such as solar cells, nanolasers, and nano-LEDs based on $p$-type Ge.

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INTRODUCTION
Germanium is a semiconductor that has applications in several technology fields including nano-electronics, photovoltaics, and photonics. Due to its relatively high carrier mobility compared to silicon, it is considered an attractive alternative channel material for 3 nm and beyond gate-all-around field-effect transistors (GAAFET) based on nanowires and (stacked) nanosheets.1 In photovoltaics, Ge is interesting as a light absorber due to its relatively small bandgap. Monocrystalline Ge has been used as a rear absorber in multijunction solar cells2–5 and amorphous SiGe alloys have been used in thin film solar cells.6–9 Furthermore, germanium has the possibility to exhibit direct bandgap photoluminescence9–12 and it is relatively well compatible with the existing silicon CMOS.10,12–14 This makes it currently a frequently investigated material for monolithically integratable optoelectronic devices like nano-LEDs,15 nanolasers,16,14 and photodetectors.15–17

In the aforementioned devices, whose surface-to-volume ratio is continuously increasing, defects at the interface between the semiconductor and the adjacent layer lead to electronic states in the bandgap, which can be detrimental to device performance. In field-effect transistors (FETs), these interface states can lower the sub-threshold slope16–20 and lead to a lower carrier channel mobility.21,22 Moreover, the charge exchange between the semiconductor and interface states or gate oxide states can lead to noise in the drive current (“1/f noise”)19,24 and shifts in threshold voltage (bias
temperature instability). In solar cells, nanolasers and photodetectors interface states can act as non-radiative recombination centers for electrons and holes, which decreases the conversion efficiency. Surface passivation of Ge is essential to mitigate these effects.

In the last few decades, surface passivation of germanium has mainly been investigated in the context of metal–oxide–semiconductor field-effect transistors (MOSFETs). In the case of MOSFETs, surface passivation mostly entails a reduction of the interface defect density \( [D_{\text{it}} \text{ (eV}^{-1} \text{cm}^{-2})] \) between the gate oxide and the germanium channel. Several approaches have been investigated to reduce the \( D_{\text{it}} \) including the use of an ultrathin epilayer silicon interlayer, a germanium oxide \( (\text{GeO}_x) \) interlayer, surface sulfurization, and nitride-based interlayers. Of these approaches, the \( \text{GeO}_x \) interlayer approach, in particular, has been investigated extensively in the last two decades yielding promising \( D_{\text{it}} \) values for \( \text{GeO}_x \) interlayers grown by plasma oxidation \( \left( D_{\text{it}} \approx 4.5 \times 10^{10} \text{ cm}^{-2} \text{ eV}^{-1} \right) \) and thermal oxidation in \( \text{O}_2 \) or \( \text{O}_3 \left( D_{\text{it}} \approx 7.5 \times 10^{10} \text{ cm}^{-2} \text{ eV}^{-1} \right) \).

For optoelectronic devices, passivation entails a reduction in the surface recombination rate of electrons and holes, which depends not only on \( D_{\text{it}} \) but also on the capture cross sections of these states and the fixed charge concentration \( Q \). This makes passivation for such applications somewhat different from passivation for MOSFETs. Moreover, the additional criteria for passivation layers in optoelectronic devices (transparency, carrier selectivity, etc.) are distinct from those for passivation layers in MOSFETs (high \( k \)-value, low leakage current, etc.). The surface recombination rate is commonly quantified by a metric called surface recombination velocity \( S_{\text{eff}} \) \( \text{(cm s}^{-1}) \). An effective reduction of \( S_{\text{eff}} \) can be realized by decreasing the interface state density \( D_{\text{it}} \) between the semiconductor and the adjacent layer (chemical passivation) and/or by shielding the surface from one type of free charge carrier. The latter can occur due to the presence of a built-in electric field induced by, for example, charge that is trapped in the film adjacent to the semiconductor or charge trapped at the interface between these two layers. This surface passivation mechanism is called field-effect passivation and the trapped charges are typically quantified by a fixed charge density \( Q \) \( \text{(cm}^{-2}) \).

In contrast to Ge, extensive literature on surface passivation in the context of optoelectronic applications exists for Si, especially in the context of solar cells. Amorphous silicon \( (\text{a-Si:H}) \) and aluminum oxide \( (\text{Al}_2\text{O}_3) \) have proven to be well-suited and very successful. Amorphous silicon has been reported to reach very low recombination velocities on Si. Values for the recombination velocity below \( S_{\text{eff}} \leq 10 \text{ cm s}^{-1} \) are rare except and also several values below \( S_{\text{eff}} \leq 1 \text{ cm s}^{-1} \) have been reported. These low values are mainly realized due to a very high level of chemical passivation \( \left( D_{\text{it}} \approx 10^9 \text{ cm}^{-2} \text{ eV}^{-1} \right) \). This chemical passivation is likely provided by the relatively high hydrogen content of a-Si:H, which can passivate the main defect at the c-Si interface: silicon dangling bonds. Owing to its high chemical passivation, amorphous silicon played a key role in enabling the highest c-Si solar cell conversion efficiency reported thus far. For Ge solar cells and photodetectors, a-Si:H has been used and investigated as a passivation layer as well, although to a far lesser extent than for Si. A dedicated research study on surface passivation of Ge by a-Si:H from Posthuma et al. shows that surface recombination velocities as low as \( S_{\text{eff}} = 17 \text{ cm s}^{-1} \) can be achieved on p-type Ge \( (11 \text{ cm}) \) using a relatively thick \( (20–80 \text{ nm}) \) a-Si:H film deposited by plasma-enhanced chemical vapor deposition (PECVD). Like a-Si:H on Si, thin films of \( \text{Al}_2\text{O}_3 \) on Si can also achieve very low surface recombination velocities, which are frequently reported below \( S_{\text{eff}} \leq 10 \text{ cm s}^{-1} \) (Ref. 54) and in some cases as low as \( S_{\text{eff}} \leq 1 \text{ cm s}^{-1} \). The mechanism behind this is reported to be a combination of a high negative fixed charge density \( (10^{12} \text{ cm}^{-2} < Q_i < 10^{11} \text{ cm}^{-2}) \), which induces field-effect passivation, and relatively low density of interface states \( (D_{\text{it}} \approx 5 \times 10^{19} \text{ cm}^{-2} \text{ eV}^{-1}) \). Inspired by the success of \( \text{Al}_2\text{O}_3 \) for the surface passivation of c-Si surfaces, we investigated in our previous work the surface passivation of Ge by ALD \( \text{Al}_2\text{O}_3 \) for optoelectronic applications. We found a surface recombination velocity of \( S_{\text{eff,max}} = 170 \text{ cm s}^{-1} \) on p-type Ge \( (0.2 \text{ cm}) \) after optimization of the ALD substrate temperature, film thickness, and post-deposition annealing (PDA) temperature. Moreover, we found a negative fixed charge density of \( Q_i \approx -2 \times 10^{12} \text{ cm}^{-2} \), which contributed to field-effect passivation.

To reduce the surface recombination velocity of Ge even further, one should ideally apply a film on Ge that exhibits very good chemical passivation and a high degree of field-effect passivation. For this purpose, we have investigated a passivation stack that combines a thin PECVD a-Si:H layer for chemical passivation with a capping layer of ALD \( \text{Al}_2\text{O}_3 \) for field-effect passivation. Both thermal and plasma-enhanced ALD \( \text{Al}_2\text{O}_3 \) were investigated since differences in the magnitude and behavior of the fixed charge density have been reported on Si by several authors. Symmetric lifetime wafers were made and analyzed by transient photocurrent technique and corona-lifetime measurements to determine the surface recombination velocities and the fixed charge densities, respectively. These measurements were supplemented with capacitance voltage profiling to determine \( D_{\text{it}} \) and transmission electron microscopy (TEM) to analyze the interfaces. We show that state-of-the-art surface passivation of Ge can be reached using a-Si:H/\( \text{Al}_2\text{O}_3 \) stacks \( (S_{\text{eff}} = 2.7 \text{ cm s}^{-1}) \) and that this is partly related to a very high negative fixed charge density \( (|Q_i| \geq 9 \times 10^{12} \text{ cm}^{-2}) \).

**EXPERIMENTAL DETAILS**

Double side polished n-type Ge wafers \( (325 \pm 25 \mu \text{m}, <100>, \rho = 1–3 \Omega \text{ cm}) \) and p-type Ge wafers \( (304 \pm 2 \text{ and } 150 \pm 10 \mu \text{m}, <100>, \rho = 1–3 \Omega \text{ cm}) \) were procured from Umicore as substrates. From earlier work, it is known that an oxide free Ge surface prior to the deposition of a-Si:H is important to obtain good passivation. For this purpose, we investigated two wet-chemical surface cleans to remove the native oxide from Ge surface prior to deposition of a-Si:H \( (1\% \text{ aqueous hydrofluoric acid (HF)} \) for \( 90 \text{ s} \) and \( 20\% \text{ aqueous hydrogen bromide (HBr)} \) for \( 90 \text{ s} \)) and compared these to the case of no surface clean. We found an inverse correlation between the amount of germanium oxide on the surface prior to a-Si:H deposition and the lifetime of the Ge wafer passivated by a-Si:H. This indicates that removal of germanium oxide is indeed important to achieve good surface passivation by a-Si:H.
Although HBr shows slightly better results compared to HF, we have chosen HF as standard clean because it was routinely available. The intrinsic a-Si:H layers were deposited at a table temperature of 200 °C by PECVD at a pressure of 10 mTorr using argon diluted silane in a remote inductively coupled plasma (ICP). An Oxford Instruments Plasmalab System 100 ICP PECVD was used for this purpose. With Raman spectroscopy, we confirmed that the PECVD process yields amorphous films on HF cleaned Ge substrates (see Fig. S3 of the supplementary material). The Al$_2$O$_3$ films were deposited at a table temperature of 200 °C by atomic layer deposition in a FlexAL$^\text{TM}$ system from Oxford Instruments.$^7$ The first half cycle of the plasma-enhanced ALD (PEALD) process consists of vapor drawn dosing of the Al-precursor trimethylaluminum [TMA, Al(CH$_3$)$_3$], 99.999% pure, Dockweiler Chemicals] at a background pressure of 23 mTorr. A remote inductively coupled oxygen plasma at 15 mTorr is used as co-reactant in the second half cycle of this ALD process. The first half cycle of the thermal ALD process consists of vapor drawn dosing of TMA at a background pressure of 200 mTorr. Water vapor at 200 mTorr is used as a co-reactant in the second half cycle of this ALD process. At the start of each a-Si:H and Al$_2$O$_3$ deposition, the wafers were subjected to a warmup step in the reactor of 4 min under N$_2$ flow. After deposition, the wafers received a post-deposition annealing (PDA) treatment in a Jipelec Rapid Thermal Anneal furnace. The annealing took place for 10 min at 325 °C in N$_2$ ambient unless stated otherwise. The thicknesses of the a-Si:H and Al$_2$O$_3$ films throughout this work were determined by spectroscopic ellipsometry using a J.A. Woollam Co., Inc. M2000 rotating compensator spectroscopic ellipsometer.

Symmetric lifetime wafers [Ge covered on both wafer sides by the passivating film under investigation, depicted in Fig. 1(a)] were analyzed by transient inductively coupled photoco nductance decay measurements$^7$ using a WCT-120 Photoconductance Lifetime Tester. This tool, originally designed to measure Si wafers, was made suitable for Ge using the work of Cornagliotti et al.$^7$ and Martin et al.$^7$ From the average effective carrier lifetime measured by this technique [$\tau_{\text{eff}} (s)$], the upper limit of the surface recombination velocity [$S_{\text{eff,max}}$ (cm s$^{-1}$)] can be obtained by assuming the surface lifetime $\tau_s$ to be limiting compared to the bulk lifetime $\tau_b$ (i.e., $\tau_s \gg \tau_b$),

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_s} + \frac{1}{\tau_b},$$

where $W$(cm) represents the wafer thickness and $\Delta n$ (cm$^{-2}$) the excess carrier density. We used $\Delta n = 10^{15}$ cm$^{-2}$ to report $S_{\text{eff,max}}$ throughout this work (a value of $\Delta n$ conventionally used in Si passivation studies).$^{74-76}$ The uncertainty in $S_{\text{eff,max}}$ originates from the uncertainties in the parameters of the carrier mobility model and the eddy current conductance sensor, both used to calculate the lifetime and surface recombination velocity from the measured quantities of the WCT-120 Photoconductance Lifetime Tester.

Fixed charges in the passivation layer with a density $Q_f$ (cm$^{-2}$) induce a space charge region in Ge near the surface resulting in field-effect passivation due to the suppression of the surface minority carrier concentration. To determine the fixed charge density corresponding to the Al$_2$O$_3$ layer and the a-Si:H/Al$_2$O$_3$ stack, we conducted corona-lifetime experiments$^{77-79}$ using the Corona Charging System of Delph Spectral Technologies. In this experiment, incremental positive or negative charge was deposited on both sides of symmetric lifetime samples using ionized air molecules generated by a needle at a potential of ±10 kV with respect to the sample. The surface recombination velocity $S_{\text{eff,max}}$ and the deposited surface charge density were measured after each charging step using photoconductance and Kelvin probe potential measurements, respectively. Repetition of these steps allowed us to plot $S_{\text{eff,max}}$ vs the deposited corona charge ($Q_f$). The fixed charge density $Q_f$ equals approximately $-Q_i$ at the point where $S_{\text{eff,max}}$ reaches its maximum value.

For the capacitance–voltage (CV) measurements, a-Si:H/Al$_2$O$_3$ and Al$_2$O$_3$ films were deposited on one side of $n$-type ($\rho = 1-3$ Ω cm) and $p$-type ($\rho = 0.1-0.3$ Ω cm) Ge substrates and consequently contacted by 700 μm diameter Al dots which were thermally evaporated through a shadow mask. An ohmic contact was established on the rear side of the wafer using GaIn eutectic paste. High-frequency (1 MHz) and quasi-static CV measurements were performed using an HP 4284A precision LCR meter and an HP 4140B picoammeter/DC voltage source. $D_q$ as a function of energy was derived from the quasi-static capacitance following Berglund,$^{81}$ and $Q_f$ was calculated from the shift in flatband voltage.$^{82}$

Cross-sectional TEM samples were made using a standard lift-out Focused Ion Beam (FIB) preparation protocol.$^{25}$ The transmission electron microscopy (TEM) study was performed using a probe-corrected JEOL ARM operated at 200 kV and equipped with a 100 nm$^2$ Centurio SDD energy dispersive x-ray (EDX) spectroscope detector.

RESULTS

Figure 1 shows the effect of the amorphous Si interlayer thickness on the Ge surface passivation by the a-Si:H/Al$_2$O$_3$ stack after they were annealed at an optimum temperature of 325 °C to activate the passivation (Fig. S4 of the supplementary material). Data are presented for a-Si:H (red), for a-Si:H with thermal ALD Al$_2$O$_3$ capping layer (green), and for a-Si:H with plasma-enhanced ALD Al$_2$O$_3$ capping layer (blue). Both the thermal and plasma-enhanced ALD Al$_2$O$_3$ capping layers were grown for 50 cycles resulting in thicknesses of 5.6 nm and 4.8 nm, respectively. The stack with plasma-enhanced ALD Al$_2$O$_3$ shows a relatively high surface recombination velocity $S_{\text{eff,max}} \approx 650$ cm s$^{-1}$ when no a-Si:H interlayer is present (most left data point of the blue curve). Insertion of an a-Si:H layer as thin as 1.7 nm decreases $S_{\text{eff,max}}$ over nearly two orders of magnitude down to $\approx 6.9$ cm s$^{-1}$. Increasing the a-Si:H interlayer up to 10 nm did not further improve $S_{\text{eff,max}}$. The thermal ALD Al$_2$O$_3$ film without a-Si:H interlayer (most left data point of the green curve) yields a maximum surface recombination velocity of $\approx 80$ cm s$^{-1}$, which is significantly lower than the $S_{\text{eff,max}}$ value of the Ge/Al$_2$O$_3$ (PEALD) sample. Also, in this case,
The insertion of an a-Si:H interlayer leads to an improvement of $S_{\text{eff, max}}$ (∼29 cm s$^{-1}$). A second stepwise improvement is observed for this stack when the interlayer thickness exceeds 4 nm. The surface recombination velocity is about the same for both types of Al$_2$O$_3$ capping layers. The a-Si:H films without the Al$_2$O$_3$ capping layer show a decreasing surface recombination velocity with increasing film thickness. Significantly higher $S_{\text{eff, max}}$ values are observed compared to the Al$_2$O$_3$ capped samples until the a-Si:H film reaches 10 nm thickness. Note that for the 10 nm thick a-Si:H layer with and without Al$_2$O$_3$ capping we consistently observed local delamination of the film (“blistering”) after annealing [see Figs. S5(a) and S5(b) of the supplementary material]. For certain process and annealing conditions, others have also reported this phenomenon for a-Si:H and Al$_2$O$_3$ films. For thinner films, no blistering was observed in this work.

The 2.3 nm a-Si:H interlayer with a 5.6 nm Al$_2$O$_3$ PEALD capping layer has been studied in more detail. Next to the passivation on lowly doped n-type Ge, this condition was also tested on p-type Ge featuring the same resistivity and crystal orientation (∼2 Ω cm, <100>). The $S_{\text{eff, max}}$ value for this condition is 8.3 cm s$^{-1}$ as shown by the open blue symbol in Fig. 1. Besides this, the inverse effective carrier lifetime of passivated p-type Ge wafers has been plotted vs their inverse wafer thickness in Fig. 2(a). For this

**FIG. 1.** The maximum effective surface recombination velocity $S_{\text{eff, max}}$ measured on Ge (∼2 Ω cm n-type, <100>) as a function of a-Si:H interlayer thickness. Data are presented for a-Si:H without the Al$_2$O$_3$ capping layer (red), with 50 cycles Al$_2$O$_3$ capping layer by thermal ALD (green), and with 50 cycles nm Al$_2$O$_3$ capping layer by plasma-enhanced ALD (blue). The inset is a schematic representation of a symmetric lifetime wafer used for the measurements. The open blue data point represents $S_{\text{eff, max}}$ on p-type Ge (∼2 Ω cm, <100>) instead of n-type Ge. Samples related to this data point are examined in more detail in Fig. 2.

**FIG. 2.** (a) The inverse effective carrier lifetime in p-type Ge wafers (∼2 Ω cm, <100>) vs the inverse wafer thickness. From the slope of the linear fit, the surface recombination velocity $S_{\text{eff}}$ (not $S_{\text{eff, max}}$) has been determined to be 2.7 ± 0.8 cm s$^{-1}$ at $\Delta n = 10^{15}$ cm$^{-3}$. The intersection of the fit with the vertical axis revealed a wafer bulk lifetime of 3.0 ± 0.7 µs. (b) The carrier lifetime measured in one of the passivated 304 and 150 µm thick p-type Ge wafers used in (a) as a function of excess carrier density. The derived bulk lifetime ($\tau_{\text{Bulk}}$) based on these two wafers is shown as well. Ranges for the intrinsic lifetime limits due to radiative recombination ($\tau_{\text{Rad}}$) (Refs. 86–89) and Auger recombination ($\tau_{\text{Aug}}$) (Refs. 86 and 90) are indicated by gray shaded areas. (c) The surface recombination velocity as a function of excess carrier density derived from the data of (b).
purpose, the supplier of the Ge wafers thinned down wafers cut from the same ingot using a surface grinding step which was followed by a polishing step. The plot of Fig. 2(a) allows fitting the lifetime data using Eq. (1) and hence report $\tau_{\text{eff}}$ instead of the upper limit $S_{\text{eff,max}}$. From the slope of the linear fit, the surface recombination velocity $S_{\text{eff}}$ was found to be $2.7 \pm 0.8 \text{ cm s}^{-1}$, which is considerably lower than the upper limit reported before. This is due to the finite bulk lifetime of the wafers. From the intersection of the fit with the vertical axis, the bulk lifetime of the particular wafer type used was found to be $3.0 \pm 0.7 \text{ ms}$. Despite having only two wafer thicknesses, the errors in the values are reasonably low as the six wafers passivated showed good reproducibility. The excess carrier dependence of the lifetime in one of the passivated 304 μm thick p-type Ge wafers used in Fig. 2(a) can be found in Fig. 2(b). Figure 2 also shows the excess carrier dependence of the bulk lifetime [Fig. 2(b)] and surface recombination velocity [Fig. 2(c)] based on these two single wafers. In addition, the ranges for the intrinsic lifetime limits due to radiative recombination ($\tau_{\text{rad}}$) and Auger recombination ($\tau_{\text{Aug}}$) are indicated by gray shaded areas.

In Fig. 3(a), the effect of the a-Si:H interlayer on the fixed charge density $Q_f$ is shown. The Ge/Al$_2$O$_3$ stack with PEALD Al$_2$O$_3$ (red) shows a peak for a deposited positive corona charge density of $Q_c = 0.2 \times 10^{12} \text{ cm}^{-2}$, which means that this stack holds a negative fixed charge density of $Q_f = -0.2 \times 10^{12} \text{ cm}^{-2}$; a relatively low value. Additional data concerning this value are presented in Fig. S6 in the supplementary material. Note that aging of the Ge/Al$_2$O$_3$ stack increases this $Q_f$ value (Fig. S7 of the supplementary material). The latter explains the difference in the $Q_f$ value reported in this work and our earlier work.  The insertion of a 2.3 nm a-Si:H film between the Ge and the PEALD Al$_2$O$_3$ (blue) appears to have a considerable effect on the $Q_f$; the fixed charge density increases with more than an order of magnitude from $Q_f = -0.2 \times 10^{12} \text{ cm}^{-2}$ up to $Q_f \approx -9 \times 10^{12} \text{ cm}^{-2}$. The thermal ALD Al$_2$O$_3$ film deposited directly on Ge (orange) yields a negative fixed charge density of about $Q_f = -3.5 \times 10^{12} \text{ cm}^{-2}$. The insertion of a 2.3 nm a-Si:H interlayer between this layer and the Ge (green) lowers the $Q_f$ to a value of $Q_f \approx -1 \times 10^{12} \text{ cm}^{-2}$, which is the opposite trend as found by PEALD Al$_2$O$_3$.

With regard to the experiment presented in Fig. 3, it is worthwhile to mention that we verified our PEALD Al$_2$O$_3$ process and our corona-lifetime procedure by also performing a corona-lifetime experiment on a Si substrate passivated by the PEALD ALD Al$_2$O$_3$ similar to in our earlier work. The result of the experiment is shown in Fig. S9 of the supplementary material. In this experiment, we found a fixed charge density of $Q_f \approx -4.5 \times 10^{12} \text{ cm}^{-2}$, which is similar to the earlier reports of PEALD Al$_2$O$_3$ on Si substrates using similar process conditions and deposition tools ($Q_f \approx -5 \times 10^{12} \text{ cm}^{-2}$).

Capacitance-voltage measurements were performed to further analyze the Ge/Al$_2$O$_3$ (PEALD) and Ge/a-Si:H/Al$_2$O$_3$ (PEALD) interfaces. The capacitance–voltage data are presented in Figs. S11 and S12 of the supplementary material. For the Ge/Al$_2$O$_3$ (PEALD) interface, an interface state density $D_{\text{it}} \approx 1 \times 10^{12} \text{ cm}^{-2} \text{eV}^{-1}$ was extracted at midgap. From the shifts in flatband voltage, a negative fixed charge density of $Q_f \approx -0.3 \times 10^{12} \text{ cm}^{-2}$ was derived, which is in good agreement with the value determined by the corona-lifetime experiments (Fig. 3). For the Ge/a-Si:H/Al$_2$O$_3$ stack, the observed flatband shifts were consistent with the value of $Q_f$ obtained from corona measurements as well. Further interpretation of the Ge/a-Si:H/Al$_2$O$_3$ data in terms of $Q_f$ proved, however, difficult and no reliable value for $D_{\text{it}}$ could be extracted.

In Figs. 4 and 5, the results on the film thicknesses, interface properties, and chemical composition of the Ge/a-Si:H/Al$_2$O$_3$ passivation stacks are presented. Figure 4(a) shows a cross-sectional bright-field scanning transmission electron microscopy (BFTEM) image of the a-Si:H/Al$_2$O$_3$ (PEALD) stack deposited on Ge $<$100$>$ with 2.3 nm a-Si:H and 50 cycles ($\sim$5.6 nm) PEALD Al$_2$O$_3$ (the same condition as in Fig. 2). Figure 4(b) shows a cross-sectional BFTEM image of an a-Si:H/Al$_2$O$_3$ stack in which Al$_2$O$_3$ has been deposited by thermal ALD. The a-Si:H interlayer was chosen to have a similar thickness as in Fig. 4(a) (2.3 nm a-Si:H) and the Al$_2$O$_3$ film was grown with the same number of ALD cycles as in Fig. 4(a). This resulted in a slightly thinner film ($\sim$4.8 nm) due to the lower growth per cycle of the thermal ALD process. The upper layer of SiO$_2$ in Figs. 4(a) and 4(b) has been deposited as a protection layer for the FIB procedure.

From Fig. 4(a), it becomes clear that a substantial SiO$_2$ layer forms between the a-Si:H and the Al$_2$O$_3$ layers during the PEALD process. The thickness of this layer and the thicknesses of the other layers are estimated by an intensity profile (see Fig. S13 of the supplementary material) made of the cross-sectional TEM image.
presented in Fig. 4(a). The layers in Fig. 4(a) measure 1.8 ± 0.2 nm a-Si:H, 1.4 ± 0.2 nm SiOx, and 6.2 ± 0.2 nm Al2O3, respectively. This is close to the earlier mentioned thicknesses determined by ellipsometry. A similar procedure was performed for Fig. 4(b) (see Fig. S13 of the supplementary material) revealing 1.7 ± 0.2 nm a-Si:H, 1.0 ± 0.2 nm SiOx, and 4.7 ± 0.2 nm Al2O3. The SiOx layer is thinner in this case and therefore hardly visible in Fig. 4(b).

Figure 5 shows the corresponding EDX profiles of the Ge/a-Si:H/Al2O3 stacks shown in the TEM images in Fig. 4. At the Ge surface, no significant oxygen peak is present, which is in line with the fact that the HF removes the majority of the native GeOx prior to the PECVD process of a-Si:H (Fig. S1 of the supplementary material). At about 1.8 nm from the germanium surface, the oxygen signal sets in. The aluminum signal starts to increase slightly further away from the substrate than the oxygen signal. This indicates that there is a thin SiOx layer between a-Si:H and Al2O3. For plasma-enhanced ALD Al2O3, the difference between O− onset and Al− onset is larger (~1.2 nm) than for thermal ALD Al2O3 (~0.8 nm), indicating a thicker SiOx layer. This is consistent with what we found from the TEM images. With regard to the Al2O3 layer, it was observed that the O/Al ratio of the thermal ALD Al2O3 layer is higher than the O/Al ratio of the PEALD Al2O3 layer. This could be attributed to the presence of more oxygen in the form of OH− groups.92

**DISCUSSION**

From Fig. 1 of the Results section, it becomes clear that the maximum surface recombination velocity of the Ge surface
passivated by PEALD Al$_2$O$_3$ decreases substantially (from $S_{\text{eff,max}} \approx 650 \text{cm}\cdot\text{s}^{-1}$ to $S_{\text{eff,max}} \approx 6.9 \text{cm}\cdot\text{s}^{-1}$) by the insertion of an a-Si:H interlayer as thin as 1.7 nm. This demonstrates that this approach greatly improves the surface passivation. As $S_{\text{eff,max}}$ assumes an infinite bulk lifetime, the actual $S_{\text{eff}}$ is even lower as was shown by the experiment with different thicknesses as reported in Fig. 2(a).

The latter also allowed us to make a comparison with (the limited) the existing literature. We found a value of $S_{\text{eff}} \approx 2.7 \pm 0.8 \text{ cm}\cdot\text{s}^{-1}$ for the a-Si:H/Al$_2$O$_3$ stack on 1–3 Ω cm p-type Ge. This is relatively low compared to, for example, the passivation by pure a-Si:H ($S_{\text{eff}} \approx 17 \text{ cm}^2\cdot\text{s}^{-1}$) reported by Posthuma et al. on p-type Ge featuring a resistivity of 11 Ω cm. It is furthermore low compared to the values reported by Chen et al. ($S_{\text{eff}} \geq 70 \text{ cm}^2\cdot\text{s}^{-1}$) who investigated thermally grown GeO$_2$ (47 nm) as a passivation layer on (1–3 Ω cm, <100>).

We also aimed to investigate the effect of the a-Si:H interlayer on the chemical and field-effect passivation of Ge by Al$_2$O$_3$. For this purpose, we performed corona-lifetime experiments. From the corona-lifetime curves (Fig. 3), information regarding the chemical passivation can be extracted from the peak height of the curves. The height of the peak occurs, namely, at approximately flatband conditions for which $S_{\text{eff,max}}$ depends only on the number of defects and their capture cross sections. From the peak heights, it becomes clear that the chemical passivation of the Ge/Al$_2$O$_3$ (PEALD) and Ge/a-Si:H/Al$_2$O$_3$ (PEALD) stack is not so much different, i.e., there are no indications that a large improved chemical passivation after insertion of a thin a-Si:H interlayer. Yet, remarkably, the passivation by the a-Si:H/Al$_2$O$_3$ (PEALD) stack yields significantly lower surface recombination velocities than the passivation by only Al$_2$O$_3$ (PEALD). This means that the improvement in surface passivation after insertion of a thin a-Si:H layer must stem from an increased field-effect passivation. The latter proved to be the case since the negative fixed charge density increased from $0.2 \times 10^{12}$ to $9 \times 10^{12} \text{ cm}^{-2}$ after insertion of an ~2 nm a-Si:H interlayer. From the c-Si literature on Al$_2$O$_3$ and other dielectrics, it becomes clear that the $Q_f$ of the Ge/a-Si:H/Al$_2$O$_3$ (PEALD) stacks reported in this work ($\approx 10^{13} \text{ cm}^{-2}$) can be considered exceptionally high. Further analysis of the stack [presented in Figs. 4(a) and 5] revealed that PEALD of Al$_2$O$_3$ on a-Si:H leads to the formation of a SiO$_x$ interlayer ($\approx 1.4$ nm). It may very well be that the fixed charge resides very near or at the resulting SiO$_x$/Al$_2$O$_3$ interface. This is plausible as these locations have been reported as locations for the negative $Q_f$ in SiO$_2$/Al$_2$O$_3$ passivation layers deposited on c-Si. Several possible origins of the fixed charges are reported in the literature including charged point defects near the SiO$_2$/Al$_2$O$_3$ interface like aluminum vacancies ($V_{Al}$), oxygen interstitials (O$_i$), and hydrogen interstitials (H$_i$). Moreover, recent work has proposed that SiO$_2$ and Al$_2$O$_3$ intermix at the interface and lead to Al atoms embedded in SiO$_2$, which can create acceptor states that are negatively charged by electrons. The exceptionally high fixed charge density found in this work raises, however, questions about the possible differences in the SiO$_x$ layer formed by the plasma oxidation of a-Si:H compared to c-Si.

The a-Si:H/Al$_2$O$_3$ stack with thermal ALD Al$_2$O$_3$ shows a higher surface recombination velocity ($S_{\text{eff,max}} \approx 29 \text{ cm}\cdot\text{s}^{-1}$) than the a-Si:H/Al$_2$O$_3$ stack with PEALD Al$_2$O$_3$ for a-Si:H interlayer thicknesses lower than 4 nm. The inferior passivation can be attributed to some extent to a slightly lower level of chemical passivation (somewhat higher peak in Fig. 3), but mainly to a lower fixed charge density ($Q_f \approx 1.2 \times 10^{12} \text{ cm}^{-2}$). Dingemans and Kessels pointed out that Al$_2$O$_3$ on c-Si yields, in general, a lower $Q_f$ when synthesized with thermal ALD instead of plasma-enhanced ALD, which agrees with our findings. For thermal ALD Al$_2$O$_3$ on c-Si annealed at ~300°C (like in this work), they report $Q_f \approx 1 \times 10^{12} \text{ cm}^{-2}$, which is very close to $Q_f \approx 1.2 \times 10^{12} \text{ cm}^{-2}$ of thermal ALD Al$_2$O$_3$ measured in this work on a-Si:H. The reason for the lower $Q_f$ of the a-Si:H/Al$_2$O$_3$ stack by thermal ALD compared to the one with plasma-enhanced ALD is not clear yet, but may be related to the thinner SiO$_x$ layer between a-Si:H and Al$_2$O$_3$ (Figs. 4 and 5). While the chemical passivation of Ge by PEALD Al$_2$O$_3$ and a-Si:H/Al$_2$O$_3$ by PEALD is similar, the chemical passivation of a-Si:H/Al$_2$O$_3$ stack by thermal ALD is substantially worse when the a-Si:H interlayer is omitted. This can be seen in Fig. 3 from the significantly higher peak of the Al$_2$O$_3$ curve (orange, scaled by a factor 0.007) compared to the a-Si:H/Al$_2$O$_3$ curve (green). Hence, in this case of thermal ALD Al$_2$O$_3$, a-Si:H does play an important role in the chemical passivation of the Ge surface.

CONCLUSION

In this work, we found that a stack of a-Si:H and Al$_2$O$_3$ can provide excellent passivation of Ge surfaces. Using an a-Si:H layer as thin as 1.8 nm and an Al$_2$O$_3$ film of ~6 nm, we achieved a recombination velocity as low as 2.7 cm s$^{-1}$. The plasma-enhanced ALD process for the Al$_2$O$_3$ capping layer proved superior to the thermal ALD process since it resulted in an exceptionally high negative fixed charge density ($Q_f \approx 10^{13} \text{ cm}^{-2}$), which proved to be a key factor in achieving a low surface recombination velocity. The formation of a SiO$_x$ layer between the a-Si:H and Al$_2$O$_3$ layers was found as a likely candidate for the origin of this high fixed charge density. This passivation scheme is considered highly interesting for optoelectronic applications based on p-type Ge such as solar cells, nanolasers, and nano-LEDs.

SUPPLEMENTARY MATERIAL

See the supplementary material for Figs. S1 until S13.

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AUTHOR DECLARATIONS
Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES


