Thermomechanical properties of aluminum oxide thin films made by atomic layer deposition

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ABSTRACT

In microelectromechanical system devices, thin films experience thermal processing at temperatures some cases exceeding the growth or deposition temperature of the film. In the case of the thin film grown by atomic layer deposition (ALD) at relatively low temperatures, post-ALD thermal processing or high device operation temperature might cause performance issues at device level or even device failure. In this work, residual stress and the role of intrinsic stress in ALD Al2O3 films grown from Me3Al and H2O, O3, or O2 (plasma ALD) were studied via post-ALD thermal processing. Thermal expansion coefficient was determined using thermal cycling and the double substrate method. For some samples, post-ALD thermal annealing was done in nitrogen at 300, 450, 700, or 900 °C. Selected samples were also studied for crystallinity, composition, and optical properties. Samples that were thermally annealed at 900 °C had increased residual stress value (1400–1600 MPa) upon formation of denser Al2O3 phase. The thermal expansion coefficient varied somewhat between Al2O3 made using different oxygen precursors. For thermal-Al2O3, intrinsic stress decreased with increasing growth temperature. ALD Al2O3 grown with plasma process had the lowest intrinsic stress. The results show that ALD Al2O3 grown at 200 and 300 °C is suitable for applications, where films are exposed to post-ALD thermal processing even at temperature of 700 °C without a major change in optical properties or residual stress.

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I. INTRODUCTION

Thin films made by atomic layer deposition (ALD)1–4 are used as both passive and active layers, for example, in microelectromechanical system (MEMS) devices.10–12 ALD thin films are typically made at relatively low temperatures, below 400 °C, and after coating, these films might be exposed to subsequent thermal processing at temperatures higher than the actual growth temperature. In addition, the device operation temperatures might occasionally exceed the fabrication temperature depending on the environment of use. In these cases, thin films might experience measurable permanent changes, for example, in the sense of the residual stress, composed of intrinsic and extrinsic stress components5–10 causing performance issues at device level or even device failure.

Even though residual stress data for ALD Al2O3 films are published on silicon11–13,24 and on polymers15–20 in a wide temperature range, it is unclear how a large quantity of the residual stress originates from extrinsic source (mainly thermal origin) and what is the role of intrinsic, growth-related stress in the film. The residual stress of thermal ALD Al2O3 is temperature dependent: residual stress decreases with increasing growth temperature.26,31
From residual stress, we are able to differentiate the intrinsic stress part with thermal cycling, as the residual stress measured at the growth temperature can be assumed to be equal to intrinsic stress.24 By thermal cycling, the coefficient of the thermal expansion (CTE) of the thin film can be extracted using the so-called double substrate method.50,51 In the double substrate method, the studied material is grown on two substrates with different CTE values. When the double substrate method is used, the coefficient of the thermal expansion of the film, $\alpha_f$, is calculated as follows:50

$$\alpha_f = \frac{\alpha_2 - \alpha_1}{\frac{\sigma_2(T) - \sigma_1(T)}{T}} \cdot \frac{\sigma_1}{C_0} - \frac{\sigma_2}{C_0} \cdot \frac{\Delta T}{T},$$

where $\sigma_1$ is the residual stress of the first film on a first substrate, $\sigma_2$ is the residual stress of the second film on a second substrate, $\alpha_1$ is the CTE of the first substrate, $\alpha_2$ is the CTE of the second substrate, and $\Delta T$ is the selected temperature range for which the measured stress-temperature slopes $\sigma/(\Delta T)$ should be linear.

The residual stress and mechanical properties of ALD thin films can be tuned by changing the growth temperature by adding interlayers into the material or by using laminated thin films.12,28,44,52,53 Post-ALD thermal processing affects residual stress via changes in film morphology, density, or impurity content.52 In some cases, the post-ALD thermal processing might cause additional problems, for example, blistering due to outgassing of trapped hydrogen, especially known to appear with pinhole-free ALD Al2O3 films, and also delamination problems due to the CTE mismatch between the substrate and the film. Crystallization of ALD Al2O3 requires high annealing temperatures, and it has been reported to start at around 950 °C for 30 min in nitrogen prior to ALD. The purpose with pre-ALD thermal annealing was to prevent possible blistering occurring in the films during post-ALD thermal processing. Selected samples were post-ALD thermal annealed at 300, 450, 700, or 900 °C for 30 min using the 1000 SCCM nitrogen flow. The annealing furnace was ATV Technologie GmbH PEO-603.

Optical characterization on full range (from UV to NIR) was done using FilmTek4000 spectroscopic reflectometry. Furthermore, the samples were analyzed with x-ray reflectivity (XRR), x-ray diffraction (XRD),28 and time-of-flight elastic recoil detection analysis (TOF-ERDA)64,65 for density, crystalline structure, and impurities, respectively. The wafer curvature measurements were done on blank silicon wafers before ALD, after ALD, and after post-ALD thermal annealing using the Toho Technology FLX 2320-S laser-based wafer curvature measurement tool. The residual stress was calculated via Stoney’s equation. The wafer curvature was measured in two directions, in parallel and perpendicular to the wafer flat. The residual stress values given here are average values from these two measurements and are given with maximum measurement uncertainty.25

Some wafers were thermally cycled from room temperature up to 500 °C and back to room temperature with in situ wafer curvature measurement using Toho Technology FLX 2320-S. As this measurement is destructive, the measurement was done only in parallel to the wafer flat, along so-called x-axis. The wafer was held at maximum temperature, 500 °C for 1 min before cooling started. The heating ramp rate was 10 °C/min. Thermal cycling was repeated non-stop maximum of three times. During thermal cycling, the wafers were under continuous nitrogen flow, but the atmosphere was not completely oxygen free.

The thermal expansion coefficient of ALD Al2O3 was evaluated using the double substrate method. Silicon (100) and single-crystal sapphire wafers were used as a substrate material. Single side polished sapphire wafers (100 mm, 526 ± 9 µm from Kyocera) were cleaned with SCI (NH2H2O:H2O2 1:5:1, 65 °C, 10 min) followed by SC2 (H2CH2O:H2O2 1:5:1, 60 °C, 10 min) prior to the ALD process. The ALD process on sapphire was identical compared to coatings made on silicon wafers. Backsides of the wafers were protected during the ALD growth using another wafer, rough side against the backside. The backside growth was larger for 100 mm sapphire wafers about.
<table>
<thead>
<tr>
<th>ALD growth</th>
<th>Residual stress</th>
<th>Post-ALD annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ALD growth</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Thickness (nm)</td>
<td>On silicon</td>
</tr>
<tr>
<td>Me₃Al-H₂O</td>
<td>30 1316 101.0 0.5</td>
<td>366 18</td>
</tr>
<tr>
<td></td>
<td>50 1266 98.2 0.2</td>
<td>229 14</td>
</tr>
<tr>
<td></td>
<td>70 1205 97.8 0.1</td>
<td>412 18</td>
</tr>
<tr>
<td></td>
<td>90 1149 97.5 0.1</td>
<td>482 23</td>
</tr>
<tr>
<td></td>
<td>110 1087 98.5 0.2</td>
<td>490 20</td>
</tr>
<tr>
<td></td>
<td>110 1283 97.8 3.2</td>
<td>472 36</td>
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<td>478 37</td>
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<td>220 15</td>
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<td>222 15</td>
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<td>548 36</td>
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<tr>
<td></td>
<td>300 1150 99.4 1.0</td>
<td>274 17</td>
</tr>
<tr>
<td>Me₃Al-O₂</td>
<td>110 1090 109.6 4.4</td>
<td>564 45</td>
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<td></td>
<td>200 1168 109.7 3.5</td>
<td>424 33</td>
</tr>
<tr>
<td></td>
<td>300 1142 95.9 2.2</td>
<td>191 17</td>
</tr>
</tbody>
</table>

*O₂ plasma.
5–10 mm compared to the backside growth of 150 mm silicon wafers, giving a somewhat larger measurement uncertainty for sapphire wafers. The magnitude of the backside growth to residual stress was not analyzed on sapphire wafers. After the ALD growth, the sapphire wafers were thermally cycled with the same equipment and parameters as the silicon wafers. Film thickness was assumed to be the same on silicon and sapphire. The thermal expansion coefficient of 3.08 and 5.37 ppm/°C was used for silicon and sapphire, respectively, at temperature range from about room temperature (RT) to 180 °C. And at temperature range from about RT to 500 °C, CTE values of 3.45 and 7.0 ppm/°C were used for silicon and sapphire, respectively. Different substrate CTE values were used at different temperature ranges because substrate CTE varies with temperature. Temperature range from RT to 500 °C was selected because most ALD Al₂O₃ CTE values are published on this temperature range.

III. RESULTS AND DISCUSSIONS

ALD Al₂O₃ thin films were characterized for thickness, refractive index, density, and residual stress after ALD and after post-ALD thermal annealing; results are presented in Table I. For as-grown samples made from Me₃Al and H₂O, there was a positive correlation between growth temperature (temperature from 30 to 300 °C) and film density. The density increased with increasing ALD temperature. Surface roughness measured by XRR was independent of the ALD temperature. Low-temperature sample grown at 30 °C had high amount of hydrogen, about 30 at. %. The amount of hydrogen decreased with increasing ALD temperature. The amount of residual carbon decreased with increasing ALD temperature from 2.6 to 0.08 at. %. There was a linear negative correlation between hydrogen in the film and the film density and between the residual carbon and the film density. Low-temperature samples grown at 30–110 °C had small amount of residual chlorine (not included in the Table I) from the reactor, amount being highest at 0.16 ± 0.03 at. % at 110 °C. Film grown at 30 °C was oxygen-rich O/Al ratio being 2.07. High-temperature films had O/Al ratio near stoichiometric Al₂O₃.

For different ALD Al₂O₃ precursor combinations, impurity content (Table I) decreased with increasing ALD temperature. Plasma ALD Al₂O₃ from Me₂Al-O₂ had the low hydrogen content for sample processed at 110 °C of 6.7 at. % compared to about 11 at. % for thermal ALD processes. Thermal Al₂O₃ from Me₂Al-O₃ had high, 6.3 at. % carbon concentration for sample grown at 110 °C. At this temperature density was lower compared to samples made using other oxygen sources. Me₂Al-O₂ and Me₂Al-O₃ were oxygen rich grown at low temperature, at 110 °C. Samples grown at higher temperatures were closer to stoichiometric Al₂O₃. In every case, density increased with increasing ALD temperature. All as-grown samples were amorphous in XRD.

Thickness decrease was observed upon post-ALD thermal annealing for Me₃Al-H₂O samples grown at 110, 200, and 300 °C. Notable thickness change was observed for samples annealed at highest temperature at 900 °C, where also highest values for refractive index (1.71 nm) and density (3.60 g/cm³) were measured. Thickness reduction with increasing post-ALD thermal annealing temperature was due to film densification; thickness reduction upon annealing has been previously reported by several sources. Upon annealing, the hydrogen content decreased with increasing annealing temperature, being at lowest value after annealing at 900 °C. In carbon content, no change upon annealing was detected. The O/Al ratio decreased about 7% for sample grown at 110 °C and annealed at 900 °C.

Refractive index and extinction coefficients were measured as a function of wavelength for as-grown and post-ALD thermally annealed Me₃Al-H₂O samples. The sample grown at 110 °C had lowest refractive index values through the wavelength range from 190 to 1650 nm [Fig. 1(a)]. In refractive index, no major changes were measured after thermal annealing up to 700 °C. Thermal annealing at 900 °C caused a notable change in refractive index for samples grown at 110 and 300 °C. In the extinction coefficient, however, the only nonzero value throughout the wavelength range was observed upon annealing up to 700 °C.
was measured for the sample grown at 110 °C and thermally annealed at 900 °C, and all other samples were nonabsorptive [Fig. 1(b)]; this was the only sample where blistering was detected.

Residual stress results for as-grown Al₂O₃ samples and samples after post-ALD thermal annealing are presented in Table I. For thermal Al₂O₃ made from Me₃Al-H₂O, in a temperature range from 90 to 300 °C, there was a linear negative correlation (−0.99) between ALD growth temperature and residual stress. The residual stress decreased with increasing ALD temperature. This was in line with previously published results. The residual stress of the samples grown at temperatures from 30 to 70 °C showed linear positive correlation (0.96) with increasing ALD temperature. The reason for this behavior is unknown. In this temperature range, from 30 to 70 °C, residual stress had linear positive correlation with film density (0.98) and linear negative correlation with O/Al ratio (−0.98) and impurity content of the film (−0.97 for H and −0.92 for C). For plasma-Al₂O₃ from Me₃Al-O₂, the residual stress decreased linearly with increasing ALD growth temperature (correlation of −0.99). For thermal Me₃Al-O₂ process, there was no linear correlation between the residual stress and ALD growth temperature detected (correlation of −0.49). The residual stress result for repeated thermal Me₃Al-O₂ sample was alike.

For samples grown at 300 °C, highest residual stress was measured for thermal-O₂-based Al₂O₃ process, and residual stress value for the film was 274 ± 17 MPa compared to residual stress of a thermal H₂O-based material of about 220 MPa and a plasma-O₂-based material of 190 MPa. Comparison to published residual stress values for films made by plasma-ALD from Me₃Al and O₂ gives no comprehensive image of the residual stress as published residual stress values vary from compressive to tensile even at the same ALD temperature. High dispersion of published residual stress values in plasma ALD Al₂O₃ is most probably related to many variables in plasma processes. For the thermal Me₃Al-O₂ process, only a single publication covering residual stress was found. The residual stress (Table I) increased due to post-ALD thermal annealing already at temperatures of 450 °C; a high-rise was observed on samples annealed at 900 °C. In literature up to 2000 MPa, tensile residual stress has been measured for ALD Al₂O₃ film annealed at 850 °C. Here, maximum values of about 1400–1600 MPa were measured upon thermal annealing at 900 °C. At this temperature, high values have been measured also for elastic modulus and hardness, and ALD Al₂O₃ has been reported to be polycrystalline, depending on film thickness, containing islands with mixture of different crystalline phases surrounded by an amorphous film. Cubic γ-Al₂O₃ has been reported at 950 °C and crystallization to alpha-Al₂O₃ requires annealing at 1150 °C.

Thermal cycling results (numerical data are given in the supplementary material) of ALD Al₂O₃ on silicon, residual stress as a function of temperature, are presented in Fig. 2 for thermal H₂O and O₂ and plasma-O₂-based samples. There was no difference in thermal behavior between Me₃Al-H₂O samples that were preannealed before ALD growth or samples without preannealing. Only preannealed Me₃Al-H₂O sample results are presented here and data for samples without preanneal are presented in the supplementary material. The sample grown at 110 °C was the only sample where irreversible changes in the stress-temperature curve were observed during the first heating cycle. Samples with other precursor combination and growth temperature had a reversible stress-temperature curve, indicating good stability of the material over the used temperature range. In each case, the stress values headed toward more compressive values with increasing annealing temperature, meaning that Al₂O₃ films have larger CTE than the silicon substrate. These results are in line with published ALD Al₂O₃ thermal cycling results on silicon, although for much thinner films opposite results have been published.

Sapphire was used as an alternative substrate material. Figure 3 presents stress-temperature curves for Al₂O₃ on sapphire wafers grown using different oxygen precursors H₂O, O₃, and O₂. The curvature data as a function of temperature were more scattered on sapphire compared to what were measured on silicon. All the samples showed a reversible stress-temperature curve. Although large residual stress values were observed for plasma Me₃Al-O₂ and thermal Me₃Al-H₂O samples at thermal cycling temperatures close to 500 °C, no permanent changes in the residual stress were observed when samples were cooled back to room temperature. Upon annealing, the residual stress of Al₂O₃ on sapphire shifted toward more tensile values indicating higher CTE of the sapphire substrate compared to the CTE of the film. We did not define thermal stress values for Al₂O₃ on sapphire as there was large scatter between the results of consecutive measurements; this was also the reason why actual residual stress value were not given for Al₂O₃ on sapphire.

Table II presents the CTE values calculated for the ALD Al₂O₃ films using the double substrate method. The CTE values were determined from slopes (result from linear fitting) on a temperature range from about RT to 180 °C and on some samples on a temperature range from RT to 500 °C. There was no clear difference between the CTE values in thermal processes using either O₃ or H₂O as the oxygen source, nor between thermal and plasma processes on a temperature range of RT to 180 °C. The standard error from linear fitting on a sapphire substrate was in such a large role that no general conclusions could be made on the CTE value as a function of the ALD growth temperature. Moreover, because of the large standard error, the CTE value calculated for Me₃Al-H₂O grown at 110 °C should not be considered reliable. On a broader temperature range, from RT to 500 °C, thermal Me₃Al-O₂ had largest CTE value, and difference to CTE value of thermal Me₃Al-H₂O was significant.

The CTE values presented here are approximately in line with published CTE values. In literature decreasing CTE as a function of increasing ALD temperature has been reported for ALD Al₂O₃. Here, the magnitude of standard error in the linear fit was large for sapphire wafers causing uncertainty in CTE determination and no such conclusion could be made.

Intrinsic stress (Table II) defined at annealing temperature corresponding to the actual film growth temperature had a linear negative dependence to growth temperature (correlation −0.99); intrinsic stress decreased with increasing ALD temperature. Decreasing intrinsic stress with increasing ALD temperature is in line with theoretical calculations presented earlier. Intrinsic stress varied for samples made using different oxygen precursors and
thermal/plasma processes: for the plasma-O$_2$ process, about 44% of the stress was from intrinsic origin, while for the thermal H$_2$O-based material, about 55% of the stress was from intrinsic origin. As intrinsic stress was examined as a function of growth temperature, we see that intrinsic stress was in major role, as around 95% of the stress was from intrinsic origin for films grown at 110 and 200 °C and this is most probably related to higher impurity content of the film.

**FIG. 2.** Residual stress as a function of thermal cycling temperature for ALD Al$_2$O$_3$ on silicon from Me$_3$Al and H$_2$O grown at (a) 110, (b) 200, and (c) 300 °C and (d) from Me$_3$Al and O$_3$ grown at 300 °C and (e) Me$_3$Al and O$_2$ (plasma) grown at 300 °C.
FIG. 3. Change in residual stress as a function of thermal cycling temperature from about room temperature up to 500 °C for ALD Al₂O₃ on sapphire from (a) Me₃Al and H₂O grown at 110, 200, and 300 °C, (b) Me₃Al and O₃ grown at 300 °C, and (c) Me₃Al and O₂ (plasma) grown at 300 °C.

TABLE II. Slopes \( \Delta \sigma/\Delta T \) measured for ALD Al₂O₃ from different precursor combinations on silicon and on sapphire wafers. Temperature range was from about RT to 180 °C and for samples grown at 300 °C from RT to 500 °C. Intrinsic stress was approximated on thin films on silicon from the stress-temperature curve during first heat cycling at temperature corresponding to actual growth temperature. Thermal expansion coefficient values were calculated from \( \Delta \sigma/\Delta T \) values using the double substrate method.

<table>
<thead>
<tr>
<th>Temperature range</th>
<th>Precursors</th>
<th>ALD temperature (°C)</th>
<th>Stress (MPa/°C) ± Standard error</th>
<th>Slope (MPa/°C) ± Standard error</th>
<th>Intrinsic stress (MPa) ±</th>
<th>Thermal expansion coefficient ppm/°C ±</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT–180 °C</td>
<td>Me₃Al + H₂O</td>
<td>110</td>
<td>−0.1203 ± 0.1756</td>
<td>−0.2600 ± 0.0183</td>
<td>520 ± 520</td>
<td>7.340 ± 7.020</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
<td>0.3862 ± 0.1202</td>
<td>−0.1108 ± 0.0223</td>
<td>340 ± 390</td>
<td>3.590 ± 0.525</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>0.4758 ± 0.1484</td>
<td>−0.2974 ± 0.0177</td>
<td>115 ± 115</td>
<td>3.960 ± 0.380</td>
</tr>
<tr>
<td></td>
<td>Me₃Al + O₃</td>
<td>300</td>
<td>0.4530 ± 0.1811</td>
<td>−0.2335 ± 0.0218</td>
<td>180 ± 180</td>
<td>4.055 ± 0.200</td>
</tr>
<tr>
<td></td>
<td>Me₃Al + O₂ plasma</td>
<td>300</td>
<td>0.4227 ± 0.1077</td>
<td>−0.3136 ± 0.0134</td>
<td>80 ± 80</td>
<td>4.480 ± 0.430</td>
</tr>
<tr>
<td>RT - 500 °C</td>
<td>Me₃Al + H₂O</td>
<td>300</td>
<td>1.7536 ± 0.0844</td>
<td>−0.4388 ± 0.0135</td>
<td>— ± —</td>
<td>3.840 ± 0.100</td>
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<td>300</td>
<td>0.3230 ± 0.0613</td>
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<td>— ± —</td>
<td>4.480 ± 0.430</td>
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<td>Me₃Al + O₂ plasma</td>
<td>300</td>
<td>1.0450 ± 0.1031</td>
<td>−0.4802 ± 0.0153</td>
<td>— ± —</td>
<td>4.055 ± 0.200</td>
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</tbody>
</table>
IV. CONCLUSIONS

The thermal behavior of ALD Al2O3 grown from trimethylaluminum with different oxygen precursors (H2O, O3, and O2 plasma) was studied via post-ALD thermal annealing and thermal cycling. The thermal stability of the films grown at 200 and 300 °C was good, as no permanent changes were observed in the residual stress, also the refractive index and extinction coefficient remained stable upon thermal annealing at 700 °C. Samples annealed at 900 °C had increased residual stress and clear rise in the refractive index [and in the extinction coefficient (sample grown at 110 °C)]. The thermal expansion coefficient varied somewhat between different oxygen precursors in the temperature range from about RT to 350 °C. At narrower temperature range from about RT to 180 °C, there was no statistical difference in the thermal expansion coefficients between different ALD temperatures or oxygen precursors detected. Intrinsic stress decreased with increasing growth temperature. Comparison between Al2O3 samples grown at 300 °C using different oxygen precursors revealed clear differences in intrinsic stress; lowest intrinsic stress was with ALD Al2O3 grown with O2 plasma. The results show that ALD Al2O3 is suitable for applications where the films are exposed to moderate subsequent thermal load with major change in optical properties or residual stress.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

O.Y. designed the experiments with A.L. and R.L.P. O.Y. fabricated thermal Me3Al-H2O samples at a temperature range from 110 to 300 °C and made thickness and residual stress characterization and thermal annealing and cycling and related data analysis under supervision of R.L.P. A.L. made refractive index and extinction coefficient measurements on a wavelength range from 190 to 1645 nm. S.E. fabricated samples with thermal Me3Al-O3 and plasma Me3Al-O2 processes. J.M. fabricated thermal Me3Al-H2O samples at a temperature range from 30 to 110 °C. J.J. and M.L. performed the ToF-ERDA measurements and the analysis under the supervision of T.S.A. and S.S. made the XRR and GIXRD measurements and the data analysis under supervision of H.L.; Project management, supervision, and resource management were done by R.L.P. O.Y. did writing of the original draft and editing of the review. All authors discussed the results and commented the manuscript by O.Y.

Oili M. E. Ylivaara: Conceptualization (equal); Data curation (equal); Formal analysis (lead); Writing – original draft (lead); Writing – review & editing (lead). Andreas Langner: Conceptualization (equal); Data curation (supporting); Formal analysis (supporting); Writing – review & editing (supporting). Satu Ek: Data curation (supporting); Writing – review & editing (supporting). Jari Malm: Data curation (supporting); Formal analysis (supporting); Writing – review & editing (supporting). Jaakko Julin: Data curation (supporting); Formal analysis (supporting); Writing – review & editing (supporting). Mikko Laitinen: Data curation (supporting); Formal analysis (supporting); Writing – review & editing (supporting). Saima Ali: Data curation (supporting); Formal analysis (supporting); Writing – review & editing (supporting). Harri Lipsanen: Supervision (supporting); Writing – review & editing (supporting). Timo Sajavaara: Supervision (supporting); Writing – review & editing (supporting). Riikka L. Puurunen: Conceptualization (equal); Formal analysis (supporting); Funding acquisition (lead); Supervision (lead); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are openly available in Zenodo at http://doi.org/10.5281/zenodo.7105571, Ref. 73. The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES
