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ABSTRACT

Desirable intrinsic properties, namely, narrow bandgap and high carrier mobility, make germanium (Ge) an excellent candidate for various applications, such as radiation detectors, multi-junction solar cells, and field effect transistors. Nevertheless, efficient surface passivation of Ge has been an everlasting challenge. In this work, we tackle this problem by applying thermal atomic layer deposited (ALD) aluminum oxide (Al₂O₃), with special focus on the process steps carried out prior to and after dielectric film deposition. Our results show that instead of conventional hydrofluoric acid (HF) dip, hydrochloric acid (HCI) pre-treatment is an essential process step needed to reach surface recombination velocities (SRVs) below 10 cm/s. The main reason for efficient surface passivation is found to be a high dielectric charge that promotes the so-called field-effect passivation. Furthermore, the results demonstrate that the post-deposition anneal temperature, time, and ambient play a role in passivating Ge-dangling bonds, but surprisingly, good surface passivation (SRV below 26 cm/s) is obtained even without any post-deposition annealing. The results pave the way for high-performance *n*-type Ge optoelectronic devices that could use induced junctions via negatively charged Al₂O₃ layers.

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INTRODUCTION

Germanium (Ge) is a highly promising material for various semiconductor devices due to its intrinsic material properties such as high electron (\leq 3900 cm² V⁻¹ s⁻¹) and hole mobilities ($\leq 1900 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) as well as a narrow bandgap (0.66 eV). The high mobility allows high switching speeds in complementary metal-oxide-semiconductor (CMOS) transistors, while the narrow bandgap makes Ge attractive in optoelectronic applications, such as infrared detectors and multi-junction solar cells.^{1–11} Despite the prominent merits offered by Ge, its adoption in both CMOS and optoelectronic devices has been challenging, primarily due to the difficulty in passivating Ge surfaces. For instance, thermally grown Ge oxides are known to be highly unstable and water soluble, preventing their utilization for this purpose.^{5,12-18} Consequently, numerous research efforts have been devoted to developing externally deposited thin films that could provide efficient surface passivation for Ge.^{19,1}

Atomic layer deposition (ALD) is one of the most promising methods for high-quality thin film fabrication needed for efficient Ge surface passivation. In particular, ALD deposited high-k materials have been extensively studied in field-effect transistors, aiming for improved device performance.¹⁹ Those studies have focused primarily on the chemical passivation properties of the thin film, which involve the termination of dangling bonds at the Ge-dielectric interface and are often characterized with the parameter called interface defect density (D_{it}) . The interface quality has varied a lot, but eventually, D_{it} as low as 3×10^{11} cm⁻² has been achieved using ALD HfO2.²¹ In addition to D_{it}, there is also another parameter that deserves attention, that is, Qtot of the dielectric film. This parameter impacts the so-called field-effect passivation, which relies on the manipulation of minority carrier density at the interface. This passivation mechanism is especially attractive in optoelectronic devices as in addition to efficient surface passivation, it could also be utilized in the formation of an inversion layer that enables efficient charge collection.²² Quite surprisingly, the field-effect passivation has been mostly neglected in prior Ge passivation studies. Nevertheless, there are preliminary results by Isometsä followed by more systematic studies by Berghuis et al. who had reported promising field effect passivation in Ge by ALD aluminum oxide (Al₂O₃), as demonstrated by a surface recombination velocity (SRV) of 170 cm/s.^{20,23} For high efficiency devices, values below 10 cm/s are typically preferred, so there is still room for improvement. Furthermore, the latter results have been reported only for *p*-type Ge surfaces while *n*-type surface passivation would be interesting in induced junction radiation detectors.²²

While the previous field-effect passivation study by Berghuis et al. had focused mainly on the optimization of ALD parameters,²⁰ it is equally important to pay attention to the processing steps carried out prior to and after dielectric thin film deposition as both these steps affect D_{it} and Q_{tot} and thus the final surface passivation efficiency. Prior to the film deposition, the wafers are typically exposed to some chemical solution. This solution serves the purpose of (1) removing contamination, such as organic and metal impurities and native oxide layer and (2) surface treatment, such as hydride and halide termination. In the case of Ge, neither standardclean 1 (SC-1) nor standard-clean 2 (SC-2) is applicable due to the extremely high etch rate of Ge in hydrogen peroxide (H2O2) solution, which leads to massive material consumption.13 Therefore, only hydrofluoric acid (HF) dip has often been applied. However, the use of HF solution can be rather disadvantageous for preparing Ge surfaces due to inefficient removal of impurities (e.g., oxygen, carbon, and copper) and surface roughness enhancement.^{13,24-28} In addition, the hydrogen (H)-termination coverage on the Ge surface is known to be HF-concentration dependent.²⁴ Furthermore, the H-termination has been found to be unstable under air, which leads to possible exposure of Ge to contamination prior to thin film deposition.^{15,24,29,30} In contrast, hydrochloric acid (HCl), especially in high concentration (e.g., >20%), could be an alternative solution for preparing Ge surfaces for subsequent thin film deposition due to the efficient removal of carbon and oxide layers.^{13,17,28,30,31} Moreover, dipping in HCl results in a smooth Ge surface with monochloride and dichloride termination.^{17,24,30,32} Based on this, it would be worth comparing HF and HCl pre-treatment and their impact on the Ge surface passivation quality. The same applies to the post-ALD treatment. It would be interesting to study, in more detail, how temperature, time, and ambient gas of post-deposition annealing affect the field effect passivation of Ge surfaces.

In this paper, our goal is to develop an efficient surface passivation process for *n*-type Ge surfaces, targeting SRVs below 10 cm/s using a negatively charged dielectric layer that allows the formation of an inversion layer. We start by investigating the impact of HF and HCl surface pre-treatment on the Ge/Al₂O₃ interface properties (D_{it} and Q_{tot}) as well as on the SRV. Then, we examine the impact of post-deposition annealing on the same parameters and focus especially on the role of H by comparing nitrogen (N₂) and forming gas (95% N₂ + 5% H₂) ambient. The impact of temperature and duration of post-deposition annealing on field effect passivation is also investigated. Finally, we discuss the mechanisms behind the effect of pre- and post-treatment parameters on surface passivation and their utilization in actual devices.

EXPERIMENTAL

The process flow of samples studied in this work is outlined in Fig. 1. A batch of 185 µm thick, double-sided polished 4-in. *n*-type {100} Czochralski-grown (CZ) Ge wafers with 18–25 Ω cm base resistivity was used in the experiments. First, the samples underwent a chemical pre-treatment to remove possible surface contamination and the native oxide layer. Two different pre-treatment processes were studied: the first was 31.6% v/v HCl dip for 60 s, whereas the second was 1% v/v HF dip for 90 s; these were followed by de-ionized water (DIW) rinsing for another 90 s. The HCl-treated samples did not receive any DIW rinsing to ensure a Cl terminated surface (more details in the section titled Discussion).²⁹ After the chemical pre-treatment step, an Al₂O₃ layer (n = 1.65 at 633 nm and thickness = 23 nm) was subsequently deposited by thermal ALD at 200 °C using 200 cycles of H₂O and trimethylaluminum (TMA) precursors. Finally, the samples were post-deposition annealed at 400 °C for 30 min to activate Al₂O₃ passivation as such annealing is known to be essential for the Al₂O₃-passivation of silicon (Si).³ Since the optimal temperature and time may be different in Ge, the impact of post-deposition annealing temperature (350-500 °C) and time (10-30 min) was also further examined. Two ambient gases, namely, nitrogen (N₂) and forming gas (95% N₂ + 5% H₂), were separately investigated.

Both the injection-dependent effective minority carrier lifetime (τ_{eff}) and the Ge–Al₂O₃ interfacial properties were extracted using a Semilab PV2000A semiconductor characterization tool.³⁴ τ_{eff} , which reflects the overall recombination activities of a sample, was



FIG. 1. Process flow for the studied samples showing different surface pretreatment and post-deposition annealing conditions. The red arrow represents the selected processing path used in studying the post-deposition annealing time and temperature (in Figs. 3 and 4).

measured by the quasi-steady-state microwave detected photoconductance decay technique (QSS-µPCD).³⁵ The SRV was calculated using the following equation:

$$SRV(\Delta n) = \left(\frac{1}{\tau_{\text{eff}}(\Delta n)} - \frac{1}{\tau_{\text{bulk}}(\Delta n)}\right) \cdot \frac{W}{2} \approx \frac{W}{2 * \tau_{\text{eff}}(\Delta n)}, \quad (1)$$

where $\Delta n \text{ (cm}^{-3})$ is the excess minority carrier density and W (cm) is the wafer thickness.³⁶ The value of SRV was extracted at an injection level of $7 \times 10^{14} \text{ cm}^{-3}$. The above-mentioned calculation assumes that bulk recombination is negligible (i.e., τ_{bulk} is infinite), which is likely a valid assumption as we use high quality substrates. Consequently, the calculated value represents the upper limit of SRV.

The Ge–Al₂O₃ interfacial properties, specifically the thin film charge (Q_{tot}) and D_{it} , were monitored by corona oxide characterization of semiconductor (COCOS) measurement.³⁷ The principle of COCOS measurement is similar to that of the traditional capacitance–voltage (CV) measurement, i.e., the sample surface is swept from accumulation to inversion or vice versa, and simultaneous measurements of surface band bending (V_{sb}) allow extraction of Q_{tot} and D_{it} . Unlike the CV measurement, COCOS measurement is a contactless method as the surface potential difference is measured using a Kelvin probe and the sample surface state is modified by varying the external corona charge (Q_c). The steepness of the V_{sb} curve as a function of Q_c at the inflection point correlates with D_{it} at the semiconductor–dielectric interface, and the amount of shift in the curve with respect to $Q_c = 0$ indicates Q_{tot} in the thin film.

RESULTS

Pre-treatment and post-deposition annealing ambient

Figure 2(a) presents the injection-dependent τ_{eff} for the Al₂O₃ coated samples that experienced different combinations of

pre-treatment (either HF or HCl based solution) and postdeposition annealing ambient (either N₂ or forming gas). The postdeposition annealing temperature and time were fixed to 400 °C and 30 min, respectively. As can be seen from Fig. 2(a), the Al₂O₃ deposition (red and blue markers) results in substantial improvement in surface passivation compared to the reference sample that has no ALD Al₂O₃ layer (black markers), i.e., τ_{eff} increases from 30 µs to hundreds of µs and even above 1 ms in specific samples. Consequently, the extracted SRV, as indicated in the figure, is reduced by more than an order of magnitude for all the ALD Al₂O₃ coated samples.

The impact of pre-treatment on the passivation quality is surprisingly large. The samples that received the HCl pre-treatment (closed markers) show superior SRV (well below 10 cm/s) as compared to the HF pre-treatment counterparts (~15 cm/s), demonstrating that the typical HF pre-treatment is not optimal for Ge surface passivation. The impact of ambient gas during post-deposition annealing is less clear as the forming gas is found to improve $\tau_{\rm eff}$ for the HF pre-treated samples, while the opposite is observed for the HCl pre-treated samples. However, the changes in both cases are relatively small compared to the effect of chemical pre-treatment. In summary, these results suggest that chemical pre-treatment, rather than the ambient gas during post-deposition annealing, plays a much more significant role in achieving good passivation for Ge surfaces. More specifically, the best SRV (6.55 cm/s) is obtained with HCl pre-treatment combined with post-deposition annealing under N₂ ambient.

To shed further light on the passivation mechanisms of the samples, COCOS measurements [see Fig. 2(b)] were performed, aiming to reveal any changes in Ge–Al₂O₃ interfacial properties amongst the samples. The figure shows that positive corona charges (Q_c) are needed in order to achieve a flat-band condition $(V_{sb} = 0)$, which confirms that Q_{tot} is negative in all samples. Interestingly, the samples that experienced HCl pre-treatment show higher Q_{tot} (-2.3 × 10¹² cm⁻²) than those that had HF pre-treatment



FIG. 2. (a) Injection-dependent τ_{eff} of ALD Al₂O₃ coated samples with different combinations of pre-treatments (HCI and HF-based solutions) and post-deposition annealing ambient (either N₂ or forming gas). τ_{eff} measured from a sample without any ALD Al₂O₃ layer is shown as a reference. The value labeled for each curve represents the corresponding SRV extracted at the 7 × 10¹⁴ cm⁻³ injection level. (b) Measured V_{sb} as a function of Q_c of the same samples. The inset shows Q_{tot} extracted from the measured curves.



FIG. 3. (a) Injection-dependent τ_{eff} of the HCI-pre-treated samples post-deposition annealed at different temperatures under N₂ ambient. The value labeled for each curve is the corresponding SRV extracted at the 7 × 10¹⁴ cm⁻³ injection level. The sample that experienced only ALD Al₂O₃ deposition but no post-deposition annealing is shown as a reference. (b) Measured V_{sb} as a function of deposited corona charge (Q_c) of the same samples. The inset shows Q_{tot} extracted from the measured curves.

 $(-1.15 \times 10^{12} \text{ cm}^{-2})$. On the other hand, the steepness of the curve at the inflection point remains relatively unchanged for all samples, indicating that D_{it} is barely affected by the pre-treatment. The COCOS analysis thus indicates that the superior SRV measured on samples with the HCl pre-treatment is due to enhanced field effect passivation as a result of increased Q_{tot} .

Post-deposition annealing temperature and duration

This section aims to further investigate the sensitivity of the Al_2O_3 surface passivation quality to the post-deposition annealing conditions by varying both the annealing temperature and duration. We have selected N_2 ambient and HCl pre-treatment for these experiments because as shown in Fig. 2, this combination resulted

in the best surface passivation. First, we study the impact of postdeposition annealing temperature on the surface passivation quality [Fig. 3(a)]. It is surprising that relatively efficient surface passivation, i.e., an SRV of around 25 cm/s, is achieved even without any postdeposition annealing. Nevertheless, the post-deposition annealing improves the passivation quality further in all samples. While 400 °C temperature results in the best SRV (6.55 cm/s), rather similar surface passivation efficiency is obtained also after 350 and 450 °C post-deposition annealing (~8 cm/s). Increasing the post-deposition annealing temperature further to 500 °C starts to decrease the passivation as $\tau_{\rm eff}$ drops below 1 ms. Once again, the COCOS measurements, as shown in Fig. 3(b), provide further insight into the root-cause for the observed changes in SRV. There is a clear



FIG. 4. (a) Injection-dependent τ_{eff} of the HCI-pre-treated samples post-deposition annealed under different anneal durations in N₂ ambient. The value labeled for each curve is the corresponding SRV extracted at the 7 × 10¹⁴ cm⁻³ injection level. The sample that experienced only ALD Al₂O₃ deposition but no post-deposition annealing is shown as a reference. (b) Measured V_{sb} as a function of deposited corona charge (Q_c) of the same samples. The inset shows Q_{tot} extracted from the measured curves.

correlation with Q_{tot} as a function of post-deposition annealing temperature: the higher the temperature, the higher the Q_{tot} value. It is also clear that the post-deposition annealing generates negative charge in the film as the reference sample without any postdeposition annealing shows only a small negative Q_{tot} . On the other hand, the slope of the $V_{sb}-Q_c$ curve behaves different from that of Q_{tot} : the interface quality seems to remain unchanged until the temperature reaches 450 °C, beyond which a drastic decrease in the interface quality is observed (green curve). These results highlight the complexity of achieving good surface passivation on Ge using ALD Al₂O₃: the high Q_{tot} is not enough for efficient passivation, but the interface quality needs to remain high as well. In our result, the best compromise between these two is achieved at 400 °C.

We also studied how the post-deposition anneal duration affects the passivation and whether shorter annealing would be sufficient in the case of Ge surfaces. Figure 4(a) shows that, indeed, 30 min results in the best passivation but 20 min is already enough to reach 1 ms (SRV of 10 cm/s). Based on the COCOS measurements, it can be seen that Q_{tot} is not affected much between the samples with different post-deposition anneal durations. Somewhat lower SRV (~16 cm/s) after 10 min of annealing could be explained with the lower quality of the Al₂O₃/Ge interface as the V_{sb} slope is less steep in this sample.

DISCUSSION

The results presented in this study demonstrate that chemical pre-treatment prior to ALD plays a critical role in achieving good surface passivation for Ge. In particular, the samples that received the HCl pre-treatment, as opposed to the HF pre-treatment, show a significantly lower SRV. It has been shown that HF pretreatment results in a rougher surface than the HCl counterpart,²⁴⁻²⁸ although the difference (tens of Å rms roughness) can be considered insignificant in the context of surface passivation. In addition, HF pre-treatment has been shown to be less efficient in removing the sub-stoichiometric native oxide and impurities (e.g., carbon and copper) on the Ge surface.^{13,24,25,30,38-40} Based on the aforementioned results, one would expect that the HF-treated surface leads to higher D_{it} and hence higher SRV. The results shown in this study, however, indicate that the primary difference in SRV seems to originate from the difference in Q_{tot} . Finally, to make things a bit more complicated, Qtot measured here after HCl pre-treatment is only slightly higher $(-2.3 \times 10^{12} \text{ cm}^{-2})$ than that in the HF pretreated films measured by Berghuis et al. $(-1.8 \times 10^{12} \text{ cm}^{-2})$.²⁰ This hints that our D_{it} is smaller than that in their study, which could be due to the difference in the ALD deposition mode (thermal vs plasma).

Chemical pre-treatment also affects the termination of Ge atoms at the surface prior to thin-film deposition. It has been shown that a Ge surface treated with 10% HCl resulted in 0.29 \pm 0.06 monolayer (ML) monochloride coverage and 0.50 \pm 0.1 ML dichloride coverage, leading to an ~0.8 ML total chloride coverage.²⁹ In the same study, it has been demonstrated that no more than 0.2 ML coverage was achieved for the sample treated with 2%–14% HF.²⁹ Furthermore, in our study, DIW rinsing was subsequently applied to HF-pre-treated samples due to practical reasons and safety consideration, which may further impair the surface termination. On the other hand, since the HCl

concentration (31.6% v/v) used here is significantly higher than that used in the aforementioned study, it is reasonable to assume that the total chloride coverage on the HCl pre-treated sample is no less than 0.8 ML. In addition, a considerable amount of negatively charged Cl⁻ might remain on the surface prior to Al₂O₃ deposition as no DIW rinsing was applied. Therefore, it is suggested that the high total chloride coverage, coupled with the negatively charged Cl⁻, results in higher negative Q_{tot} at the Ge–Al₂O₃ interface, leading to higher τ_{eff} measured on the HCl pre-treated samples. However, further investigation is required to understand the root cause of the high Q_{tot} measured on the HCl pre-treated Ge surface.

The results presented in this paper also imply that the role of H is different in Ge from Si. Forming gas post-deposition annealing, a widely used process in passivating Si dangling bonds, was found to be less efficient for Ge. In fact, $\tau_{\rm eff}$ was found to be reduced for the HCl-pre-treated sample with the forming gas post-deposition annealing when compared to the N₂ post-deposition annealing counterpart, although the difference was relatively small. The effectiveness of the Ge dangling bond hydrogenation process, provided by the forming gas post-deposition annealing, was demonstrated to be inefficient. It is in agreement with the results by Berghuis *et al.*, where a similar conclusion was drawn from a study on ALD deposition temperature, which is known to affect the H concentration in the film.²⁰

The inefficiency of passivating Ge dangling bonds using H may be explained by considering the dominant charge-state for the key species involved. The donor level $\varepsilon(+/0)$ is defined as the level where H^+ and H^0 have equal formation energy.⁴¹ H^+ or H^0 is stable when the Fermi level (E_f) is below or above $\overline{\epsilon}(+/0)$.⁴¹ Similarly, the acceptor level $\varepsilon(0/-)$ is defined as the level where H⁰ and H⁻ have equal formation energy.⁴¹ H^0 or H^- is stable when the Fermi level (E_f) is below or above $\varepsilon(0/-)$.⁴¹ In most semiconductors, including Si and Ge, the H donor level is located above the acceptor level, leading to a so-called "negative-U" center.⁴¹ In this scenario, H⁰ is never thermodynamically stable, and the charge state of H is better described by the transition level $\varepsilon(\pm)$ between the positive and the negative charge state.⁴² While the $\varepsilon(\pm)$ of H was found to be within the bandgap of Si, it was calculated to be 0.04 eV below the valance band of Ge.⁴² In consequence, H was found to act exclusively as an acceptor in Ge regardless of the doping type.⁴² Coincidently, it was suggested that the dangling bond in Ge also acts exclusively as an acceptor, and hence, it cannot be efficiently passivated by other acceptor-like atoms (e.g., H).42

Finally, it is important to consider what the obtained results mean from the Ge device perspective. It is well known that the best SRV obtained here, 6.55 cm/s, is more than enough for a high-performance device.⁴³ Such a low SRV reduces dark current and improves the internal quantum efficiency. Another benefit is the high negative Q_{tot} measured in ALD Al₂O₃ on the *n*-type Ge surface. With a substrate doping density of 1×10^{14} cm⁻³, the charged insulator is likely to produce a *pn*-junction underneath the surface. Simulations show a depletion region as wide as 1 µm at zero bias voltage in this case. Such an induced junction could be used for charge collection with minimal recombination losses, similar to what has been reported earlier for Si,^{44,45} further boosting the device performance. Another aspect from the device perspective is the post-deposition annealing. Now, we have shown that the best

outcome is obtained with 30 min 400 $^{\circ}$ C post-deposition annealing in N₂, which nicely matches typical metal sintering annealing. Therefore, it is likely that the post-deposition annealing treatment can be combined with metal sintering and there is no need to carry out a separate process step to activate the passivation. Actually, in case the device is sensitive to high temperatures, a good compromise would be to omit the post-deposition annealing step as SRV as low as 25 cm/s was obtained without any post-treatment.

CONCLUSION

In this paper, an efficient passivation method for *n*-type Ge surfaces was developed. SRV as low as 6.55 cm/s was achieved using HCl pre-treatment prior to ALD Al₂O₃ deposition. It was found that the main reason for the high surface passivation efficiency was due to the field-effect passivation: samples that received HCl pretreatment had consistently higher negative Qtot than the HF-pretreatment counterpart. The high Cl termination coverage, coupled with the excess Cl⁻ ions remaining on the surface, was speculated to be the root-cause for the higher negative Qtot measured on the HCl-pre-treated Ge surface. Rather surprisingly, the impact of forming gas post-deposition annealing was found to be less significant for the Ge surface than what has been reported for Si. This could be explained by considering the dominant charge-state for the key species involved: both H and dangling bonds were suggested to be exclusively negatively charged in Ge. Regarding the post-deposition annealing temperature and time, typical metal sintering parameters resulted in the best performance, but rather surprisingly, the surface passivation was already good before the post-deposition annealing. To conclude, the excellent surface passivation combined with highly charged thin film demonstrated in this study paves the way for high efficiency Ge devices, such as multi-junction solar cells and infrared detectors.

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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.

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