Thin films of the $\alpha$-quartz $Si_xGe_{1-x}O_2$ solid solution

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$SiO_2$ with the $\alpha$-quartz structure is one of the most popular piezoelectrics. It is widely used in crystal oscillators, bulk acoustic wave (BAW) devices, surface acoustic wave (SAW) devices, and so on. $GeO_2$ can also be crystallized into the $\alpha$-quartz structure and it has better piezoelectric properties, with higher piezoelectric coefficient and electromechanical coupling coefficients, than $SiO_2$. Experiments on bulk crystals and theoretical studies have shown that these properties can be tuned by varying the Si/Ge ratio in the $Si_xGe_{1-x}O_2$ solid solution. However, to the best of our knowledge, thin films of $Si_xGe_{1-x}O_2$ quartz have never been reported. Here we present the successful crystallization of $Si_xGe_{1-x}O_2$ thin films in the $\alpha$-quartz phase on quartz substrates ($SiO_2$) with $x$ up to 0.75. Generally, the films grow semi-epitaxially, with the same orientation as the substrates. Interestingly, the $SiO_{0.75}GeO_{0.25}O_2$ composition grows fully strained by the quartz substrates and this leads to the formation of circular quartz domains with an ordered Dauphiné twin structure. These studies represent a first step towards the optimization of piezoelectric quartz thin films for high frequency (> 5 GHz) applications.

$\alpha$-quartz, $SiO_2$, crystals are currently used as clocks in basically all integrated circuits and as frequency stabilizers in radio transmitters and receivers. The availability of $\alpha$-quartz films with sub-micron thickness and quality factor similar to those of the single crystals, would enable the new generation of devices for information and communication technology beyond 5 GHz. Efforts in this direction are still in their infancy guided by seminal work on thin films of $SiO_2$ synthesised by chemical solution deposition methods.

The structure of $\alpha$-quartz is a network of ordered corner-sharing tetrahedra. It is believed that the piezoelectric properties of quartz are enhanced by the distortion of the structure, which can be represented by two interrelated angles: the bridging angle, $\theta$, between the neighboring tetrahedra and the tilt angle, $\delta$, which is the order parameter of the $\alpha$-$\beta$ quartz phase transition and corresponds to the tilt of the tetrahedra away from its position in $\beta$-phase, where $\delta = 0.816$. The quartz family includes compounds with formulae $TO_2$ (T = Si, Ge) and $MZO_4$ (M = B, Al, Ga, Fe, Mn and X = F, As). Among them, $GeO_2$ and GaPO$_4$ have the most distorted structure, with $GeO_2$ displaying a $d_{11} = 6.2 pC/N$ compared with the $2.31 pC/N$ of $SiO_2$. Theoretical calculations of a quartz-type $GeO_2$ SAW device estimate an electromechanical coupling coefficient $K^2$ that can reach a maximum value of about 0.34%, compared to the 0.16% of the well-known ST-cut $SiO_2$ crystals.

In the $Si_xGe_{1-x}O_2$ solid solution, it is expected that its structure, and thus the piezoelectric properties, can be tuned continuously via varying the Si/Ge ratio. Moreover, $GeO_2$ quartz has better thermal stability than $SiO_2$ quartz. The piezoelectric properties of $SiO_2$ start to deteriorate about 300 °C, due to the presence of the $\alpha$-$\beta$ phase transition at 573 °C, above which the $d_{11}$ of $SiO_2$ vanishes. On the other hand, the $\alpha$-$\beta$ phase transition point of $GeO_2$ is reported to be as high as 1049 °C by Sarver and Hummel. However, Lignie et al. measured $GeO_2$ single crystals by Differential Scanning Calorimetry, showing that $\alpha$-quartz is the only phase present until melting at 1116 °C. This contradiction may arise from size or surface effects: Lignie et al. measured $GeO_2$ single crystals while Sarver and Hummel presumably used powders. In addition, a study has shown that nano-crystals of $SiO_2$ display a continuous $\alpha-\beta$ phase transition, in contrast to the first-order transition in macroscopic quartz ($SiO_2$). In any case, the $\alpha$-quartz phase of $GeO_2$ is more stable than that of $SiO_2$ and a study also shows that in the $SiO_{0.75}GeO_{0.25}O_2$ composition, the $\alpha$-$\beta$ transition temperature is increased to about 1026 °C. However, Brillouin spectroscopy measurements of elastic constants up to 1000 °C show preservation of piezoelectricity in $GeO_2$ in the measured range.

Several efforts have been devoted to the growth of bulk single crystals of $Si_xGe_{1-x}O_2$ by hydrothermal synthesis and flux growth methods. It was found that when $GeO_2$ crystals are grown in aqueous media, hydroxyl groups catalyze it into the more stable rutile phase. Experimental studies show that, at 1200 °C and 1 GPa, a maximum of about 40 mole% Ge can be dissolved into quartz in the bulk. Recently, using an evaporative-recirculation method, Balitsky et al. have succeeded to grow 4–12 mm thick quartz-like $GeO_2$ crystals.
Results and discussion

Epitaxial growth of GeO2 on quartz (SiO2) substrates. We first discuss the growth of the end members of the \( \text{Si}_x\text{Ge}_{1-x}\text{O}_2 \) solid solution. For \( x = 0 \), GeO2 thin films can grow directly in the quartz phase on quartz (SiO2) substrates at high temperatures. Figure S1 (see supplementary material) shows the evolution of RHEED patterns during the deposition of GeO2 on Z-cut and Y-cut quartz substrates. After several tens of pulses, the RHEED pattern turns into grids of dots, suggesting island-like rather than layer-by-layer growth. This is in agreement with the surface morphology obtained by AFM (see Fig. S2 of the supplementary material), showing that the film is composed of grains of about 30 nm in size. The thicknesses of the films are estimated from XRR scans (Fig. S3 of the supplementary material) to be 46 nm and 47 nm for Z-cut and Y-cut substrates, respectively. XRD measurements show the thin film has crystallized into the quartz phase and has the same agreement with the surface morphology obtained by AFM (see Fig. S2 of the supplementary material), showing that the film is composed of grains of about 30 nm in size. The thicknesses of the films are estimated from XRR scans (Fig. S3 of the supplementary material) to be 46 nm and 47 nm for Z-cut and Y-cut substrates, respectively. XRD measurements show the thin film has crystallized into the quartz phase and has the same
orientation as the substrate in both cases. Indeed, Fig. 1a includes an RSM around the (10\bar{1}3) Bragg peak of Z-cut quartz, which shows that the thin film shares the in-plane lattice parameters of the substrate, therefore, growing epitaxially under strain. The lattice mismatch between the film and the substrate can be estimated as
\[
\frac{a_{SiO_2} - a_{GeO_2}}{a_{GeO_2}} = \frac{4.916 - 4.989}{4.989} = -1.5\% 
\]
indicating that the films are under compressive strain. However, for the thin films grown on Y-cut quartz, as shown in Fig. 1b,c, only the in-plane [1\bar{2}10] direction of the thin film grows coherently strained, being the [0001] in-plane direction only partially strained. This is due to the anisotropic lattice mismatch: it is about -1.5\% for the [1\bar{2}10] direction, while it amounts to about -4.3\% for the [0001] direction.

Figure 2 shows the change in the lattice parameters of an epitaxial GeO_2 thin film grown on a Z-cut quartz substrate, extracted from the 2\theta - \omega scans of the (0003) Bragg peak and shown in Table S2 (see supplementary material). It can be observed that the SiO_2 substrate follows the same temperature dependence as reported in the literature\textsuperscript{37}: the lattice of \(\alpha\)-quartz expands continuously till 573 °C where the \(\alpha\)-\(\beta\) phase transition occurs, and the \(\beta\)-phase shows almost zero and slightly negative thermal expansion\textsuperscript{38}. For the GeO_2 thin film, the out-of-plane lattice parameter (c, [0001]) shows a slight increase for temperatures below about 400 °C, above which it starts to flatten. However, before the \(\alpha\)-\(\beta\) phase transition of the SiO_2 substrates, the out-of-plane lattice of GeO_2 thin film is larger than the bulk value. This can be explained by the competition between the thermal expansion and the relieve of in-plane compression from the substrate lattice: as shown in Fig. 2, bulk crystals of GeO_2 show a monotonically increasing lattice with increasing temperature. On the other hand, the in-plane lattice mismatch (a, [1210]) becomes smaller with increasing temperature, leading to a decrease of the out-of-plane lattice expansion. The combination of these two factors results in the complex temperature dependence observed in the GeO_2 thin films.

As observed in Fig. 2, measurements up to 1070 °C in bulk GeO_2 display a continuous increase of the lattice with temperature, evidencing the absence of an \(\alpha\)-\(\beta\) phase transition\textsuperscript{39}. This is, however, not the case for the GeO_2 thin films. The GeO_2 thin film does show signatures of the \(\alpha\)-\(\beta\) transition, following the trend of the SiO_2 substrate. We believe this can only be explained by the fact that the GeO_2 has transformed into \(\beta\)-quartz under...
the influence of the substrate. Under the assumption that the $\beta$-quartz phase of Ge$_2$O$_3$ has similar zero thermal expansion as $\beta$-quartz SiO$_2$, the volume expansion due to the in-plane lattice mismatch would remain similar. Since the contribution from thermal expansion and volume expansion are both negligible, the lattice of Ge$_2$O$_3$ thin film after the phase transition of the substrate also remains unchanged. Experimental studies have shown that in the quartz family, only the least distorted homotypes, such as SiO$_2$, AlPO$_4$ and FePO$_4$ undergo a $\alpha \rightarrow \beta$ phase transition. It is generally accepted that the $\alpha \rightarrow \beta$ phase transition is related to phonon mode softening and for the highly distorted homotypes, such as Ge$_2$O$_3$, the frequency of this mode is temperature independent. Our findings suggest that, due to the strain imposed by the substrates, the distortion of the Ge$_2$O$_3$ thin film structure is less than in its bulk form, with the tilt angle close to the SiO$_2$ value.

**Crystallization of Si$_x$Ge$_{1-x}$O$_2$. Stoichiometric control of the thin films.** Although PLD is known for its good stoichiometry transfer of material from a single target, compared to other thin film deposition techniques, in our study we have found preferential ablation in our Si$_x$Ge$_{1-x}$O$_2$ targets at all accessible fluence values. As shown in Table S1 (see supplementary material), the stoichiometry of the Si$_x$Ge$_{1-x}$O$_2$ targets before and after the laser ablation was studied by EDS. It is clear that for the targets which are made from mixed SiO$_2$ and GeO$_2$ powder, the corresponding thin films lost significant amount of Si comparing to the original composition. Figure S4a (see supplementary material) shows an example of the ablated area of one of these targets. The ablated powder has crystallized into the cristobalite phase (Fig. S8 in supplementary material), which displays stronger signs of melting and re-solidification, compared to the targets made from SiO$_2$ or GeO$_2$. Obviously, the overall morphology is much flatter, with signs of melting and re-solidification, compared to the targets made from SiO$_2$ powder. Moreover, the particulates on the thin film surface increases, while GeO$_2$ films are free from particulates.

To solve these problems, the SiO$_2$ powder was replaced by SiO powder in one of the mixture targets and the improvement is clear: the stoichiometry of the thin films grown from this new target is comparable to that of the target (see Table S1 in supplementary material). This is due to the fact that, after synthesis, the amorphous SiO powder has crystallized into the cristobalite phase (Fig. S8 in supplementary material), which displays stronger absorption for the 248nm laser wavelength. Figure S4b (see supplementary material) shows the morphology of this target after laser ablation under the CBS SEM detector, where the dark flat pockets are the mixture of this target after laser ablation under the CBS SEM detector, where the dark flat pockets are

Si$_x$Ge$_{1-x}$O$_2$ on quartz (SiO$_2$) substrate. A series of Si$_x$Ge$_{1-x}$O$_2$ thin films with compositions x = 0, 0.08, 0.16, 0.75, 1 (for Cs-free targets) and x = 0.20, 0.21 and 0.48 (for Cs-doped targets) are deposited at 600 °C on Y-cut quartz substrates. Surprisingly, no difference between thin films doped with Cs or without it on quartz substrates has been observed. Therefore, in this section we will discuss them together.

After the deposition, the crystallization of these thin films is examined by X-ray diffraction (XRD). In all cases, the films are amorphous, as expected at the relatively low temperatures used (see “Methods”). The thin films are annealed at 900 °C, where the Cs is reported to become activated as network modifier. After annealing for 30 min, the RHEED pattern is recovered for all compositions, except for the SiO$_2$ thin films (Fig. S9 in supplementary material). The amorphous films have crystallized into the $\alpha$-quartz phase with the same orientation as the substrate.

For the Si$_x$Ge$_{1-x}$O$_2$ films, the crystallization takes place in a similar manner. Figure 3 shows the morphology of these films: For the GeO$_2$, Si$_{0.08}$Ge$_{0.92}$O$_2$ and Si$_{0.16}$Ge$_{0.84}$O$_2$ compositions, the films are composed by small grains of about 50 to 150 nm in diameter and the surfaces are flat with root mean square surface roughness $R_k$ ranging from 0.9 to 1.5 nm. With increasing Si amount, such as in Si$_{0.20}$Ge$_{0.80}$O$_2$ and Si$_{0.21}$Ge$_{0.79}$O$_2$, columnar features with height varying from 50 to 100 nm are present, while the rest of the surface displays small grains, similar to the previous two compositions (see Fig. S10 of supplementary material). With further increase of Si content, as in Si$_{0.48}$Ge$_{0.52}$O$_2$, the height of the columnar features increases to about 150 nm, as shown in Fig. 3f. For all these films, the crystallization is complete and the described morphology is homogeneous across the substrate.

This evolution in morphology is also reflected in the RXXR curves as shown in Fig. 4. The film thickness is calculated from period of the Kikuchi fringes. While all the films are deposited with the same total number of laser pulses, those with Si$_{0.20}$Ge$_{0.80}$O$_2$, Si$_{0.21}$Ge$_{0.79}$O$_2$ and Si$_{0.48}$Ge$_{0.52}$O$_2$ compositions, are significantly thinner than the rest. This can be attributed to the fact that part of the deposited material is used to form the columns.
Figure 3. AFM images of $Si_{x}Ge_{1-x}O_{2}$ thin films grown on Y-cut quartz substrates, with (a) $x = 0$, (b) $x = 0.08$, (c) $x = 0.16$, (d) $x = 0.20$, (e) $x = 0.21$ and (f) $x = 0.48$. Note the columnar features growing in number and height with increasing Si content. Scale bar is 600.0 nm for the first row and 2.0 μm for the second row.

Figure 4. X-ray reflectivity (XRR) curves of $Si_{x}Ge_{1-x}O_{2}$ thin films grown on Y-cut quartz substrates, from which the film thickness and electron density are extracted. They show that the thicknesses of the thin films decrease with increasing silicon content, as a result of the displacement of the material on to the columns. The electron density change of the series can also be easily observed from the shift of the critical angles. The thickness is estimated to be 151 nm, 120 nm, 106 nm, 65 nm, 74 nm and 77 nm, for $x = 0$, 0.08, 0.16, 0.20, 0.21, 0.48 and 0.75, respectively.
shown in the Fig. 3. The presence of these taller features also increases the roughness of the film resulting in a quicker drop in intensity at higher angles of the reflectivity curve. The critical angles, which are determined by the electron density of the thin films, decrease with the increase of silicon content, as expected, which suggest the thin films are a homogeneous mixture of $\text{Si}_x \text{Ge}_{1-x} \text{O}_2$.

On the other hand, the $\text{Si}_{0.75} \text{Ge}_{0.25} \text{O}_2$ composition shows a different type of crystallization. As shown in Fig. 5, unlike in the previous films, only about 90% of the sample area is crystallized. Moreover, instead of giving rise to a continuous crystallized film with small grains, it is crystallized into oriented domains. AFM images in Fig. 5b,c show that nucleation starts at the center of the domain. After some further crystallization, stripes with width of about 1 μm form and expand radially. In between these stripes, there are flat and dense crystalline areas, which are about 10 nm lower in height than the stripes. When these stripes reach the domain boundary, bumps as high

**Figure 5.** (a) SEM images of a $\text{Si}_{0.75} \text{Ge}_{0.25} \text{O}_2$ film grown on Y-cut quartz substrate shows the crystallization of domains surrounded by low crystallinity areas (i) and amorphous areas (ii). The black arrows point to the new domains nucleated at the edge of a bigger domain. (b) AFM image of a domain boundary where bumps are formed when the stripes meet the boundary. Notice the stripes are about 10 nm higher than the areas in between them. (c) AFM image showing the middle part of the domains with the nucleation point is a central point in area from which stripes arise.
as 100 nm form at the end of the stripes, suggesting accumulation of excess material. Interestingly, the stripes have the same height as the area outside of the domain in Fig. 5b. SEM images with higher magnification show that the stripes have a porous structure and are composed of small holes about 50 nm in diameter (see Fig. S11 in supplementary material).

These kind of radial structures and circular domains resemble the spherulitic crystallization of GeO$_2$ thin films on Al$_2$O$_3$ reported in our previous study$^{29}$. However, after further examination by EBSD, it turns out that these domains are single crystals as shown in Fig. 6, which agrees with the oriented RHEED pattern collected for the same films. Furthermore, GIXRD did not show any peaks confirming the epitaxial nature of the domains (see Fig. S12a in supplementary material). Moreover, some of the areas surrounding the domains (marked as i) in Fig. 5a, appear not to be amorphous, but instead they display poly-crystals with poor crystallinity, as it is shown by their vague Kikuchi patterns. In fact, the crystallinity of this area is so low that it cannot be indexed properly by EBSD. Comparing to area (i) in Fig. 5a, where substructures with different contrast can be observed (see Fig. S11 in supplementary material for higher magnification), area (ii) has a homogeneous contrast, suggesting that this area is amorphous.

Figure 6a is the Image Quality (IQ) map of a EBSD scan, where the contrast represents the crystallinity: the brighter the contrast, the higher the crystallinity. The stripes can be clearly observed in the IQ map and they have worse crystallinity than the rest of the area on the domains. Interestingly, from Fig. 6b, all the domains are composed of Dauphiné twins, as clearly indicated by the blue-green color in the orientation map. The Dauphiné twins detected by EBSD are related to each other by a 60° rotation around the c-axis, such as the two unit cells drawn in Fig. 6b. By comparing the pattern in the domains in Fig. 6a,b, it can be observed that the twin boundaries are related to the stripes as sometimes the twin boundaries overlap with the stripes. SEM images show these stripes are well-organized structures as they can connect to each other across the domain boundaries (see Fig. S11 in supplementary material). Moreover, it can be observed that the twin boundaries evolve with the growth of the domains: For the smallest domains, the twin boundaries are straight lines close to the 11-5 o’clock direction. With further growth of the domain, the twin boundaries are still straight but rotate counter-clockwise,
eventually forming a “Yin Yang” pattern with a jerky Dauphiné twin boundary in the big domains (see Fig. S13 in supplementary material for another example with higher magnification).

Dauphiné twins can form during the $\beta$-quartz to $\alpha$-quartz phase transition, as growth twins, or when the crystal is under mechanical stress, as mechanical twins$^{46-48}$. $\alpha$-Quartz crystal is highly anisotropic in stiffness, with the stiffest orientation being close to negative rhombohedral (z) (011) with a Young’s modulus of 109 GPa, while the positive rhombohedral (r) (10\bar{1}1) has a Young’s modulus of about 71.5 GPa$^{48}$. It is generally accepted that when a constant stress is applied on a quartz domain, the twins will react in a way to maximize the stored elastic strain energy of the domain in a way to minimize the internal energy of the system, and the stored elastic energy is proportional to the difference between the elastic energies of the two parts of the twins$^{49,50}$. Compression studies have shown that if a compressive stress is applied perpendicular to the rhombohedral (z) planes, twins will form. However, if it is applied perpendicular to the rhombohedral (r) planes, twinning will not form, since it is already in a thermodynamic stable state$^{46,48,50}$. We believe the Dauphiné twins in our films are induced by the epitaxial stress from the substrates because of their highly ordered structures. However, in our case, the crystal orientation is fixed by the epitaxial growth and only twin boundaries can move. As domains grow bigger, the accumulated stress due to the epitaxial relationship increases with increasing domain size. Moreover, the accumulated stress is not equal in the two in-plane directions, with the compressive strain along [0001] being about 4 times larger than that along the [12\bar{1}0] direction, as will be explained in the later sections. We believe this is the reason for the changing of twinning patterns with domain growth. The details of the mechanism will be discussed in a separate paper.

For the SiO$_2$ thin films made using the same annealing procedure, the RHEED pattern is not recovered, suggesting they are amorphous. Unfortunately, it is difficult to check this by XRD because if crystallized, the film peak will overlap with the substrate peak. Under the optical microscope, the film looks homogeneous, without any features, and the AFM scans show the surface is flat with $R_q = 0.3$ nm. Moreover, an XRR scan shows an uniform layer with density of about 2.2 g/cm$^3$ is grown on the substrate, to be compared with the 2.64 g/cm$^3$ value of SiO$_2$ quartz (see Fig. S14 in the supplementary material). All this evidence supports the amorphous nature of the SiO$_2$ thin films.

Figure 7 displays X-ray RSMs around the (31\bar{4}0) and (30\bar{3}1) Bragg peaks of the Y-cut quartz substrates, in which the peaks of the Si$_x$Ge$_{1-x}$O$_2$ film peaks are also visible. Table S3 (see supplementary material) contains the thin film lattice parameters that are extracted from those maps by means of Lorentzian fitting (see Fig. S15 of the supplementary material for one example of the procedure), which are also plotted in Fig. 8. In this figure, the bulk lattice parameters for different compositions, obtained from Refs. $^{17}$ and $^{25}$, are also plotted. According to these results, none of these thin films are fully relaxed: the in-plane lattice parameters are smaller than those of the bulk single crystals due to the in-plane compressive stress applied by the substrates. Consequently, the out-of-plane lattice is elongated with respect to the bulk value.

From Fig. 7, it can be observed that, for the thin films with low Si content ($x = 0, 0.08$ and 0.16), the film peaks shift towards the substrate peaks in the out-of-plane direction [10\bar{1}0] and both in-plane directions, [12\bar{1}0] and [0001], with increasing Si content, as expected due to the larger unit cell volume of GeO$_2$. However, with $x$
increasing further (x = 0.20 and 0.21), the in-plane lattice keeps decreasing while the out-of-plane lattice spacing remains comparable to that of the film with x = 0.16. This can be explained by the very large compressive strain along the in-plane $[\bar{1}2\bar{1}0]$ direction, as shown in Fig. 8, where the lattice drops dramatically from x = 0.16 to 0.20 in the $[\bar{1}2\bar{1}0]$ direction. In response of that, the lattice expands on the strain-free, out-of-plane direction.

With further increase of Si content to x = 0.48, the thin films are fully strained by the substrate as shown in Fig. 7. Interestingly, in the [0001] direction, the tail of the thin film peaks reaches the substrate indicating that a part of the film is fully strained. Using the lattice parameter data from the bulk single crystals at various compositions17, we can estimate the strain for the x = 0.48 thin film to be about − 0.7% and − 2.2% along the $[\bar{1}2\bar{1}0]$ and [0001] directions, respectively. For the first few layers, the strain imposed by the substrate forces the film to have the same lattice as the substrate both in the $[\bar{1}2\bar{1}0]$ and [0001] directions. However, with the crystallization continuing upwards, the elastic energy contributed along the [0001] direction is too large to be accommodated, relaxing the lattice gradually towards the bulk values, and contributing to the main intensity of the $(30\bar{3}1)$ peak. On the other hand, in the $[\bar{1}2\bar{1}0]$ direction, the mismatch strain of about − 0.7% can be accommodated and the lattice is completely strained for the entire thickness.

Finally, when x increases to 0.75, the $Sn_{0.75}Ge_{0.25}O_2$ thin films are fully strained by the substrate in both in-plane directions, as shown in Fig. 7. Using similar arguments, we can estimate the strain magnitudes to be − 0.2% and − 0.8% along the $[\bar{1}2\bar{1}0]$ and [0001] directions, respectively. From Fig. 8, it can be observed that, generally speaking, the lattice along the [0001] direction has a composition dependence more similar to the bulk than the lattice in $[\bar{1}2\bar{1}0]$ direction, due to the strain anisotropy described above.

$Si_xGe_{1-x}O_2$ on sapphire (Al$_2$O$_3$) substrates. A series of $Si_xGe_{1-x}O_2$ films with x = 0.08, 0.16, 0.75, 1 (for Cs-free targets) and x = 0.20, 0.21, 0.48 (for Cs-doped targets) were also deposited on Al$_2$O$_3$ substrates with the same growth parameters as those used for the growth on quartz substrates (see previous section). In our earlier study25, we have reported crystallization of GeO$_2$ on Al$_2$O$_3$ substrates: quartz crystals with diameter of about 100 μm are achieved, but most of the crystalline area is covered by wavy patterns that start from the edge of the sample and sweep inwards until crystallization of the entire film is completed. GIXRD shows that these crystals...
are randomly oriented poly-crystals (see Fig. S16 in supplementary material). However, these continuous wavy features are absent in the Si-containing Si$_x$Ge$_{1-x}$O$_2$ films. Figure 9 shows the Si$_x$Ge$_{1-x}$O$_2$ thin film with x = 0.08 after annealing. Some quartz poly-crystals with diameter of about 20 μm are present while the rest of the film is still amorphous. Films with x = 0.16 show a similar behavior, with the difference of having smaller crystals with diameters below 10 μm (see Fig. S17 in supplementary material). The decrease of the size of the quartz crystals with increasing Si content indicates an enhancement of the crystallization barrier, as expected.

EDS point analysis on the crystals as well as the amorphous area results in the same composition (see Fig. S17 in supplementary material) suggesting that the crystals are solid solutions of Si$_x$Ge$_{1-x}$O$_2$. As observed from Fig. 9 and S18 (see supplementary material), the center of the crystal, the nucleation point, can be as flat as the surrounding area or it can protrude above the surface. Moreover, in the amorphous area, similar round bumps are observed, perhaps denoting nucleation points for the new crystals that have not grown yet. Interestingly, EDS point analysis on these cores and bumps often shows a different stoichiometry than the nominal x value (Ge/Si ratio) of the thin film, while the rest of the film does show the expected stoichiometry (Fig. S17 in supplementary material).

For the rest of the Si$_x$Ge$_{1-x}$O$_2$ thin films with x = 0.20, 0.21, 0.48 (for Cs-doped targets) and x = 0.75, 1 (for Cs-free targets), no crystallization is observed on the Al$_2$O$_3$ substrates (see Fig. S13b in supplementary material). This may indicate that the crystallization barrier is so high that 900 °C is not sufficient or the amount of Cs (about 1 at.%) is not enough, to fully break the network.

Crystallization mechanism of Si$_x$Ge$_{1-x}$O$_2$. We have shown that the films on quartz and sapphire substrates display different morphologies: the thin films on quartz substrates are composed of small grains, while on sapphire substrates, they crystallize into more extended crystals with clear nucleation points. Moreover, we have found that changing the deposition temperature from 600 to 800 °C, GeO$_2$ thin film can still crystallize successfully on the quartz substrates. However, this is not the case on sapphire substrates. On these substrates, the thin film starts evaporating from the edge of the sample, and circular evaporation pits can be observed (see Fig. S19 in supplementary material). AFM images of the film reveal a flat surface without any features, suggesting it is still amorphous (Fig. S19 in the supplementary material) and GIXRD confirms the amorphous state of the thin film. This evidence indicates that at 800 °C, the high temperature suppresses the nucleation process of GeO$_2$, leading to no crystallization.

In the Si$_x$Ge$_{1-x}$O$_2$ thin films, the crystallization kinetics appears to change with composition. The melting point of GeO$_2$ is 1116 °C, compared to about 1600 °C of SiO$_2$, and the annealing temperature is 900 °C in both cases. One would expect that the melting point in the composition series increases with increasing silicon content. As the size of the crystals on sapphire substrates decreases from about 100 μm (x = 0), 20 μm (x = 0.08), to below 10 μm (x = 0.16), this indicates that the growth rate of Si$_x$Ge$_{1-x}$O$_2$ decreases with increasing Si content in this range, and is likely to decrease further with additional increase of silicon content. On the contrary, the nucleation rate is increasing in this range as the number of crystals on sapphire substrates increases (see Fig. S20 of supplementary material). When x reaches x = 0.20, the growth rate on sapphire is so low that no crystallization occurs. On the quartz substrates, the growth rate is also likely decreasing with increasing x. Nevertheless, the growth rate is still high enough to fully crystallize the Si$_{0.48}$Ge$_{0.52}$O$_2$ thin films. The fact that the Si$_{0.75}$Ge$_{0.25}$O$_2$ composition only shows partial crystallization, suggests that at this Si concentration the growth rate is significantly reduced compared to that of GeO$_2$.

Thus, we propose the following crystallizing mechanisms: for the Si$_x$Ge$_{1-x}$O$_2$ (0 ≤ x ≤ 0.48) thin films on quartz substrates, the substrates can serve as a seed for crystallization. Thus, there is no need for additional nucleation points and the Si$_x$Ge$_{1-x}$O$_2$ (0 ≤ x ≤ 0.48) can grow on the quartz substrate homo-epitaxially, as also shown for bulk GeO$_2$. In this case, the whole film crystallizes in a planar and continuous fashion from bottom to top: at the film-substrate interface, the atoms diffuse and attach to the substrate to crystallize, forming small
Si0.48Ge0.53O2 and SiO2 on SrTiO3 substrates. Unexpectedly, our experiments on quartz and sapphire substrates shown on the previous sections do not reveal the functionality of Cs in the network. Next to Cs, Sr is reported to act as a network modifier, which can also help crystallization by bonding with oxygen atoms. In our previous study, we have found that when GeO2 is deposited on SrTiO3 (STO) substrates, during the annealing at 830 °C, Sr from the substrate will diffuse into the film and react with it forming a colorful germanate SrGe1-xO2, on top of which a quartz layer forms. To study the role of the network modifiers in the SiGe1-xO2 network, we have deposited Si0.48Ge0.52O2 films on STO substrates. After annealing for 30 min at 800 °C, some crystals appear (Fig. 10a), accompanied by some circular pits (Fig. 10b). Further investigation by EBSD reveals the polycrystallinity of the quartz crystal, and the nature of circular spots are evaporation pits, where all the film material evaporates, revealing the bare substrate surface (see Fig. S22 in supplementary material).

Comparing to the lack of crystallization of the same composition on sapphire at 900 °C, the presence of crystals in this case suggests that, indeed, Sr can break the network and help crystallization. However, if the film thickness is reduced by one-half, the number of the evaporation pits increases significantly, while the number of crystals remains very much unchanged (see Fig. S23 in supplementary material). Moreover, a gradient for crystallization/evaporation exist across the surface. Close to the edge, the density of crystals and evaporation pits is the highest, with a gradual decrease towards the center of the film.
The structure of GeO$_2$ (SiO$_2$) glass can be viewed as a network of randomly distributed corner-sharing GeO$_4$ (SiO$_4$) tetrahedra. However, the GeO$_2$ tetrahedra are more distorted and the GeO$_2$ network contains significantly more 3-membered tetrahedral rings$^{33}$. In the 50:50 SiO$_2$-GeO$_2$ glass, an Oxygen-17 NMR study has shown that the three species of bridging oxygen of Si-O-Si, Si-O-Ge, and Ge-O-Ge appear in a ratio of about 27%, 46% and 27%, respectively, favouring the random mixture of the network$^{34}$. However, Raman spectroscopy shows that the mixture is not ideal in terms of the mixing of the tetrahedra: the small (3- and 4-membered) SiO$_4$ rings are lost as they convert to large mixed GeO$_4$-SiO$_4$ rings. As a result of that, the mixed network is composed of SiO$_2$-like, GeO$_2$-like and mixed SiO$_2$-GeO$_2$-like areas. Moreover, at high temperature, the large mixed rings break up into 3-membered GeO$_4$ rings and 6-membered SiO$_4$ rings rather than the original 3- and 4-membered SiO$_4$ rings$^{55}$.

When alkali and alkaline earth ions are added, both non-bridging oxygens can be formed with Si and Ge. However, due to the larger radius of Ge$^{4+}$, GeO$_2$ octahedra can also form, as in many crystalline germanates, depending on the concentration of the modifier$^{34,36}$. On the thin film of Si$_{0.48}$Ge$_{0.52}$O$_2$, we did not observe the formation of SrGe$_{3.3}$O$_{5.6}$, in which some of Ge is likely to be 6-coordinated, as in the thin film of GeO$_2$$^{29}$. This suggests that Si may prevent Ge to form high coordination compound by forming the Ge-O-Si bonds instead. On the other hand, since the mixing of the tetrahedra is not ideal due to the size mismatch, it is likely that the Sr acts differently in different areas: in a Ge$_{2}$O$_{7}$-like region, since it cannot form a germanate and the local melting point may be lowered, the material starts evaporating forming the observed pits; while in a Si$_{2}$O$_{7}$-like region, Sr is more stable. As with crystallization, the evaporation process is also determined by nucleation of the new phase: the Ge$_{2}$O$_{7}$-like regions initially evaporated serve as nuclei of the vapor phase and the pits expand. Figure 10 and S23 (see supplementary material), show an evaporated area clearly exceeding 50% of the total area, suggesting that with the breaking of the Ge-O-Si bonds and the leaving of Ge (Ge-O), the remaining O-Si (Si) with dangling bonds will also become unstable and evaporate. In the competition between crystallization (attachment) kinetics and evaporation (detachment) kinetics, the latter wins in the film shown in Fig. 10. Beside Si$_{0.48}$Ge$_{0.52}$O$_2$, we have also deposited thin films of SiO$_2$ on STO, and neither crystallization nor evaporation was observed with an annealing temperature of 1000 °C, which proves that the SiO$_2$ network is more rigid than GeO$_2$.

**Conclusions**

We have deposited amorphous thin films of Si$_x$Ge$_{1-x}$O$_2$ by PLD. We have found non-stoichiometric material transfer between the target and the substrate for targets made from SiO$_2$ (quartz phase) and GeO$_2$ (quartz phase) powders, with SiO$_2$ being more resistant to the laser ablation. We solved this problem by replacing the SiO$_2$ powders with SiO powders, which crystallize into cristobalite phase during the synthesis, and offer better laser absorption than the quartz phase.

We have successfully crystallized Si$_x$Ge$_{1-x}$O$_2$ with $x \leq 0.75$ into quartz phase on quartz (SiO$_2$) substrates, which provides highly anisotropic strain conditions, achieving a higher solubility ratio than possible in the bulk crystals. These thin films crystallize at the substrate surface and grow towards the film free surface. Due to the small lattice mismatch between film and substrate, the films grow homo-epitaxially, with the same orientation of the substrate. All of these thin films are compressively strained, with the lattice in the out-of-plane direction being larger than the bulk value. With the increase of $x$, the mismatch between the film and the substrate is reduced. When the Si content increases to $x = 0.48$, the in-plane lattice is fully strained only along the direction with low-mismatch ([1210]). When the Si content increases beyond $x = 0.75$, the film is fully strained. On the other hand, with the same growth procedure, the SiO$_2$ thin film shows no sign of crystallization. This indicates that by replacing Si with Ge in the network, the flexibility of the network can be enhanced, facilitating the crystallization process.

With a view to extend the type of piezoelectric devices that can be foreseen, growth on non-piezoelectric substrates was also attempted. For Si$_x$Ge$_{1-x}$O$_2$ on Al$_2$O$_3$ substrates, only compositions with $x \leq 0.16$ show signs of crystallization. We believe this can be attributed to the additional nucleation barrier and worse molecular adhesion on sapphire, compared to quartz. In these thin films, the nucleation starts at the top film surface and then expand laterally, forming crystals with sizes of tens of μm.

For thin films deposited on SrTiO$_3$, SiO$_2$ still shows no crystallization with annealing temperatures of 900 °C. On the contrary, for the GeO$_2$ composition, crystallization of quartz is possible with a lower annealing temperature of 800 °C and a layer of SrGe$_{3.3}$O$_{5.6}$ is formed at the interface with the substrate, prior to the nucleation of quartz. With Si:Ge ratio of about 1, local evaporation and crystallization are observed with an annealing temperature of 800 °C. Our findings support the idea that in a Si$_x$Ge$_{1-x}$O$_2$ glass, the mixing of the SiO$_4$ and GeO$_4$ tetrahedra is not ideal due to size mismatch. At 800 °C, evaporation seems to starts at the GeO$_2$-like regions, where the network is the least connected, due to the bonding to Sr. The loss of material destabilizes the surroundings, leading to further evaporation, and formation of pits.

To conclude, the very different nucleation barriers of the two components of the Si$_x$Ge$_{1-x}$O$_2$ solid-solution makes the crystallization of the these materials greatly challenging. However, it is possible to partially overcome this by using quartz substrates, on which successful growth of oriented Si$_x$Ge$_{1-x}$O$_2$ single crystals have been achieved for Ge-rich compositions. These films are promising for future SAW devices where acoustic waves propagate at the surface of the film with a penetration depth comparable to the wavelength of the acoustic wave (hundreds of nm).

**Methods**

The process starts with the synthesis of poly-crystalline pellets to be used as targets for laser ablation during PLD growth: fine powders of GeO$_2$ (Alfa Aesar, 99.9999%, α-quartz phase) with SiO (Alfa Aesar, 99.8%, amorphous) or SiO$_2$ (Alfa Aesar, 99.9%, α-quartz phase) were mixed together with different ratios. For some of them, a small amount of C$_{29}$SiO$_2$ was added in. The powders were milled for 90 min at 150 rpm and then pressed into a pellet.
with 20 mm in diameter by a cold pressing at 10 tons. Finally, they were annealed at 900 °C for 4 h. The compositions of the synthesised Si₇₋ₓGeₓO₂ targets are shown in Table S1 of the supplementary material.

Thin films were deposited by pulsed laser deposition using a 248 nm KrF laser (Lambda Physik COMPex Pro 205). The substrates were heated by an infrared laser (DILAS Compact-Evolution, wavelength 808 nm) and the temperature was monitored by a pyrometer. The substrates used in this study are Z-cut (0001) and Y-cut (1010) α-quartz (SiO₂), Al₂O₃ (0001) and SrTiO₃ (STO) (001) (CrysTec GmbH). All the substrates are 5 mm x 5 mm in lateral dimensions and 0.5 mm thick. For the epitaxial growth of GeO₂, the deposition parameters were: growth temperature of 470 °C, laser repetition rate of 1 Hz, a total number of 1800 pulses, and cooling rate of 5 °C/min.

For the Si₇₋ₓGeₓO₂ films (0 ≤ x ≤ 0.75), first the amorphous thin film was deposited at 600 °C, with repetition rate of 5 Hz. If not specified, the total number of pulses is 3600. After deposition, the films were annealed at 900 °C for 30 min and then cooled down with rate of 5 °C/min. In thicker films or with higher silicon content, the annealing time needed to reach full crystallization is expected to be longer. Among the series presented here, GeO₂ is the easiest composition to crystallize, with crystallization being achieved after 30 min of annealing at 800 °C. And annealing at 900 °C for 30 min can successfully crystallize thicker GeO₂ films, even for thicknesses up to 400 nm (not included in this work).

The rest of the deposition parameters were the same in both recipes: a target-substrate distance of 46 mm, a laser fluence between 2.5 and 3.5 J/cm². Oxygen was present in the chamber during growth with pressure 0.1 mbar. The annealing atmosphere was 200 mbar of oxygen. The growth process was monitored by high-energy electron diffraction (RHEED) set-up, including differential pumping of the incident electron beam path.

The film crystallinity and orientation, as well as the epitaxial relationship between the thin films and the substrates were studied by X-ray diffraction (XRD) 2θ - ω scans and reciprocal space mapping (RSM). The thickness is estimated from X-ray reflectivity (XRR) scans. These studies were performed on a Panalytical X’Pert electron diffraction (RHEED) set-up, including differential pumping of the incident electron beam path. (EDAX EBSD system equipped with a Hikari CCD camera). EDAX OIM Analysis 8.1 and Matlab® based toolbox MTEX were used for EBSD data analysis.

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Author contributions
S.Z. and B.N. designed the project. S.Z. synthesized the materials, performed most of the data analysis and wrote the first version of the manuscript. J.A-L. helped with the analysis of the XRD and Reflectivity data. V.O. helped with the EBSD measurements and the analysis. All the authors discussed the data and gave feedback on the manuscript.

Competing interests
The authors declare no competing interests.

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