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Plasma-enhanced atomic layer deposited SiO₂ enables positive thin film charge and surface recombination velocity of 1.3 cm/s on germanium

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Abstract

The excellent field-effect passivation provided by aluminum oxide (Al₂O₃) on germanium surfaces relies on the high negative fixed charge present in the film. However, in many applications a neutral or a positive charge would be preferred. Here we investigate the surface passivation performance and the charge polarity of plasma-enhanced atomic layer deposited (PEALD) silicon oxide (SiO₂) on Ge. The results show that even a 3 nm thick PEALD SiO₂ provides a positive charge density (Q_{tot} , $\sim 2.6 \times 10^{11} \text{ cm}^{-2}$) and a relatively good surface passivation (maximum surface recombination velocity $SRV_{\text{max}} \sim 16 \text{ cm/s}$). When the SiO₂ thin film is capped with an ALD Al₂O₃ layer, the surface passivation improves further and a low midgap interface defect density (D_{it}) of $\sim 1 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ is achieved. By varying the SiO₂ thickness under the Al₂O₃ capping it is possible to control the Q_{tot} from virtually neutral ($\sim 2.8 \times 10^{10} \text{ cm}^{-2}$) to moderately positive ($\sim 8.5 \times 10^{11} \text{ cm}^{-2}$) values. Consequently, an excellent SRV_{max} as low as 1.3 cm/s is obtained using optimized SiO₂/Al₂O₃ layer thicknesses. Finally, the origin of the positive charge as well as the interface defects related to PEALD SiO₂ are discussed.

Germanium (Ge) is well known for its higher carrier mobility and optical absorptance compared to silicon (Si), which makes it a promising material for high-performance optoelectronic devices. However, it has been challenging to integrate Ge into optoelectronic devices essentially due to the abundant defect states present at Ge surfaces and the lack of a stable oxide that would efficiently passivate the surface defects. Therefore, developing an efficient surface passivation scheme for Ge is crucial.

Recently, the surface passivation issue for Ge has been addressed by utilizing atomic layer deposited (ALD) aluminum oxide (Al₂O₃) thin films. Isometsä et al.¹ focused on thermal ALD Al₂O₃ and investigated the effect of wet-chemical pre-treatments and post-annealing and eventually achieved a high effective minority carrier recombination lifetime (τ_{eff}) over 1.4 ms and a maximum surface recombination velocity (SRV_{max}) of $\sim 10 \text{ cm/s}$. Berghuis et al.² optimized the deposition and post-anneal conditions for plasma-enhanced ALD (PEALD) Al₂O₃ and obtained an SRV_{max} as low as $\sim 2.7 \text{ cm/s}$ by introducing a thin (1.8 nm) hydrogenated amorphous silicon (a-Si:H) interlayer between Ge and Al₂O₃. Martin et al.³ studied the impact of an amorphous silicon carbide (a-SiC_x) interlayer to Al₂O₃ passivation and achieved an SRV_{max} of 18 cm/s with a 1 nm thick a-SiC_x film. These results demonstrate that ALD Al₂O₃ provides excellent surface passivation. However, all the above mentioned results show

low SRV_{max} relying on so-called field-effect passivation induced by the high density of negative charges (Q_{tot} , $\sim 2\text{-}10 \times 10^{12} \text{ cm}^{-2}$) present in the Al_2O_3 -based films. This high negative oxide charge does not work in all applications, a good example is a device that has a highly n-doped surface which requires either neutral or positive charge – or transistors that would benefit from neutral oxide charge^{4,5}. There is hence a clear need of positively charged (or tailorable charge) commonly available thin films that would provide low SRV_{max} for Ge surfaces.

Materials that are well known for having a positive charge when deposited on Si include e.g. plasma-enhanced chemical vapor deposited (PECVD) silicon nitride (SiN_x)⁶ (Q_{tot} of $\sim 2.5 \times 10^{12} \text{ cm}^{-2}$), PEALD or PECVD silicon oxide (SiO_2)^{7,8} (Q_{tot} of $\sim 6\text{-}8 \times 10^{11} \text{ cm}^{-2}$) and ALD phosphorus oxide (PO_x)/ Al_2O_3 stack⁹ (Q_{tot} of $\sim 3\text{-}5 \times 10^{12} \text{ cm}^{-2}$). However, it is not guaranteed that these films would behave identically when deposited on Ge. Indeed, PECVD SiN_x was recently discovered to have a negative charge on Ge^{10,11}. ALD PO_x has not yet been reported on Ge surface, most likely because it is not a common process used in microelectronics. SiO_2 has been studied on Ge surfaces but the results are controversial regarding the charge polarity^{12,13,14}. Furthermore, there are no direct SRV measurements available for SiO_2 films on Ge surfaces in literature, making it worth of detailed investigation whether SiO_2 could provide good surface passivation combined with positive/tunable charge.

In addition to field-effect passivation, it is important to have as high interface quality as possible between the passivation layer and Ge substrate. The interface quality is often characterized with interface defect density (D_{it}) and is referred as chemical passivation. The chemical passivation becomes of utmost importance in case of neutral or small positive charge. One well known method to reduce D_{it} is to deposit a hydrogen-rich capping layer such as ALD Al_2O_3 on top of the actual passivation film, which often reduces SRV_{max} and thus makes stacks favorable as the final passivation scheme. For instance, an ALD Al_2O_3 capping has been shown to reduce the SRV significantly in both Ge and Si as compared to bare SiN_x ¹¹.

Here our target is to find a surface passivation scheme for Ge with a positive Q_{tot} and a low SRV_{max} . We focus on SiO_2 -based passivation as based on literature it is a promising material that has been speculated to have a positive charge on Ge. We start by investigating the passivation performance and the charge polarity of PEALD SiO_2 . Then we examine the effect of an Al_2O_3 capping layer on the passivation and try to find an optimum SiO_2 thickness, which still provides a high enough positive Q_{tot} and a low enough D_{it} to result in a low SRV_{max} . Finally we discuss the mechanisms behind the obtained results.

The Ge substrates used in the experiments were n-type Czochralski-grown wafers with 17-39 Ωcm resistivity. PEALD SiO_2 films with varying thickness (3-45 nm range) were deposited on both sides symmetrically. Some wafers were additionally coated with 20 nm thermal ALD to study the impact of a capping layer. All the samples went through post-deposition anneal (PDA) at 400 °C for 30 min in N_2 ambient to activate the passivation. Injection-level-dependent τ_{eff} was measured by photoconductance decay method and corresponding SRV_{max} was determined by the equation:

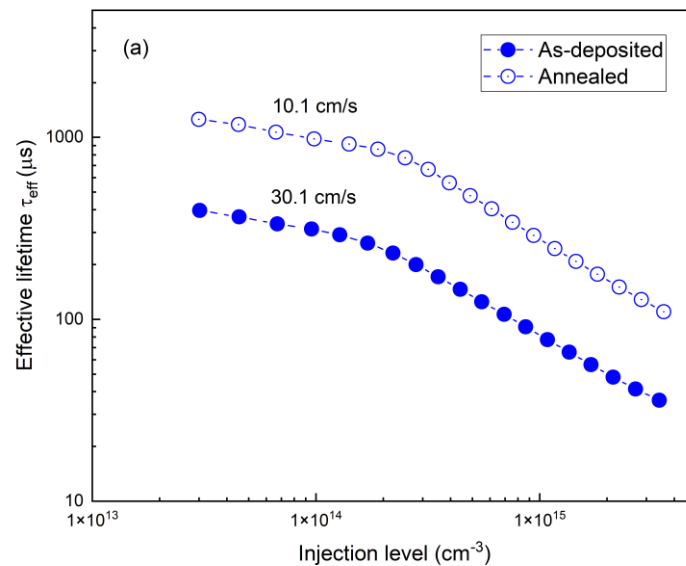
$$SRV_{max} = \frac{W}{2 * \tau_{eff}},$$

where W is the wafer thickness. Q_{tot} and/or D_{it} were assessed using corona oxide characterization of semiconductor (COCOS) method. For more detailed experimental description, please refer to the supplementary.

Fig. 1(a) presents the measured τ_{eff} of the samples passivated with a 20 nm SiO_2 film. For the as-deposited SiO_2 passivated sample, a τ_{eff} of $\sim 313 \mu\text{s}$ ($SRV_{max} = 30.1 \text{ cm/s}$) is achieved at $\Delta n = 1 \times 10^{14} \text{ cm}^{-3}$

³, which can be considered to be already a good value. It is well known that a PDA improves the surface passivation of ALD films^{15,16}, which seems to be the case also for PEALD SiO₂ on Ge as shown in **Fig. 1(a)**. The SRV_{max} is reduced by a factor of 3 to ~10.1 cm/s after the PDA. Thickness of the SiO₂ layer does not seem to impact the SRV_{max} much as evidenced by **Fig. 1(c)**. Actually, rather surprisingly, even as thin as a 3 nm thick SiO₂ layer provides reasonably good passivation increasing SRV only to ~16 cm/s.

While the lifetime results demonstrate that the SiO₂ films passivate Ge surfaces efficiently, the charge polarity of the film needs to be investigated. Therefore, the surface barrier (V_{sb}) was measured as a function of deposited corona charge (Q_c) in the samples, several examples being shown in **Fig. 1(b)**. The flat-band point ($V_{sb} = 0$) was determined in annealed samples and corresponding Q_{tot} polarity and density was obtained. We can see from **Fig. 1(c)** that the measured Q_{tot} is positive and in the range of $2.6\text{-}4.6 \times 10^{11} \text{ cm}^{-2}$ and only slightly increases with SiO₂ thickness. In order to determine the impact of PDA on the charge, Q_{tot} was also measured in as-deposited 45 nm thick SiO₂ sample. The results show that PDA increases Q_{tot} from 2.4×10^{11} to $4.6 \times 10^{11} \text{ cm}^{-2}$, which could explain the difference seen in SRV_{max} via enhanced field-effect passivation. Based on all the above results, we can conclude that the SiO₂ film deposited by PEALD provides both reasonable surface passivation and a positive Q_{tot} polarity independent of the thickness.



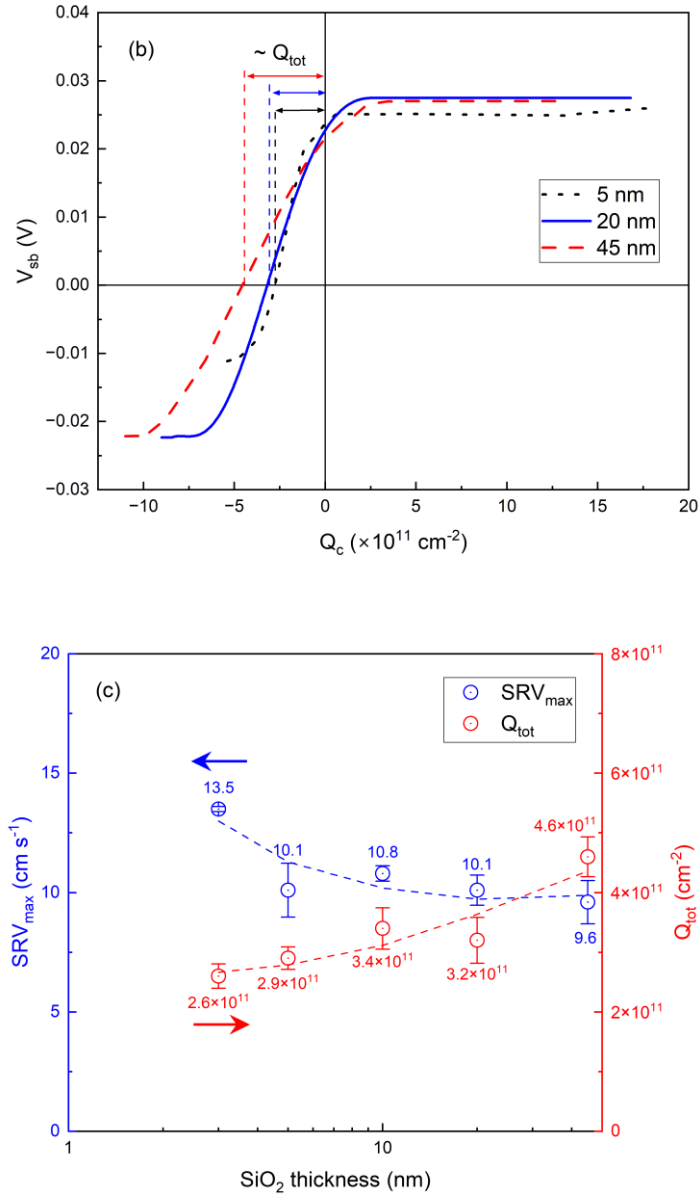


Fig. 1. (a) τ_{eff} of the as-deposited and annealed 20 nm SiO_2 passivated Ge samples. (b) The measured V_{sb} and (c) SRV_{max} and Q_{tot} of annealed samples as a function of SiO_2 thickness. The lines are guides to the eyes.

The earlier research carried out on Si has demonstrated that a hydrogen-rich capping layer on SiO_2 can improve the surface passivation^{8,17}. A similar beneficial effect has also been reported on Ge substrates e.g. by capping SiN_x with Al_2O_3 ¹¹. To investigate if such an effect would take place also in SiO_2 on Ge, 20 nm thick Al_2O_3 layer was deposited on top of SiO_2 samples. **Fig. 2** presents the SRV_{max} of $\text{SiO}_2/\text{Al}_2\text{O}_3$ samples as a function of SiO_2 thickness. If we recall that the SRV_{max} was ~ 10 cm/s in bare SiO_2 samples almost independent of the thickness, we can see that Al_2O_3 capping has indeed a clear impact on the passivation. While a thickness of 3 nm was still enough for bare SiO_2 passivation, the SRV_{max} increases close to 40 cm/s when capped with Al_2O_3 . On the other hand, with the increasing SiO_2 thickness, Al_2O_3 capping starts to show beneficial impact and finally with 45 nm SiO_2 thickness SRV_{max} reaches a value as low as 1.3 cm/s . A similar behavior for Al_2O_3 capped SiO_2 films has been reported earlier on Si, where the SRV_{max} decreased from 10 to 1.5 cm/s while SiO_2 layer thickness increased from 4 to 12 nm, respectively¹⁷.

An additional sample with Al₂O₃ passivation without any SiO₂ film was prepared for reference using identical deposition parameters than the capping layer (square symbol in **Fig. 2**). This highlights the fact that a thin SiO₂ layer is not applicable as an “interlayer” for Al₂O₃ in contrast to a-SiC_x and a-Si:H that have been successfully used to decrease the SRV_{max} of Al₂O₃ passivation^{2,3}. However, it is interesting to note that the best SiO₂ samples in this study provide even better passivation than the reference sample.

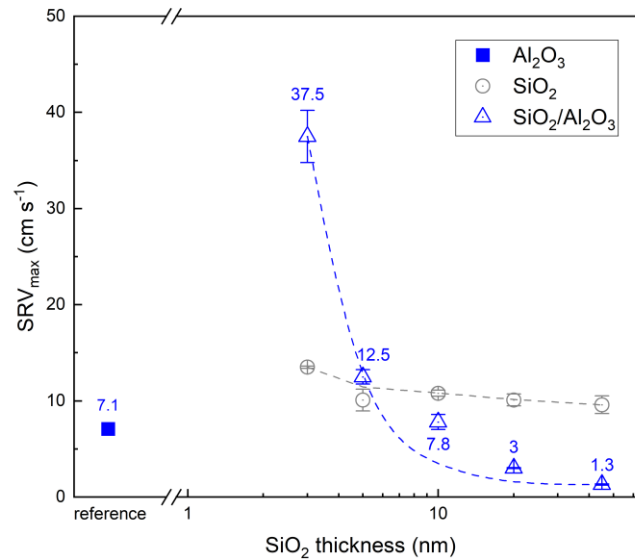


Fig. 2. SRV_{max} of annealed SiO₂/Al₂O₃ samples as a function of SiO₂ thickness. The thickness of Al₂O₃ is 20 nm, and the leftmost square symbol represents the bare Al₂O₃ passivated Ge reference sample. The gray symbols are bare SiO₂ samples replotted from Fig. 1(c).

In addition to a good surface passivation, the main goal in this study is to maintain a positive charge in the passivation film. Since Al₂O₃ is known to exhibit a negative charge, one needs to pay attention to the total charge of the SiO₂/Al₂O₃ stack. On the other hand, Al₂O₃ capping was recently shown to turn the high negative Q_{tot} present in bare SiN_x to virtually neutral¹¹, thus, the total charge seems to be an interplay between the passivation and capping layer and is not always intuitive. Nevertheless, **Fig. 3(a)** shows that in all our SiO₂/Al₂O₃ samples the charge remains positive, although there is a clear thickness dependency. The most noteworthy observation is that even as thin as 3 nm SiO₂ is enough to block out the negative charge of Al₂O₃. On the other hand, with such a thin SiO₂ layer, the charge is only slightly positive, which explains the relatively high SRV_{max} because of the weak field-effect passivation. When the thickness of the SiO₂ layer beneath the Al₂O₃ increases, the Q_{tot} starts to increase further and finally reaches $\sim 8.5 \times 10^{11} \text{ cm}^{-2}$. The Q_{tot} trend as a function of thickness matches well with the SRV_{max} variation: the higher the Q_{tot} the higher the passivation quality i.e. the field-effect passivation increases. In other words, the oxide thickness seems to provide a means to control the Q_{tot} present in the stack.

Intuitively, one needs to optimize the thickness of the passivation layer beneath to maintain the positive charge without having the capping layer too far from the interface¹⁸ so that the capping layer can still have a positive impact on D_{it}. The midgap D_{it} as a function of the SiO₂ thickness in our samples is shown in **Fig. 3(b)** where the SiO₂/Al₂O₃ samples reach very low midgap D_{it} values. Even a value as low as $\sim 1 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ is achieved in samples with 3 nm SiO₂ thickness, which indicates a high-quality dielectric-Ge interface. This is comparable to e.g. thermally grown and/or ozone oxidized GeO₂

interlayer reported earlier in Ge-MOS applications^{19,20}. The midgap D_{it} slightly increases with a thicker SiO_2 and reaches $\sim 5 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ with 45 nm thick SiO_2 , which is expected as the capping layer is moved further away from the Ge/ SiO_2 interface. We speculate that most likely the D_{it} would eventually saturate to a value that should represent the D_{it} in bare SiO_2 samples, which unfortunately could not be determined by COCOS due to unstable corona charge on top of SiO_2 layer. Nevertheless, the results imply that D_{it} is higher in bare SiO_2 . The Al_2O_3 sample as a reference has a rather high D_{it} of $\sim 3 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$, which agrees with the earlier reports². The difference in D_{it} is even more evident in the inset of **Fig. 3(b)**, which shows the D_{it} distribution as a function of the position in the energy gap. When compared to the bare Al_2O_3 sample, $\text{SiO}_2/\text{Al}_2\text{O}_3$ stack reduces the D_{it} significantly to a very low value from the valence band edge to the midgap, which indicates that the defect states located in this energy range can be efficiently passivated by SiO_2 , resulting in a symmetric D_{it} distribution with minimum value around the midgap. From D_{it} point of view, a 3 nm SiO_2 layer seems to work efficiently as a thin interlayer to improve Al_2O_3 interface with Ge although from SRV_{max} point of view, this was not an optimal thickness due to low field-effect passivation.

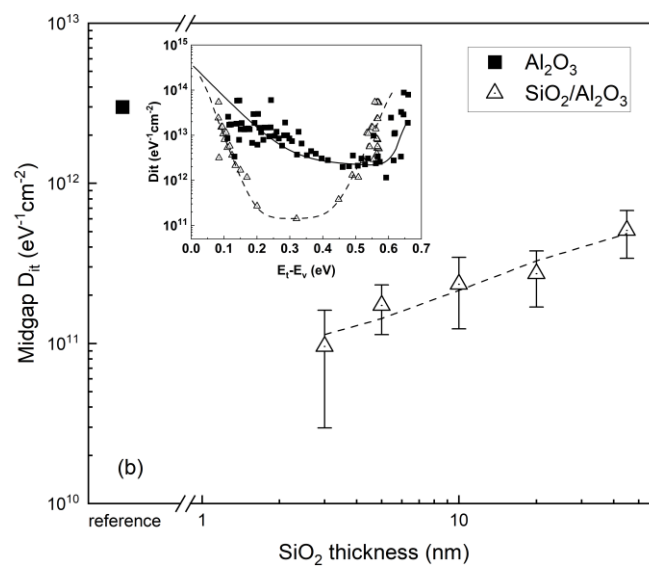
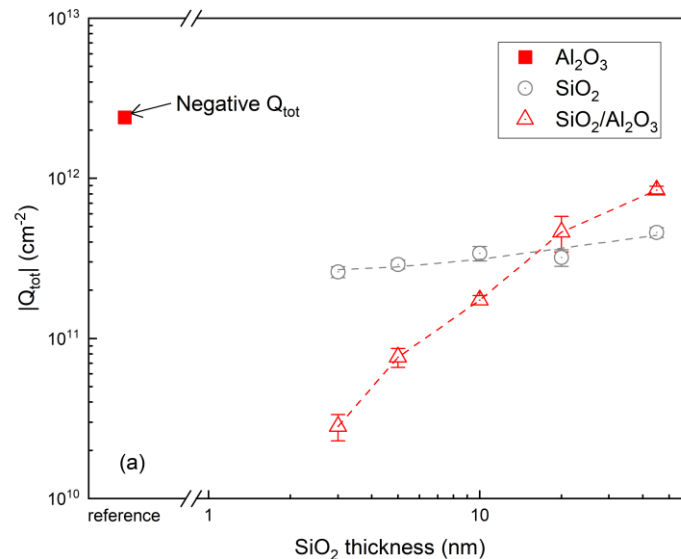


Fig.3. (a) Absolute Q_{tot} and (b) midgap D_{it} as a function of SiO_2 thickness. The thickness of Al_2O_3 is 20 nm, the leftmost square symbol represents the bare Al_2O_3 passivated Ge reference. The gray symbols in (a) are bare SiO_2 samples replotted from Fig. 1(c). The inset in (b) shows an example of the D_{it} as a function of the band gap position for the 3 nm SiO_2 sample capped with Al_2O_3 as well as bare Al_2O_3 sample. The lines are guides to the eyes.

The results in this study demonstrate that with our SiO_2 -based passivation scheme it is possible to obtain positive Q_{tot} in n-type germanium, which is rather challenging as the abundant acceptor-like states of n-type Ge surface tend to bend its energy bands upward with a high negative interface-state trapped charge density (Q_{it})²¹. This intrinsic property hinders positive Q_{tot} formation and triggers many issues e.g. challenges in ohmic metal contact formation for n-type Ge surface^{5,22} and carrier mobility degradation in MOS devices²⁰. In this work PEALD SiO_2 deposition is started with a 5 s oxygen plasma pretreatment to condition the substrate surface before the actual cycles. The highly reactive O radicals likely form a Ge/ GeO_x interface (as also indicated by preliminary XPS data, see supplementary **Figure S1**), which can suppress the defect states²³. Nakashima et al.¹⁴ have earlier reported a positive Q_{tot} of $\sim 3.4 \times 10^{11} \text{ cm}^{-2}$ for $\text{GeO}_2/\text{SiO}_2$ stacks, which is in agreement with our results (**Fig. 1(c)**.) Based on the above, the role of the actual SiO_2 layer alone is not likely that critical as the bulk charge density of SiO_2 itself seems relatively small^{24,25}. In other words, similar positive Q_{tot} could be obtained also by other materials as long as GeO_x formation takes place at the surface and the passivation layer does not have strong negative charge itself. In summary, we speculate that the origin of positive Q_{tot} by implementing PEALD SiO_2 on Ge is mainly 1) the formation of Ge/ GeO_x interface with a positive fixed charge and 2) the elimination of interface defect density resulting in a lower amount of negative Q_{it} .

The results showed a clear impact of Al_2O_3 capping on both SRV_{max} and Q_{tot} . As shown in **Fig. 3(a)** the Q_{tot} becomes heavily dependent on the SiO_2 thickness. In principle, the Q_{tot} of the stack sample consists of the Q_{it} , $Q_{\text{Ge/GeO}_x}$, Q_{SiO_2} and $Q_{\text{Al}_2\text{O}_3}$. As discussed above the $Q_{\text{Ge/GeO}_x}$ is positive. The positive Q_{SiO_2} is originated from the 3-fold bonded oxygen²⁶, magnitude of which is determined by the sum of $\text{GeO}_x/\text{SiO}_2$ interface fixed charge and the SiO_2 bulk charge^{14,24,25,27}. The $Q_{\text{Al}_2\text{O}_3}$ is reported to be related to the trapped electrons that tunnel through the SiO_2 layer and contribute to the negative charge near the $\text{SiO}_2/\text{Al}_2\text{O}_3$ interface^{25,28}. Since the charge is mostly located close to the interface, it is often considered that the thickness of Al_2O_3 would not significantly affect $Q_{\text{Al}_2\text{O}_3}$ ²⁹. As for Q_{it} , it is a thin-film thickness-independent value but determined by the D_{it} , occupational probability of available states and doping type of the germanium. The contribution of Q_{it} in Si substrates is usually omitted because a low D_{it} value ($< 1 \times 10^{11} \text{ eV}^{-1}\text{cm}^{-2}$) is achieved easily by the assistance of hydrogenation, which can effectively saturate the dangling bonds and eliminate the electronically active interface defect states^{8,17}. In the case of Ge, however, there are limited approaches of accomplishing a good interface quality, therefore D_{it} is often significantly higher than in Si. Consequently, the large amount of acceptor-like states producing negatively-charged Q_{it} can play a significant role for the Q_{tot} in case of Ge. However, after capping SiO_2 with Al_2O_3 , all of our samples have a low D_{it} ($\sim 10^{11} \text{ eV}^{-1}\text{cm}^{-2}$), as presented in **Fig. 3(b)**. This indicates that the Q_{it} is rather similar in all the samples and the chemical-passivation provided by Al_2O_3 capping is enough for even 45 nm SiO_2 thickness. Subsequently, the observation that the thinner the SiO_2 , the lower the positive Q_{tot} can be explained such that the change in the Q_{tot} is dominated by $Q_{\text{Al}_2\text{O}_3}$ with easier electron tunneling process, which counteracts the positive $Q_{\text{Ge/GeO}_x}$ and Q_{SiO_2} resulting in a virtually neutral charge density. With a thicker SiO_2 , the electron tunnelling process becomes weaker and the Q_{tot} is dominated by the $Q_{\text{Ge/GeO}_x}$ and Q_{SiO_2} . This would agree well with the tendency on Si substrates²⁵. It is also interesting to notice that even with a thin SiO_2 layer (3 nm) the Q_{tot} remains positive, which indicates that the contributor of negative charge has already been well suppressed.

In this paper, an efficient surface passivation scheme for n-type germanium with a positive Q_{tot} was developed. It was found that PEALD SiO_2 provides a good surface passivation after a 400°C PDA in N_2 ambient. The film contains a positive Q_{tot} with a density of $\sim 3 \times 10^{11} \text{ cm}^{-2}$, which was speculated to originate from the formation of Ge/ GeO_x interface by the oxygen plasma. Positively charged Q_{tot} may thus not be limited to SiO_2 only, but could be obtained with other materials as well. The Q_{tot} of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ stack is SiO_2 thickness-dependent, which can be used to control the Q_{tot} from virtually neutral ($\sim 2.8 \times 10^{10} \text{ cm}^{-2}$) to a moderately positive value ($\sim 8.5 \times 10^{11} \text{ cm}^{-2}$) with an increasing SiO_2 thickness from 3 to 45 nm. Additionally, the Al_2O_3 capping of SiO_2 was found to result in a very low midgap D_{it} of $\sim 1 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$. Consequently, SRV_{max} as low as 1.3 cm/s was achieved as a result of the combination of positive Q_{tot} and low D_{it} which is promising for Ge-based devices.

SUPPLEMENTARY MATERIAL

See the supplementary material for the details about experimental processing, COCOS method and the XPS measurements.

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AUTHOR DECLARATIONS

Conflict of interest

The authors have no conflicts to disclose.

Author Contributions

Hanchen Liu: Conceptualization (equal); Methodology (lead); Writing – original draft (lead); Writing – review & editing (lead). **Toni P. Pasanen:** Conceptualization (equal); Writing – review & editing (lead). **Oskari Leiviskä:** Conceptualization (equal), **Joonas Isometsä:** Writing – review & editing (equal). **Tsun Hang Fung:** Writing – review & editing (equal). **Marko Yli-Koski:** Writing – review & editing (equal). **Mikko Miettinen:** Writing – review & editing (equal). **Pekka Laukkanen:** Writing – review & editing (equal). **Ville Vähänissi:** Writing – review & editing (equal). **Hele Savin:** Funding acquisition (lead); Supervision (lead); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

REFERENCES

- ¹ J. Isometsä, T.H. Fung, T.P. Pasanen, H. Liu, M. Yli-koski, V. Vähänissi, and H. Savin, "Achieving surface recombination velocity below 10 cm/s in n -type germanium using ALD Al₂O₃," *APL Mater.* **9**(11), 111113 (2021).
- ² W.J.H. (Willem-J. Berghuis, J. Melskens, B. Macco, R.J. Theeuwes, L.E. Black, M.A. Verheijen, and W.M.M. (Erwin) Kessels, "Excellent surface passivation of germanium by a-Si:H/Al₂O₃ stacks," *J. Appl. Phys.* **130**(13), 135303 (2021).
- ³ I. Martín, G. López, M. Garín, C. Voz, P. Ortega, and J. Puigdollers, "Effect of the thickness of amorphous silicon carbide interlayer on the passivation of c-Ge surface by aluminium oxide films," *Surfaces and Interfaces* **31**, 102070 (2022).
- ⁴ H.-Y. Jin, and N.W. Cheung, "Forming Gas Annealing Characteristics of Germanium-on-Insulator Substrates," *IEEE Electron Device Lett.* **29**(7), 674–676 (2008).
- ⁵ A. Dimoulas, P. Tsipas, A. Sotiropoulos, and E.K. Evangelou, "Fermi-level pinning and charge neutrality level in germanium," *Appl. Phys. Lett.* **89**(25), 252110 (2006).
- ⁶ S. Dauwe, J. Schmidt, A. Metz, and R. Hezel, in *Conf. Rec. Twenty-Ninth IEEE Photovolt. Spec. Conf. 2002*. (IEEE, 2002), pp. 162–165.
- ⁷ G. Dingemans, C.A.A. van Helvoirt, D. Pierreux, W. Keuning, and W.M.M. Kessels, " Plasma-Assisted ALD for the Conformal Deposition of SiO₂ : Process, Material and Electronic Properties ," *J. Electrochem. Soc.* **159**(3), H277–H285 (2012).
- ⁸ G. Dingemans, M.C.M. van de Sanden, and W.M.M. Kessels, "Excellent Si surface passivation by low temperature SiO₂ using an ultrathin Al₂O₃ capping film," *Phys. Status Solidi - Rapid Res. Lett.* **5**(1), 22–24 (2011).
- ⁹ L.E. Black, and W.M.M. (Erwin) Kessels, "Investigation of crystalline silicon surface passivation by positively charged POx/Al₂O₃ stacks," *Sol. Energy Mater. Sol. Cells* **185**, 385–391 (2018).
- ¹⁰ W.J.H. (Willem-J. Berghuis, M. Helmes, J. Melskens, R.J. Theeuwes, W.M.M. (Erwin) Kessels, and B. Macco, "Extracting surface recombination parameters of germanium–dielectric interfaces by corona-lifetime experiments," *J. Appl. Phys.* **131**(19), 195301 (2022).
- ¹¹ H. Liu, T.P. Pasanen, T.H. Fung, J. Isometsä, O. Leiviskä, V. Vähänissi, and H. Savin, "Comparison of SiN_x -Based Surface Passivation Between Germanium and Silicon," *Phys. Status Solidi* **220**(2), 2200690 (2023).
- ¹² T. Yashiro, "Frequency and Temperature Dependence of C-V Characteristics at Ge-SiO₂ Interface and BT Treatments," *Jpn. J. Appl. Phys.* **9**(7), 740 (1970).
- ¹³ R.S. Johnson, H. Niimi, and G. Lucovsky, "New approach for the fabrication of device-quality Ge/GeO₂/SiO₂ interfaces using low temperature remote plasma processing," *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **18**(4), 1230–1233 (2000).
- ¹⁴ H. Nakashima, Y. Iwamura, K. Sakamoto, D. Wang, K. Hirayama, K. Yamamoto, and H. Yang, "Postmetallization annealing effect of TiN-gate Ge metal-oxide-semiconductor capacitor with ultrathin SiO₂/GeO₂ bilayer passivation," *Appl. Phys. Lett.* **98**(25), 252102 (2011).
- ¹⁵ B. Hoex, J.J.H. Gielis, M.C.M. van de Sanden, and W.M.M. Kessels, "On the c-Si surface passivation mechanism by the negative-charge-dielectric Al₂O₃," *J. Appl. Phys.* **104**(11), 113703 (2008).

- ¹⁶ G. Dingemans, R. Seguin, P. Engelhart, M.C.M. van de Sanden, and W.M.M. Kessels, "Silicon surface passivation by ultrathin Al₂O₃ films synthesized by thermal and plasma atomic layer deposition," *Phys. Status Solidi - Rapid Res. Lett.* **4**(1–2), 10–12 (2010).
- ¹⁷ G. Dingemans, N.M. Terlinden, M.A. Verheijen, M.C.M. Van De Sanden, and W.M.M. Kessels, "Controlling the fixed charge and passivation properties of Si(100)/Al₂O₃ interfaces using ultrathin SiO₂ interlayers synthesized by atomic layer deposition," *J. Appl. Phys.* **110**(9), 093715 (2011).
- ¹⁸ D.K. Simon, P.M. Jordan, I. Dirnstorfer, F. Benner, C. Richter, and T. Mikolajick, "Symmetrical Al₂O₃-based passivation layers for p- and n-type silicon," *Sol. Energy Mater. Sol. Cells* **131**, 72–76 (2014).
- ¹⁹ F. Bellenger, M. Houssa, A. Delabie, V. Afanasiev, T. Conard, M. Caymax, M. Meuris, K. De Meyer, and M.M. Heyns, "Passivation of Ge(100)/GeO₂/high-κ Gate Stacks Using Thermal Oxide Treatments," *J. Electrochem. Soc.* **155**(2), G33 (2008).
- ²⁰ D. Kuzum, Jin-Hong Park, T. Krishnamohan, H.-S.P. Wong, and K.C. Saraswat, "The Effect of Donor/Acceptor Nature of Interface Traps on Ge MOSFET Characteristics," *IEEE Trans. Electron Devices* **58**(4), 1015–1022 (2011).
- ²¹ A. Chroneos, U. Schwingenschlögl, and A. Dimoulas, "Impurity diffusion, point defect engineering, and surface/interface passivation in germanium," *Ann. Phys.* **524**(3–4), 123–132 (2012).
- ²² Y. Zhou, M. Ogawa, X. Han, and K.L. Wang, "Alleviation of Fermi-level pinning effect on metal/germanium interface by insertion of an ultrathin aluminum oxide," *Appl. Phys. Lett.* **93**(20), 202105 (2008).
- ²³ Q. Xie, S. Deng, M. Schaeckers, D. Lin, M. Caymax, A. Delabie, X.-P. Qu, Y.-L. Jiang, D. Deduytsche, and C. Detavernier, "Germanium surface passivation and atomic layer deposition of high-κ dielectrics—a tutorial review on Ge-based MOS capacitors," *Semicond. Sci. Technol.* **27**(7), 074012 (2012).
- ²⁴ V.S. Kaushik, B.J. O'Sullivan, G. Pourtois, N. Van Hoornick, A. Delabie, S. Van Elshocht, W. Deweerdt, T. Schram, L. Pantisano, E. Rohr, L.Å. Ragnarsson, S. De Gendt, and M. Heyns, "Estimation of fixed charge densities in hafnium-silicate gate dielectrics," *IEEE Trans. Electron Devices* **53**(10), 2627–2633 (2006).
- ²⁵ N.M. Terlinden, G. Dingemans, V. Vandalon, R.H.E.C. Bosch, and W.M.M. Kessels, "Influence of the SiO₂ interlayer thickness on the density and polarity of charges in Si/SiO₂/Al₂O₃ stacks as studied by optical second-harmonic generation," *J. Appl. Phys.* **115**(3), 033708 (2014).
- ²⁶ J. Godet, F. Giustino, and A. Pasquarello, "Proton-Induced Fixed Positive Charge at the Si₁₀₀/SiO₂ Interface," *Phys. Rev. Lett.* **99**(12), 126102 (2007).
- ²⁷ Y.Q. Cao, B. Wu, D. Wu, and A.D. Li, "Interfacial, Electrical, and Band Alignment Characteristics of HfO₂/Ge Stacks with In Situ-Formed SiO₂ Interlayer by Plasma-Enhanced Atomic Layer Deposition," *Nanoscale Res. Lett.* **12**(1), 1–7 (2017).
- ²⁸ J. Buckley, B. De Salvo, D. Deleruyelle, M. Gely, G. Nicotra, S. Lombardo, J.F. Damlencourt, P. Hollinger, F. Martin, and S. Deleonibus, "Reduction of fixed charges in atomic layer deposited Al₂O₃ dielectrics," *Microelectron. Eng.* **80**(SUPPL.), 210–213 (2005).

²⁹ N.M. Terlinden, G. Dingemans, M.C.M. Van De Sanden, and W.M.M. Kessels, "Role of field-effect on c-Si surface passivation by ultrathin (2-20 nm) atomic layer deposited Al₂O₃," Appl. Phys. Lett. **96**(11), (2010).