Effect of Ge Content on the Formation of Ge Nanoclusters in Magnetron-Sputtered GeZrO\textsubscript{x}-Based Structures

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Abstract

Ge-rich ZrO\textsubscript{2} films, fabricated by confocal RF magnetron sputtering of pure Ge and ZrO\textsubscript{2} targets in Ar plasma, were studied by multi-angle laser ellipsometry, Raman scattering, Auger electron spectroscopy, Fourier transform infrared spectroscopy, and X-ray diffraction for varied deposition conditions and annealing treatments. It was found that as-deposited films are homogeneous for all Ge contents, thermal treatment stimulated a phase separation and a formation of crystalline Ge and ZrO\textsubscript{2}. The “start point” of this process is in the range of 640–700 °C depending on the Ge content. The higher the Ge content, the lower is the temperature necessary for phase separation, nucleation of Ge nanoclusters, and crystallization. Along with this, the crystallization temperature of the tetragonal ZrO\textsubscript{2} exceeds that of the Ge phase, which results in the formation of Ge crystallites in an amorphous ZrO\textsubscript{2} matrix. The mechanism of phase separation is discussed in detail.

Keywords: Germanium, Zirconium oxide, Nanoclusters, Phase separation, Magnetron sputtering, Thin films, X-ray diffraction, Ellipsometry, Raman scattering, Fourier Transform infrared spectroscopy, Auger electron spectroscopy

Background

Germanium is compatible with current complementary metal oxide semiconductor (CMOS) technology. Physical scaling of bulk germanium to nanometer range reopened the route to novel applications. Germanium nanocrystals (Ge-ncs) can be used for electronic flash memories with improved write/erase speed as well as for optical devices and light emitters in visible and near-infrared spectral ranges.

Most of the research were performed on the Ge-ncs embedded in SiO\textsubscript{2} \cite{1–5}, but a few studies of the Ge-ncs embedded in Al\textsubscript{2}O\textsubscript{3} \cite{6, 7} and HfO\textsubscript{2} \cite{8, 9} were done. Recently, the Ge-ncs embedded in ZrO\textsubscript{2} \cite{10, 11} and TaZrO\textsubscript{x} \cite{12} were investigated. However, for deeper understanding of the mechanism of the formation, growth, and crystallization of Ge-ncs in the ZrO\textsubscript{2} matrix, further investigations are required.

It is well-known that monoclinic ZrO\textsubscript{2} is the most stable crystalline phase at room temperature, while tetragonal and cubic crystal phases are stable at high temperatures \cite{13}. From the microelectronic point of view, amorphous films as dielectrics are most attractive due to lower leakage current and better reliability properties in comparison to polycrystalline films. However, both tetragonal and cubic phases show much higher dielectric constants in comparison with amorphous one \cite{14}. In this regard, it is important to stabilize tetragonal (cubic) ZrO\textsubscript{2} films at room temperature.

To achieve the stabilization of these phases at lower temperatures, their doping with aliovalent dopants (Y\textsuperscript{3+}, Sc\textsuperscript{3+}, Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Cu\textsuperscript{2+}, etc.) is usually used. Such doping provokes the formation of oxygen vacancies for charge compensation that play an important role in stabilizing the cubic and tetragonal structures \cite{15, 16}. However, the presence of additional oxygen vacancies will cause the formation of traps that affect the operation of the devices.

At the same time, doping with isovalent elements (Si, Ge, Ti, Sn, Ce, etc.) requires neither charge compensation nor oxygen vacancies’ formation. It was
demonstrated experimentally that these dopants can stabilize tetragonal zirconia against monoclinic distortion but only some compositions were studied experimentally [17, 18]. Besides, it is known that ultrathin films (with the thickness of few nanometers) crystallize more often in tetragonal ZrO₂ due to the stronger contribution of the surface energy to the free Gibbs energy or due to stress [19].

It was shown that the temperature of tetragonal-to-monoclinic transformation decreases with dopant concentration, while the crystallographic variations depend on dopant sizes. For instance, for large dopants as Ce⁴⁺, the c/a ratio of the tetragonal unit cell decreases with increasing Ce content, which causes the formation of cubic ZrO₂ for higher Ce concentration. This behavior is similar to that observed in trivalent-cation-doped zirconia systems [16]. For small dopants as Ti⁴⁺ and Ge⁴⁺, the c/a ratio increases with dopant content and these tetragonal solid solutions do not show any trend towards cubic phase formation. The stability of the tetragonal phase in Ge-doped ZrO₂ films was explained by the formation of tetrahedral coordinated Ge with a Ge-O distance of 1.81 Å that is shorter than Zr-O bond (2.10 Å) [17]. Being stronger, Ge-O bond increases tetragonality of ZrO₂ and stabilizes it.

It is worth to note that when ZrO₂ was doped with group IV elements, solid solutions were considered to be constructed from oxide units as (MO₂)ₓ(ZrO₂)₁₋ₓ, where M = Ce, Ti, Ge [20, 21]. This did not assume the formation of Ge-ncs in Ge-doped ZrO₂.

Recently, we have shown the formation of the Ge-ncs via phase separation of Ge-doped ZrO₂ films [10]. However, the effect of Ge content on the Ge-ncs formation as well as the stability of the host oxide towards its thermal crystallization requires more consideration.

In this work, optical and structural properties of pure ZrO₂ films and Ge-rich-ZrO₂ layers with different Ge content produced by magnetron sputtering were studied with respect to deposition parameters and annealing treatment. The goal of this work was to find the ways to control the nucleation and crystallization of Ge-ncs independently from the crystallization of the high-k host material.

**Methods**

**Sample Preparation**

Radio frequency “top-down” magnetron co-sputtering setup equipped with 3 confocal sources (Ge, ZrO₂ and SiO₂) was used to grow the films on 6 inch substrates. These latter were p-type Si (100) wafers covered by 5-nm thermal SiO₂. The sputtering was performed with pure Ar plasma (20 sccm flow) at room temperature on a rotating substrate (5 rotations per minute) allowed the deposition of homogeneous layer of the same thickness across the wafer. The power density (RFP) applied to the ZrO₂ target was fixed at RFP_ZrO₂ = 3.3 W/cm². To achieve different Ge content in the films, the power density applied to the Ge target was varied from RFP_Ge = 0.7 to 2.2 W/cm². For comparison, pure Ge and pure ZrO₂ films were deposited in addition. The film-thickness was fixed at about 500 nm, which was achieved by adjusting the deposition time. More details can be seen elsewhere [10, 11].

All films were covered with a 10 nm SiO₂ capping layer, which was sputtered from a SiO₂ target with RFP_SiO₂ = 3.3 W/cm². This manipulation was used to prevent Ge outward diffusion in Ge-doped samples upon thermal treatment [22]. After deposition, each 6-in wafer was cut into small pieces of 1 × 1 cm² (so-called hereafter as “samples”). Both schematic presentation of deposition process and the architecture of the samples are shown in Fig. 1.

![Fig. 1 Schematic presentation of “top-down” co-sputtering process (left image), sample architecture and annealing parameters (right image)](image-url)
To study the effect of thermal treatment on the sample properties, the samples were subsequently annealed at $T_A = 500$–$800 \degree C$ for 30 s in nitrogen flow using a rapid thermal processing tool. The temperature profiles are presented in Fig. 1.

**Sample Characterization**

As-deposited and annealed samples were characterized with Fourier-transform infrared (FTIR) spectroscopy, multi-angle laser ellipsometry, Auger electron spectroscopy, Raman scattering and X-ray diffraction.

FTIR spectra were measured in the range of 460–4000 cm$^{-1}$ by means of a Spectrum BX FTIR spectrometer (PerkinElmer Inc.) and a Nicolet Nexus FTIR spectrometer. The spectra were recorded in “transmission” mode at normal or Brewster (65°) incidence of excited light, using both atmospheric and Si substrate corrections. Multi-angle laser ellipsometric measurements were carried out with a LEF-3 M setup operating with a 632.8-nm light wavelength for the range of incidence angles of 45–90°. More details can be seen elsewhere [23].

X-ray diffraction data were collected with a Philips XPERT apparatus using Cu K$_\alpha$ radiation in a 2θ range of 20°–80°. An asymmetric grazing geometry was chosen to increase the volume of material interacting with the X-ray beam, as well as to reduce contributions from the Si substrate. The data were compared with standard cards of Powder Diffraction File Database (#37-1484 for monoclinic ZrO$_2$, #50-1089 for tetragonal ZrO$_2$, and #4-0545 for cubic Ge).

Raman spectra were excited with 488.0 nm radiation of an Ar$^+$-laser and recorded using a LabRam HR800 micro-Raman system in backscattering mode. The power of the laser excitation was chosen to prevent the heating of the samples.

The stoichiometry of the films was determined by Rutherford backscattering spectrometry (RBS) and Auger electron spectroscopy (AES). For RBS study, the films were deposited on carbon substrates at the same deposition conditions as described above. The RBS measurements were carried out using He$^+$ ions with energy of 1.7 MeV and a backscattering angle of 170°. For AES experiment, the Auger microprobe JAMP 9500 F (JEOL), with 3 nm resolution in the secondary electron image mode was used. The micro-probe was equipped with sensitive hemispheric Auger spectrometer with energy resolution $\Delta E/E$ from 0.05 to 0.6% and an ion etching gun for layer-by-layer analysis with diameter of Ar$^+$ ion beam 120 μm, able to move by raster 1 x 1 mm. Variation range of the beam Ar$^+$ ion energy is from 0.01 to 4 keV, while minimal beam current is 2 μA with 3 keV. More details can be found elsewhere [24].

All the measurements were performed at room temperature.

**Results and Discussion**

Ellipsometry, RBS, and AES Study

One of the most effective optical methods of researching the properties of the interface of two media and thin film heterostructures is ellipsometry. Both the thickness and optical constants of layers can be determined, when two quantitative characteristics (amplitude ratio $\Psi$ and phase difference $\Delta$) of polarized light reflected from the surface are examined simultaneously. According to the ellipsometric measurements of the polarization angles $\Psi(\varphi)$ and $\Delta(\varphi)$, the refractive index $n$, absorption coefficient $\alpha$ and thickness $d$ of the film can be extracted by solving the inverse ellipsometric task using the method of minimizing the quadratic objective function [25].

The experimental data of $\Psi(\varphi)$ and $\Delta(\varphi)$ obtained for the Ge-ZrO$_2$ samples deposited with different RFP$_{Ge}$ are shown in Fig. 2(a,b). To fit these data, a four-phase model...
optical model was applied [25, 26]. It consists of a silicon substrate, thermal SiO$_2$ layer (with the thickness of about 5 nm appeared on Si substrate surface due to wafer processing); non-stoichiometric Ge-ZrO$_2$ layer; capping SiO$_2$ layer and a surface rough layer that is composed of a mixture of void space and SiO$_2$ capping layer. Figure 3 shows the variation of $n_{\text{Ge-ZrO}_2}$ and $\alpha_{\text{Ge-ZrO}_2}$ for as-deposited Ge-ZrO$_2$ samples together with the data obtained for pure Ge and pure ZrO$_2$ films.

Figure 3 shows the evolution of the refractive index $n_{\text{Ge-ZrO}_2}$ and the absorption coefficient $\alpha_{\text{Ge-ZrO}_2}$ for Ge-ZrO$_2$ samples sputtered at various RFP$_{\text{Ge}}$. Generally, the increase of both parameters with RFP$_{\text{Ge}}$ can be seen. However, two specific ranges of the $n_{\text{Ge-ZrO}_2}$ variation can be distinguished when this latter is compared with the refractive index of ZrO$_2$, i.e., $n_{\text{Ge-ZrO}_2} < n_{\text{ZrO}_2}$ for the films grown with RFP$_{\text{Ge}} < 0.9$ W/cm$^2$ and $n_{\text{Ge-ZrO}_2} > n_{\text{ZrO}_2}$ when RFP$_{\text{Ge}} > 0.9$ W/cm$^2$. For the latter case, the $n_{\text{Ge-ZrO}_2}$ increases from 2.64 (RFP$_{\text{Ge}} = 1.1$ W/cm$^2$) to 3.16 (RFP$_{\text{Ge}} = 2.2$ W/cm$^2$). Since the refractive index of pure Ge ($n_{\text{Ge}} = 4.60$) exceeds that value of pure ZrO$_2$ ($n_{\text{ZrO}_2} = 1.98$), this tendency is in agreement with the higher Ge content in the films grown with higher RFP$_{\text{Ge}}$.

Taking into account Bruggeman effective medium approximation and considering the Ge-ZrO$_2$ samples as a mixture of pure Ge and pure ZrO$_2$ phases, i.e., Ge$_x$(ZrO$_2$)$_{1-x}$, the Ge content can be roughly estimated. More details about this procedure can be found in [10]. The obtained results show that the Ge content could be adjusted over a wide range (up to 47 at%) via the RFP$_{\text{Ge}}$ variation, while keeping other deposition parameters constant (Table 1). It is worth to note that any contribution of GeO$_2$ or voids was ruled out. This can result in the underestimation of Ge content in the films grown with RFP$_{\text{Ge}} = 1.1$–2.2 W/cm$^2$.

The samples grown with the RFP$_{\text{Ge}} = 0.7$ W/cm$^2$ show a refractive index of $n_{\text{Ge-ZrO}_2} = 1.75$. Such a low value supposes the formation of a phase with lower refractive index, for instance, GeO$_2$ or Ge suboxides. Assuming the Ge-rich-ZrO$_2$ film is a mixture of GeO$_2$ and ZrO$_2$ phases, the Ge content of the sample was estimated to be about 17%.

The determination of the Ge content for the sample grown with RFP$_{\text{Ge}} = 0.9$ W/cm$^2$ was more complicated. As one can see from Fig. 3a, this sample has a refractive index of $n_{\text{Ge-ZrO}_2} = 2.0$ which is close to $n_{\text{ZrO}_2} = 1.98$. Taking into account the results described above, as well as the higher absorption coefficient measured for this sample (Fig. 3b), one can assume that it should contain a Ge content higher than 17% obtained for the sample fabricated with RFP$_{\text{Ge}} = 0.7$ W/cm$^2$. However, the consideration of this sample either as Ge$_x$(ZrO$_2$)$_{1-x}$ or as (GeO$_2$)$_x$(ZrO$_2$)$_{1-x}$ did not bring any reasonable values for the Ge content. Nevertheless, taking into account the variation of Ge content obtained for all other samples, one can extrapolate the Ge content for the sample grown with RFP$_{\text{Ge}} = 0.9$ W/cm$^2$. Under these assumptions, it turned out that this sample contains about 21 at% of germanium.

Some of the samples described above were characterized by RBS and AES. The results on RBS are summarized also in Table 1. These data are in good agreement with those extracted from ellipsometry. However, some Si contamination at the level of 2–4 at% was detected. It could appear due to cross contamination of Si deposition processes carried out earlier. However, Si content decreases with increasing RFP$_{\text{Ge}}$ (Table 1).

The analysis of the samples with AES showed a homogeneous distribution of Ge and Zr in the Ge-rich-ZrO$_2$ volume (Fig. 4a). At the same time, some incorporation of Zr and Ge in the thermal and capping SiO$_2$ layers was observed (Fig. 4a) that can be due to preferential sputtering.
at the interfaces. Besides, similar to RBS experiment, some traces of Si were also detected. It is worth to point that doping with Si is considered as a way to stabilize amorphous structure of HfO$_2$ and ZrO$_2$ films [26, 27]. However, in this case, Si content should be higher than 10%. This means that Si contamination observed in our ZrO$_2$ and Ge-rich ZrO$_2$ samples is negligible to affect significantly their structural properties.

After thermal treatment the homogeneous distribution of Ge and Zr was conserved (Fig. 4b). However, some decrease of Ge content in the volume of Ge-rich-ZrO$_2$ was observed, whereas the near surface region was found to be depleted in Ge. This transformation of Ge distribution can be caused by the outward diffusion of Ge during annealing (Fig. 4b).

To investigate the effect of Ge content on the microstructure of the Ge-rich-ZrO$_2$ films and on its evolution with annealing, the samples described above as well as pure ZrO$_2$ films were investigated by FTIR.

### FTIR Study of Pure and Ge-Rich ZrO$_2$ Materials

Among express and nondestructive methods, FTIR holds an important place. It allows the evolution of the samples’ microstructure to be monitored as a function of the chemical composition and/or thermal treatment. In regard to Ge-rich-ZrO$_2$ materials, only a few groups reported about FTIR studies of bulk ZrGeO$_4$ [28] or GeO$_2$ contained glasses [29]. At the same time, the Ge-rich-ZrO$_2$ thin films were not often addressed [10, 18]. Nevertheless, the interpretation of experimental FTIR spectra can be based on the comparison of infrared spectra of ZrO$_2$ [30] and GeO$_2$ and their transformation with the increase of the contribution of high-k phase in solid solution. For our samples this means that we will compare FTIR spectra measured for pure ZrO$_2$ films with those obtained for Ge-rich-ZrO$_2$ counterparts, as well as with data available in the literature (Table 2). The validity of such an approach was demonstrated for Si-rich HfO$_2$ [26, 31], Ge-rich HfO$_2$ thin films [8], and Zr-doped Ta$_2$O$_5$ [32].

### Pure ZrO$_2$

Usually, transmission FTIR spectra are detected under normal incidence of exciting light. However, when Brewster configuration is used, additional longitude phonons can be revealed. For pure ZrO$_2$ films, transmission FTIR spectra show the vibration band in the range of

| RFP$_{Ge}$, W/cm$^2$ | Ellipsometry data | RBS data$^a$ |
|----------------------|-------------------|--------------|
|                      | n @ 632.8 nm | Ge, at.% | Zr, at % | O, at% | Si, at% | Density, at/cm$^2$ |
|----------------------|-------------|---------|---------|-------|--------|-----------------|
| 0                    | 1.970       | 0       | 0       | 26.5  | 67.0   | 6.0             | 1.35E+18       |
| 0.7                  | 1.749       | ~17     | 15.0    | 17.5  | 62.9   | 4.0             | 1.43E+18       |
| 0.9                  | 2.000       | ~21     | (22.0)  | (16.0) | (57.0) | (3.0)           | -              |
| 1.1                  | 2.641       | ~30     | 30.0    | 14.0  | 52.0   | 3.0             | 1.20E+18       |
| 1.3                  | 2.730       | ~32     | (33.0)  | (13.0) | (50.0) | (3.0)           | -              |
| 1.6                  | 2.983       | ~40     | 42.0    | 10.5  | 43.9   | 2.5             | 1.17E+18       |
| 2.2                  | 3.167       | ~47     | 53.0    | 8.0   | 35.9   | 2.0             | 1.09E+18       |

$^a$Note. The content of the elements placed in the parentheses was obtained by the extrapolation of RBS data.
380–800 cm\(^{-1}\). For amorphous films, this band is broad and featureless. For ZrO\(_2\) crystalline films, several bands can be detected (Table 2). The appearance of a vibration band peaked at 740–770 cm\(^{-1}\) is the evidence for the formation of monoclinic ZrO\(_2\).

FTIR spectra of as-deposited and annealed pure ZrO\(_2\) films are shown in Fig. 5a and b, respectively. Two broad bands in the range of 400–750 cm\(^{-1}\) and 800–1250 cm\(^{-1}\) can be seen. Since both bands are featureless, this means that as-deposited ZrO\(_2\) films are amorphous.

Annealing of pure ZrO\(_2\) samples at \(T_A \leq 700 ^\circ C\) did not cause the transformation of FTIR spectra. When \(T_A = 800 ^\circ C\), the Zr-O related band becomes narrower resulting in the appearance of the bands peaked at \(\sim 460 \text{cm}^{-1}\) and at \(\sim 700 \text{cm}^{-1}\) as well as a shoulder at about 610–620 cm\(^{-1}\) (Fig. 5a,b) corresponding to Zr-O vibrations. Since the peak related to monoclinic ZrO\(_2\) was not detected for the annealed films, one can suppose an appearance of tetragonal or cubic ZrO\(_2\) after annealing (Table 2).

Another vibration band was detected in the range of 1000–1200 cm\(^{-1}\) (Fig. 5a,b). It peaks at about 960–980 cm\(^{-1}\). Taking into account the architecture of the samples (Fig. 1), the presence of Zr ions inside SiO\(_2\) interfacial and capping layers as well as the presence of contaminated Si ions in ZrO\(_2\) core (Fig. 4), we can attribute the band peaked at 960–980 cm\(^{-1}\) to Si-O-Zr vibrations. This band is still stable upon annealing at \(T_A \leq 700 ^\circ C\). For \(T_A = 800 ^\circ C\), the transformation of Si-O-Zr band occurs via the appearance of the bands peaked at \(\sim 820 \text{cm}^{-1}\), \(\sim 1060 \text{cm}^{-1}\), and \(\sim 1160 \text{cm}^{-1}\) (shoulder) related to Si-O vibrations [33, 34] (Table 2). At the same time, some contribution of the Si-O-Zr band is still visible for the samples annealed at \(T_A = 800 ^\circ C\) (Fig. 5a,b). Besides, two weaker bands peaked at about 1400 cm\(^{-1}\) and 1600 cm\(^{-1}\) were detected for as-deposited ZrO\(_2\) films and those annealed at \(T_A \leq 700 ^\circ C\). Both of these bands are related to Zr-OH vibrations due to presence of moisture in the film, which contribution decreases with rising \(T_A\).

### Ge-Doped ZrO\(_2\) Samples

Usually, a triplet in the range of 515, 555, and 587 cm\(^{-1}\) connected with hexagonal GeO\(_2\) phase can be observed for Ge-O bonds. In the case of glassy Ge oxide, this triplet reconstructs in one broad band [35, 36]. For ZrGeO\(_4\), the position of Ge-O vibration bands can be detected at 453, 553 and 696 cm\(^{-1}\) (Table 3). Besides, the band at 860, 910, 1060 and 1080 cm\(^{-1}\) can be also originated by Ge-O bonds in crystalline material [28, 29, 37].

In the case of Ge-rich-ZrO\(_2\) films, besides Zr-O and Ge-O bond, one can expect the incorporation of Ge into Zr-O-Zr bond and an appearance of the Zr-O-Ge band.

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**Table 2** Assignment of Zr-O and Si-O related vibration bands

| Type of bonding | Spectral position, cm\(^{-1}\) (vibration type) | Reference |
|-----------------|-----------------------------------------------|-----------|
| Zr-O monoclinic | 350,425,520,595,740 (as-deposited) \(20 ^\circ C\) | [30] |
|                 | 335,410,505,575,740 (shoulder) \(673 ^\circ C\) |           |
|                 | 325,400,505,575 \(910 ^\circ C\)               |           |
| Zr-O tetragonal | 485, 615                                        |           |
| Zr-O cubic      | 450, 485, 615                                   |           |
| Si-O-Si         | 470 (rocking) \(\text{TO}_1\), 820 (bending) \(\text{TO}_2\) | [33] |
|                 | 1086 (asymmetric) \(\text{TO}_3\)               |           |
| Si-O\(^1^-\)    | 970 (terminal Si-O groups produced by network disruption) | [34] |

Fig. 5 Evolution of FTIR spectra with annealing temperature for ZrO\(_2\) films measured under normal (a) and Brewster (b) incidence of excited beam light. Annealing temperatures are mentioned in the figures.
The peak position of the latter one should be observed at higher wavenumbers than that of Zr-O-Zr band. This assumption is based on the fact that the vibration frequency is reciprocal to the masses of bonding ions and $m_{\text{Ge}} < m_{\text{Zr}}$.

Figure 6 shows the FTIR spectra of as-deposited Ge-rich-ZrO$_2$ samples grown with RFP = 0.9 W/cm$^2$ as well as their evolution with annealing treatment. The spectra of as-deposited sample contain two broad bands in the range of 450–800 and 900–1000 cm$^{-1}$. The featureless shape of these bands testifies to the amorphous nature of the films. It is worth to note that the higher Ge content in the as-deposited Ge-rich ZrO$_2$ films, the more featureless and broader FTIR spectra were observed.

The band peaked at about 990–1000 cm$^{-1}$ can be attributed to the Si-O-Zr vibrations similarly to the case of ZrO$_2$ samples described above. However, this band can be a superposition of Si-O-Zr and Si-O-Ge vibrations because the presence of both Ge and Zr ions was seen in SiO$_2$ interfacial and capping layers as well as some Si contamination was detected for Ge-rich-ZrO$_2$ core of the sample.

Another broad band appeared in the range of 450–800 cm$^{-1}$ (Fig. 6). The comparison of this band with that of pure ZrO$_2$ films allows its broadening to be ascribed to the Ge incorporation in ZrO$_2$ host (Fig. 5).

The FTIR spectra of the Ge-ZrO$_2$ films annealed at $T_A$ = 500 and 600 °C are similar to the ones of as-deposited films. This proves the stability of the microstructure of the samples. Annealing at $T_A$ = 700 °C leads to the transformation of Si-O-Zr (Si-O-Ge) bands and a shift of its peak position to ~1045 cm$^{-1}$ as well as an appearance of the shoulder at ~1100 and 1180 cm$^{-1}$ that is mainly due to Si-O vibrations (Fig. 6). For $T_A$ = 800 °C, this transformation is significant. The Ge-O bands peaked at about 790 and 870 cm$^{-1}$ are clearly seen. Besides the increase of the intensity at about 600 cm$^{-1}$ can be due to the overlapping of Zr-O (615 cm$^{-1}$) and Ge-O (595 cm$^{-1}$) vibration bands.

It is worth to note that the presence of OH-related band peaked at ~1440 cm$^{-1}$ was detected for the films annealed at $T_A$ = 800 °C. This can be explained by the adsorption of water by the surface of annealed films.

### Table 3: Assignment of Ge-O related vibration bands

| Type of bonding | Spectral position, cm$^{-1}$ (vibration type) | Reference |
|-----------------|---------------------------------------------|-----------|
| Ge-O            | 515, 555 and 587 (triplet of hexagonal GeO$_2$) | stretching |
| Ge-O-Ge         | 580 (bending), 870 (stretching)              | [37]      |
| Ge-O$^-$        | 1060-1080 (non-bridging)                     | [37]      |
| Ge-O            | 696 stretching (in ZrGeO$_4$)                | [28]      |
| Ge-O-Ge         | 575 bending (in ZrGeO$_4$)                   |           |
| O-Ge-O          | 453 bending (in ZrGeO$_4$)                   |           |
| Ge-O            | 410 ($v$(M-O) in [MO$_4$])                   | [29]      |
|                 | 453 ($\delta$(Ge-O) in [GeO$_4$]$_2$)       |           |
|                 | 506 ($v$(Ge-O) in [GeO$_4$]$_2$ glassy GeO$_2$) |           |
|                 | 502-580 shoulder ($v$(Ge-O) in glassy GeO$_2$) |           |
|                 | 575 ($v$(Ge-O) in [GeO$_4$]$_2$)             |           |
|                 | 586 ($\delta$(Ge-O) in [GeO$_4$]$_2$)       |           |
|                 | 696 ($v$(Ge-O) in [GeO$_4$]$_2$ in orthogermanates) |           |
|                 | doublet 773, 793 ($v$(Ge-O) in metagermanates [GeO$_4$]$_2^{2-}$) |           |
|                 | shoulder 790–890 ($v$(Ge-O) in polygermanates) |           |
|                 | 910 ($v$(Ge-O) in [GeO$_4$]$_2$)             |           |
|                 | 1060 ($v$(Ge-O) in orthogermanates [GeO$_4$]$_2^{2-}$) |           |
|                 | 1080 ($v$(Ge-O) in orthogermanates [GeO$_4$]$_3^{2-}$) |           |
These OH groups can be linked with Zr ions as shown in Fig. 6, but the appearance of Ge-OH band cannot be ruled out.

Thus, the evolution of FTIR spectra described above confirms the phase separation process in Ge-rich-ZrO$_2$ films and the formation of Ge clusters can be expected. Since such formation can be revealed rather by Raman scattering and XRD methods than FTIR ones, same samples were investigated by additional techniques.

**Raman Scattering Spectra of Ge-Rich ZrO$_2$ Materials**

The spectral positions and full-widths of Ge-related phonon modes depend on the material structure. The transition from the amorphous to the crystalline state leads to a significant narrowing of the phonons and to a shift of peak positions towards higher wavenumbers.

Usually, amorphous Ge materials show peaks at about 275 cm$^{-1}$ (TO), 200 cm$^{-1}$ (LO-LA), and 80 cm$^{-1}$ (TA) [38]. Recently, it has been shown that these bands can be distinguished not only for pure Ge films, but also for Ge-doped high-k oxides [8–10]. Thus, one can expect to observe several peaks in the range of 50–400 cm$^{-1}$ in our Ge-rich samples.

Raman scattering spectra of as-deposited pure Ge films were found to be broad and featureless with the peak position at about 275–277 cm$^{-1}$ that testifies to amorphous structure of the films (Fig. 7a). Annealing of the films at $T_A = 500$ °C did not change the film structure, while for higher $T_A$ the presence of a sharp Ge peak at about 299 cm$^{-1}$ was detected due to the crystalline phase. Its intensity increases with rising $T_A$ accompanied by a band narrowing (Fig. 7a). Based on these data one can conclude that the crystallization of sputtered Ge films sets in at $T_A = 550–600$ °C.

Raman scattering of as-deposited Ge-rich-ZrO$_2$ samples were found to be broad and featureless with a maximum at 272–275 cm$^{-1}$ (Fig. 7b). Whatever Ge content in the films, thermal treatment at $T_A \leq 600$ °C causes negligible transformation of the spectra shape. Annealing of Ge-rich-ZrO$_2$ films results in the narrowing of the spectrum as well as in the appearance of a small peak at $\sim 298$ cm$^{-1}$ due to the crystalline phase (Fig. 7b). The intensity of this band increases significantly with $T_A$ rise up to 800 °C, giving an evidence of Ge phase crystallization.

It is worth to note that for the higher Ge content, the formation of Ge clusters and their crystallization occurs at lower $T_A$. For the same $T_A$ values, the Raman peak for the films with higher Ge content becomes to be narrower (Fig. 7c). However, for $T_A = 800$ °C, significant contribution of amorphous Ge signal is still observed for the samples with high Ge content.

Thus, the analysis of Raman scattering data allows to conclude that the crystallization of Ge-ncs occurs at $T_A = 600–700$ °C, demonstrating the trend to the lowering of crystallization temperature when the Ge content increases. However, Raman scattering spectra could not provide information about the evolution of ZrO$_2$ host. For this purpose, the XRD study was performed for the same set of Ge-free and Ge-rich-ZrO$_2$ samples. Besides, information about Ge phase crystallization was also extracted and compared with Raman scattering data.

**X-ray Diffraction Study of Pure and Ge-Rich ZrO$_2$ Materials**

Figure 8 depicts the evolution of XRD patterns of pure and Ge-rich ZrO$_2$ samples. Pure ZrO$_2$ films conserve their amorphous nature up to $T_A = 700$ °C, whereas annealing at higher temperature leads to a crystallization of the films (Fig. 8a). An appearance of strong reflections at $2\Theta \approx 30$, 35, 50, and 60° testifies the formation of
tetragonal ZrO$_2$ phase at $T_A = 800\,^\circ$C (Fig. 8a). This allows concluding that temperature of crystallization of pure ZrO$_2$ films is in the range of 700–800 °C.

Besides the formation of Ge-necs in Ge-ZrO$_2$ samples, these latter showed some lowering of crystallization temperature of ZrO$_2$ host. As one can see from Fig. 8b, XRD patterns selected for Ge-rich films with $[\text{Ge}] = 22$ at.% exhibit two broad bands peaked at $2\Theta \approx 28^\circ$ and $2\Theta \approx 50^\circ$ for $T_A \leq 625\,^\circ$C. These peaks stem from amorphous Ge and ZrO$_2$. After annealing at $T_A = 650\,^\circ$C, a peak at $2\Theta \approx 27^\circ$ appeared. It corresponds to the reflection from (111) Ge family planes and testifies not only the formation of Ge phase via phase separation, but also an appearance of some amount of Ge nanocrystallites. Thermal treatment at $T_A = 675\,^\circ$C leads to the increase of the peak magnitude as well as to the development of two additional reflexes at $2\Theta \approx 45^\circ$ and $2\Theta \approx 55^\circ$, that are the signatures of (222) and (333) reflections of nanocrystalline Ge (Fig. 8b). The higher $T_A$ results in the enhancement of all Ge-related reflexes giving the evidence of pronounced Ge phase crystallization. This data are in a good agreement with Raman scattering ones (Fig. 7).

It is worth to point that whatever Ge content in the Ge-ZrO$_2$ films, the Ger crystallites form at higher $T_A$ than the temperature of the crystallization of pure Ge film (Fig. 8c). However, the peak position of broad band in the range of $2\Theta \approx 26–31^\circ$ shifts gradually from about 30.8° to 26.8° that demonstrates an increase of Ge phase contribution in the film structure.

The evolution of XRD patterns with $T_A$ showed also that an annealing at $T_A = 700\,^\circ$C stimulated an appearance of XRD peaks at $2\Theta \approx 30.4^\circ$ and 50.2°, corresponded to the reflections from (111) and (220) family planes, respectively. For $T_A = 800\,^\circ$C, these peaks became to be stronger and narrower, being accompanied by the appearance of additional peaks in the range of $2\Theta \approx 59–64^\circ$ (Fig. 8b). Analysis of these XRD patterns gives the evidence of the formation of tetragonal ZrO$_2$ phase.

When Ge content increases, the intensity of ZrO$_2$-related peaks decreases, followed by their broadening (Fig. 8c). This means that for the samples with higher Ge content, the crystallization of ZrO$_2$ phase sets in at higher $T_A$ that demonstrates the possibility to form Ge crystallites in amorphous ZrO$_2$ host. It can be assumed that for the films with high Ge content the phase separation was uncompleted and some residual Ge ions are still incorporated in Zr-O-Ge bonds. This fact is supported by the FTIR spectra of the samples annealed at 800 °C (Fig. 6). They showed the vibration band in 460–700 cm$^{-1}$ range that is featureless and broader than that of pure ZrO$_2$ films. Thus for the films with higher Ge content, either higher $T_A$ or longer annealing time (more than 30 s used in present study) are required for complete phase separation.

**General Remarks About Phase Separation Process**

The Ge-rich ZrO$_2$ ternary compounds are usually considered to be a mixture of GeO$_2$ and ZrO$_2$ unit cells as a $(\text{GeO}_2)_x(\text{ZrO}_2)_{1-x}$. In consequence, their decomposition stimulated by thermal treatment on GeO$_2$ and ZrO$_2$ phases is expected. However, if Ge-rich compound suffers from the lack of oxygen ions, phase separation can have more complex behavior. To get insight on this process in our samples, one can take into account
chemical properties of Ge and Zr ions, Ge-O and Zr-O bonds as well as thermodynamic parameters of related oxides summarized in Table 4.

It is known that thermal stability of oxide-based material depends on the coordination number of ions, M-O bond lengths and their nature (ionic or covalent). The materials with higher coordination number, shorter M-O bond length and covalent nature of this bond demonstrate usually thermal stability.

The nature of M-O bonding is determined by the difference in the electronegativity of elements (χ) composed this bond. When \( \chi_{M-XO} = 0 - 0.2 \), the bond is covalent nonpolar, while for \( \chi_{M-XO} = 0.3 - 1.4 \) it is covalent polar. For \( \chi_{M-XO} \approx 1.5 \), the bond has ionic character. Taking into account the properties of Ge and Zr ions (Table 4), one can see that the Zr-O bond is ionic one, whereas Ge-O bond is covalent polar. It is worth to note that the ionic strength increases with the increase of the \( \chi_{M-XO} \) difference, for covalent bonding this relation is opposite.

Taking into account the molar enthalpy and Gibbs energy for ZrO\(_2\), GeO\(_2\) and GeO (Table 4), one can assume that upon thermal treatment of Ge-rich ZrO\(_2\) materials the formation of ZrO\(_2\) phase is most favorable. This means that this phase will form at first upon thermal treatment. However, its crystalline type can be dependent on the appearance of pure Ge and/or Ge oxide phases.

As it was mentioned above, pure ZrO\(_2\) films can crystallize upon growing process and/or under thermal treatment. It was shown that doping with \([\text{Ge}] = 12.5 \text{ at.}\%\) allows to shift crystallization temperature of ZrO\(_2\) to higher values as well as to stabilize ZrO\(_2\) tetragonal phase [12, 27]. Our data show that pure ZrO\(_2\) films can conserve their amorphous nature up to 700 °C (Fig. 8a). The crystallization of ZrO\(_2\) occurs at \( T_A = 800 \text{ °C} \) and results in the formation of tetragonal ZrO\(_2\) domains with mean size of about 10 nm. It was reported that small ZrO\(_2\) grains crystallized usually in tetragonal and/or cubic phase [39]. Thus, the observation of tetragonal ZrO\(_2\) grains in our films can be expected.

The Ge-rich ZrO\(_2\) films showed the formation of tetragonal ZrO\(_2\) phase at lower temperature (~700 °C) (Fig. 8b). The mean size of ZrO\(_2\) domains was found to be about 6 nm that can be one of the reasons of tetragonal phase formation. Another argument for this phase formation is the difference in the Ge-O and Zr-O bond lengths. In the ordered structure, Ge ions adopt a 4-fold coordination leaving eightfold coordination to the larger cations, and the pattern for cation partition is layer-like. When Ge cations incorporate into ZrO\(_2\) host, the formation of Ge-O bonds will cause the stretching out of Zr-O ones [17] because the Ge-O bonds are shorter and stronger than Zr-O distances. Upon annealing this bonding anisotropy will result in the higher tetragonality.

One more argument for the lowering of ZrO\(_2\) crystallization temperature is metallic behavior of Zr ions themselves. Their presence makes weaker Ge-O bonds and, thus, stimulates their breaking, followed by the formation of pure Ge phase. Finally, the depletion of ZrO\(_2\) by Ge will give impact to the ZrO\(_2\) crystallization. At the same time, the formation of Ge crystallites will bring additional stretching of ZrO\(_2\) phase due to larger lattice parameter of Ge crystallites in comparison with that of ZrO\(_2\). Thus, such stretching of ZrO\(_2\) phase will favor the stabilization of its tetragonal modification.

As it was mentioned above, from thermodynamic point of view the formation of ZrO\(_2\) phase is preferable (Table 4). This means that Ge-related phase will appear either as GeO\(_2\) (for the case of (GeO\(_2\))\(_x\)(ZrO\(_2\))\(_{1-x}\) materials) or as GeO\(_x\) (for the case of lack oxygen). In the latter case, the formation of Ge nanoclusters will occur via reaction 2GeO\(_y\) \( \rightarrow \) (2-y)Ge + yGeO\(_2\). However, GeO\(_2\) is known to be transformed at \( T_A = 420 \text{ °C} \) via reaction GeO\(_2\) + Ge \( \rightarrow \) 2GeO followed by desorption of volatile GeO at higher \( T_A (~450-500 \text{ °C}) \) [22, 40]. Thus, the formation of Ge-ncs will depend not only on the Ge content in the films but also on the competition between Ge-ncs and GeO formation during annealing.

Since the Gibbs energy is lower for GeO\(_2\) than that for GeO, one can expect that this competition will be shifted towards Ge-ncs formation when Ge content is higher.

It is worth to note, that the presence of Ge crystallites of large amount in our samples annealed at \( T_A = 700 \text{ °C} \) allowed to suppose that the annealing regime caused

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**Table 4** Chemical properties of Ge, Zr, and O and thermodynamic parameters of related oxides

| Parameter                                                  | Element | Ge   | Zr   | O    |
|------------------------------------------------------------|---------|------|------|------|
| Ionic radius, Å                                            |         | 0.53 | 0.79 | 1.40 |
| Atomic radius, Å                                           |         | 1.23 | 1.60 | 0.66 |
| Electronegativity, χ                                        |         | 2.01 | 1.33 | 3.44 |
| Electronegativity difference upon bond formation, X_M-X_O  |         | 1.43 | 2.11 | 0.0  |
| Coordination number in the M-O bond                        |         | 4    | 7    | -    |
| Type of M-O bond                                           |         | covalent | ionic | -    |
| Length of M-O bond, Å                                      |         | 1.77 | 2.13 | -    |
| Standard molar enthalpy of the oxide formation at 298.15 K, ΔH\(^0\), kJ/mol |         | -261.9 (GeO) | -1000.6 (GeO\(_2\)) | -      |
| Standard molar Gibbs energy of the oxide formation at 298.15 K, ΔG\(^0\), kJ/mol |         | -237.2 (GeO) | -1042.8 (ZrO\(_2\)) | -      |

For further reading on thermal stability and crystallization processes, refer to [12, 27].
GeO formation in Ge-rich ZrO₂ films differs significantly from that described for pure GeO₂ layers [22, 40]. However, for $T_A = 800 \, ^\circ C$, the redistribution of Ge ions over film volume as well as the enrichment of capping SiO₂ layers with Ge observed by AES method can be explained by the significant contribution of GeO formation upon annealing.

Indeed, all the samples were capped with SiO₂ layers that can prevent significant outward diffusion of Ge from the layers via sublimation of GeO [22]. However, AES data showed the decrease of Ge content over film volume. Thus, the increase of $T_A$ up to 800 °C results in the strong competition between two processes (i.e., the Ge-ncs and GeO formation) that is important for the films with lower Ge content. In this regard, to achieve higher amount of Ge-ncs for the films with $[Ge] \leq 30$ at.%, the optimization of annealing treatment can be performed via optimization of annealing time. This work is in progress.

Conclusions

This work shows the utility of RF magnetron sputtering for the fabrication of undoped and Ge-doped ZrO₂ films with required properties. The Ge content in the films was controlled via the RFP Ge value at other constant deposition parameters. Rapid thermal treatment was used to form Ge crystallites in the films. The as-deposited pure ZrO₂ and Ge-ZrO₂ films and those annealed at $T_A \leq 600 \, ^\circ C$ demonstrate amorphous nature. Annealing at higher $T_A$ of Ge-rich ZrO₂ films stimulates a phase separation and the formation of Ge-ncs. The mechanism of phase separation was discussed.

The crystallization of Ge-ncs sets in at $T_A = 640–700 \, ^\circ C$ and depends on the Ge content: the higher the Ge content, the lower is the Ge crystallization temperature. The ZrO₂ matrix crystallizes at higher temperature (680–700 °C) than the Ge phase, but its crystallization temperature is lower than that of pure ZrO₂. An appearance of tetragonal ZrO₂ phase is observed. The technological window to form Ge crystallites in amorphous ZrO₂ host is demonstrated.

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Authors’ Contributions

LK, DL, and JH designed and coordinated the experiment. DL fabricated samples and performed annealing treatment. LK and ZT carried out FTIR experiment, SP performed AES experiment; OG and VP performed XRD study. OK carried out ellipsometry experiment and simulated the spectra; VYu studied Raman scattering spectra; JB performed RBS experiment. LK prepared the draft of the manuscript. All authors discussed the results and corrected the manuscript till its final version. All authors approved the final manuscript.

Competing Interests

The authors declare that they have no competing interests.

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