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# Thermal oxidation of amorphous germanium thin films on SiO<sub>2</sub> substrates

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## Abstract

In this work we report the thermal oxidation of amorphous germanium (*a*-Ge) thin films (140 nm thickness) in air. Following fabrication by conventional thermal evaporation on SiO<sub>2</sub> substrates, the samples were annealed in air at different temperatures ranging from 300 to 1000 °C. By means of x-ray diffraction, x-ray reflectivity, synchrotron grazing-incidence wide-angle x-ray scattering and cross-sectional transmission electron microscopy analysis it is found that the *a*-Ge films abruptly crystallize at 475 °C, while simultaneously increasing the thickness of the oxide (GeO<sub>2</sub>) in a layer by layer fashion. X-ray photoemission spectroscopy reveals that the oxidation state of the Ge atoms in the GeO<sub>2</sub> layer is 4<sup>+</sup>. However, a reaction at the GeO<sub>2</sub>/Ge interface occurs between 500 and 550 °C reducing the oxide layer to GeO<sub>x</sub> (x < 2) and containing Ge<sup>2+</sup> and Ge<sup>+</sup>. The thickness of the oxide layer grows with the annealing temperature following an Arrhenius behavior with an activation energy of 0.82 ± 0.09 eV up to 500 °C. Remarkably, we observed simultaneous enhancement of the oxidation and crystallization of the *a*-Ge in the temperature interval 450 °C–500 °C, in which the oxidation rate reaches a maximum of around 0.8 nm °C<sup>-1</sup> at around 500 °C.

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Keywords: germanium thin films, thermal oxidation, GeO<sub>2</sub>/Ge interface

(Some figures may appear in colour only in the online journal)

# 1. Introduction

Ge and  $GeO_2$  have been tested for different applications in electrical devices. For example, due to limitations encountered upon scaling down Si-based complementary metal– oxide–semiconductor (CMOS) transistors and metal–oxide– field effect transistors (MOSFETs), there is now great interest in testing other semiconductor materials. Among them Ge and III–V compound semiconductors such as GaAs, InP and InGaAs have attracted tremendous attention as a replacement since they have a higher electron and hole mobility than Si [1], particularly in the (110) orientation [2]. The atomic structure and electronic properties of Ge are similar to those of Si. However, it has a smaller band gap (0.66 eV) than Si (1.1 eV) and a higher carrier mobility (3900 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for electrons and 1900 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for holes) [3], although recent developments on Ge quantum well two-dimensional hole gases report an exceptionally high mobility exceeding  $1 \times 10^6$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> [4].

The amorphous form of Ge (*a*-Ge) contains a network of tetrahedrally coordinated Ge atoms (with clusters ordering up to about 1 nm) and embedded microcrystals of size 1-3 nm

[5–8]. Such a network is referred to as 'paracrystalline' [9] and it contains randomly oriented microcrystals which seem not to behave as nuclei for further growth [8]. For device applications of *a*-Ge it is necessary to transform it to high-quality crystalline films. However, techniques for crystallization of *a*-Ge are sophisticated since it easily oxidizes (see the supplemental material S1 for an extended discussion on the crystallization of *a*-Ge).

There are two types of Ge oxide: GeO and GeO<sub>2</sub>. GeO is volatile at temperatures below 500 °C [10, 11], whereas GeO<sub>2</sub> is a stable semiconductor (band gap 5.7 eV [12]). Because  $GeO_2$  on Ge surfaces usually forms in less than 1 min [13], some researchers prevent its formation by means of vacuum or reducing atmospheres, or by depositing protective layers such as  $SiO_2$  (see table S1). In the case of common metals the oxidation is referred to as the reaction of metal cations  $(M^+)$ with the surrounding  $O_2$  to form a top metal-oxide layer [14]. However, the exact mechanism for the oxidation of Ge and the nature of the Ge-oxide interface are still not well understood, because native GeO<sub>2</sub> is chemically and thermally unstable, in contrast to metal oxides [15]. In fact, GeO has been even detected during thermal oxidation of Ge [16] and it is enhanced by the reaction of the  $GeO_2/Ge$  interface [17]. Although many theoretical studies on the  $GeO_2/Ge$  interface have been performed based on calculations on SiO<sub>2</sub>/Si interfaces [18-21], the reaction mechanism still remains unsolved.

Hence, the oxidation mechanism of a-Ge films becomes a complex subject in itself. Furthermore, it is important to understand it for newly proposed  $\text{GeO}_2/\text{Ge}$  devices [22, 23]. In this work, using x-ray diffraction (XRD) and reflection, cross-sectional transmission electron microscopy, synchrotron grazing-incidence wide-angle x-ray scattering and x-ray photoemission spectroscopy, we study the thermal oxidation of a-Ge thin films (140 nm thickness) on SiO<sub>2</sub> substrates following ex situ annealing (from 300 to 1000 °C) in air. The use of an amorphous SiO<sub>2</sub> substrate ensures that if Ge crystallization occurs as a result of the the thermal treatments it is not induced by the substrate but only by self-crystallization of the a-Ge. We found that the a-Ge films abruptly crystallized at 475 °C, while simultaneously increasing the thickness of the oxide (GeO<sub>2</sub>) in a layer by layer fashion. However, a reaction occurs at the GeO<sub>2</sub>/Ge interface between 500 and 550 °C, reducing the oxide layer to  $\text{GeO}_x$  (x < 2). The thickness of the oxide layer increases with the annealing temperature following an Arrhenius behavior.

### 2. Experimental

Germanium was evaporated on polished SiO<sub>2</sub>/Si substrates using an Edwards 306 evaporator system. A relatively thick (~2  $\mu$ m) amorphous SiO<sub>2</sub> layer was used in order to avoid the use of adhesion promoters such as chromium or titanium and to ensure that the crystallization of the Ge is not induced by the substrate. The substrates (2 mm thickness) were uniformly cut into 1 cm<sup>2</sup> pieces and cleaned with acetone and isopropyl alcohol using ultrasound. Small Ge pellets (99.999% purity) were then evaporated from an alumina-coated crucible at a pressure of  $10^{-5}$  mbar. The deposition rate was maintained at 0.1 nm s<sup>-1</sup> and the thickness of the deposited Ge was measured by a quartz crystal microbalance located 10 cm above the source and next to the substrates. During the deposition process the substrates were maintained at room temperature (RT) in order to characterize only post-thermal crystallization and oxidation of the samples. The pristine samples consisted of *a*-Ge films (140 nm) on SiO<sub>2</sub>/Si(001) substrates.

Simultaneous crystallization and oxidation was carried out *ex situ* by annealing the pristine samples in a tubular oven (Lenton LTF-PTF Model 16/610) in an air atmosphere, similar to the procedure reported previously for metal films [24–26]. In the present work, the samples were annealed once at different temperatures ranging from 300 °C up to 1000 °C ( $\pm 0.5$  °C). The heating rate was set to 2 °C min<sup>-1</sup>. Once the desired maximum temperature was reached, it was maintained for 3 h to allow for oxidation and free diffusion of the Ge atoms on the surface. Finally, the quenching rate was set to 2.5 °C min<sup>-1</sup> so as to minimize the stress induced in the films. This means that the shortest annealing time was 7.5 h (for the sample annealed at 300 °C) whereas the longest time was around 18 h (for the sample annealed at 1000 °C).

The crystallization of the sample was studied by XRD. The data were collected from  $20^{\circ}$  to  $60^{\circ}$  (in  $0.02^{\circ}$  steps) using a universal powder diffractometer (Bruker D8 Focus) with Cu  $K\alpha$  radiation (1.5406 Å). X-ray reflectivity (XRR) data were collected from  $0.5^{\circ}$  to  $3.0^{\circ}$  with  $0.004^{\circ}$  step and the 'genetic algorithm' of the DIFFRAC plus LEPTOS 7 program from Bruker was used to fit the data. For the cross-sectional analysis the samples were protected with coatings of Cu (100 nm) and Pt (1  $\mu$ m). The samples were then milled and thinned with a focused ion beam (FIB) in a dual-beam Quanta 3D apparatus (Philips). The interfaces were inspected in a transmission electron microscope (TEM), Tecnai 20 (Philips), with a 200 keV beam generated by a tungsten source. The thickness of the  $GeO_2/Ge$  layers for each sample were measured ten times from each TEM image by using the program ImageJ. The ultraviolet photoelectron spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS) measurements were recorded using an Escalab 250Xi analyzer with He I (source energy 21.2 eV) and Al K $\alpha$  (source energy 1486.68 eV) radiation, respectively. In both cases the tilt and azimuth angles were  $0^{\circ}$ . The Al K $\alpha$  radiation analysis range is in the area of the top 6–12 nm, whereas the ultraviolet radiation is between 2 and 3 nm.

The crystallization was also studied by grazing-incidence wide-angle x-ray scattering (GIWAXS). The measurements were carried-out at beamline D1, Cornell High Energy Synchrotron Source (CHESS), Cornell University, Ithaca, NY, USA. The wavelength was  $\lambda = 1.15$  Å. The beam was focused to a size of  $500 \,\mu\text{m} \times 100 \,\mu\text{m}$  (horizontal  $\times$  vertical) at the sample position. A beam stop for the primary beam and the small angle x-ray scattering signal was employed. A CCD detector with a pixel size of  $46.9 \,\mu\text{m} \times 46.9 \,\mu\text{m}$  was used for GIWAXS with a sample-detector distance of 0.11 m. In order to choose the appropriate incident angle, an x-ray reflectometry scan was performed



**Figure 1.** XRD scans of Ge films on  $SiO_2/Si(001)$  substrates obtained after annealing at different temperatures between 300 and 1000 °C. The best polycrystalline Ge film is detected at 475 °C while the best polycrystalline GeO<sub>2</sub> is observed at 900 °C.

before recording the image. Images were then taken at an incident angle ( $\alpha_i$ ) of 0.4°, which is slightly higher than the critical angle of the film ( $\alpha_{cp}$ ) and lower than the critical angle of the substrate ( $\alpha_{cs}$ ). Thus the entire film was penetrated, the internal film structures could be detected and the beam was fully reflected from the sample/substrate interface. Furthermore, at these incident angles the beam footprint on the sample is similar to the whole sample size. The measurement time was 0.3 s. The samples were moved out of the beam after each measurement to avoid beam damage. The *q*-space calibration was performed by fitting the characteristic scattering signal arising from silver behenate. The conversion of the 2D images from pixels to *q*-values as well as the analysis of the 2D scattering maps were carried out using the self-written GISAS Analysis Package.

## 3. Results and discussions

Figure 1 shows the XRD scans of the samples obtained before and after annealing at different temperatures ranging from 300 to 1000 °C. Initially the sample consisted of an *a*-Ge film with its small crystalline components having no preferable orientation. The XRD can detect only the reflections belonging to the substrate. In the case of the samples annealed at 300 and 450 °C, the peak around 33° corresponds to the SiO<sub>2</sub>/Si substrate and represents the Si(002) 'ghost' peak<sup>5</sup>. As mentioned above, it has been reported that a-Ge intrinsically contains crystallites with sizes between 1 and 3 nm [5-7]. Since the occurrence density of these crystallites is very small  $(10^{6}-10^{8} \text{ cm}^{-2})$  and as they are randomly oriented in the layer [8], they are not detected by XRD. However, during annealing coalescence and growth of these crystallites occurs [7]. The latter has not been detected upon annealing below 450 °C. Furthermore, it has been proposed that a slow increase in temperature during annealing provides enough time for the crystallites to rearrange, nucleate and grow [27]. Note that in this work the rate of increase in annealing temperature was 2 °C min<sup>-1</sup> and we observe an abrupt change and the highest crystallization of the a-Ge film when it is annealed at 475 °C. The Miller indices (111), (220) and (311) reveal the cubic structure of Ge (PDF-2, card no. 04-0545, cell parameter 0.566 nm). The mean crystallite size calculated from the (111) and (220) reflections using Scherrer's equation [28] are 16 and 11 nm, respectively. It is very difficult to calculate the crystallite size from the (311) peak since it is quite hidden in the background noise of the diffractogram.

The crystallization of the Ge film persists up to 500 °C, which was expected to be the crystallization temperature  $T_{\rm C}$ in vacuum (see equation (S1)). The lower crystallization temperature obtained in this work, i.e. 475 °C, suggests that the simultaneous crystallization and oxidation may contribute to the number of nucleation sites for crystallization, as will be discussed below. Furthermore, annealing at 550 °C accelerates the oxidation of the film: the (101) reflection corresponding to the hexagonal GeO2 (PDF-2, card no. 36-1463) appears to coexist with the (111) reflection corresponding to the Ge layer. This peak grows with annealing temperature and it is clearly distinguishable in the sample annealed at 700 °C, while it appears only faintly at 550 °C. The crystallization of this oxide improves upon increasing the annealing temperature, and after annealing at 900 °C the (101), (100) and (012) reflections, at  $2\theta = 20.58^{\circ}$ ,  $26.04^{\circ}$  and  $38.2^{\circ}$ , respectively, are very sharp, indicating the best crystallization. A rough estimation of the grain size by the Scherrer equation [28] yields  $\sim 16$  and 45 nm after annealing the films at 700 and 900 °C, respectively. This indicates that the improvement in the crystallization is due to the growth of the GeO<sub>2</sub> crystallites. At higher annealing temperatures, such as 1000 °C, above the melting point of GeO<sub>2</sub> (938.25 °C [29]), the XRD scan detects only the substrate peak as parts of the film have laterally diffused away.

Figure 2 shows the cross-sectional TEM view of the films obtained before and after annealing at different temperatures ranging from 300 to 900 °C. The as-grown sample does not present any visible oxide layer, at least within the resolution of our measurements. Besides, after annealing at 300 °C, an oxide layer of  $\text{GeO}_2$  is observed on the top surface, which was

<sup>&</sup>lt;sup>5</sup> The Si (001) 'ghost' reflection consists of two peaks, a strong one at around  $32.8^{\circ}$  and a weaker one at around  $32.9^{\circ}$  and it is observed when the substrate is well aligned within the goniometer of the diffractometer.



**Figure 2.** Cross-sectional TEM view of *a*-Ge thin films on  $SiO_2$  substrates after *ex situ* annealing in air at different temperatures as indicated in the images. The top Cu layer was used as a protective layer only for TEM analysis.

not detected by the XRD scans due to its relatively small thickness ( $\sim 20 \text{ nm}$ ) compared with the *a*-Ge film ( $\sim 120 \text{ nm}$  thickness). Similar images were obtained for the samples annealed at 400 and 425 °C (not shown here) in which a homogeneous contrast in the micrographs confirms the absence of any crystalline domain, except for a slight increase in the thickness of the oxide layer (around 22 nm after

annealing the sample at 425 °C; see the list of oxide thick-

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nesses in table 1). The improvement in the Ge crystallization detected by XRD in the sample annealed at 475 °C is also reflected in its texture as observed by TEM. Note the presence of crystallites with interplanar distances of 0.32 and 0.19 nm corresponding to the Ge Miller indices (111) and (220), respectively, as detected by XRD above. A better resolved TEM image for this sample is shown in figure S1 of the supplementary material in which the crystalline (111) regions are bigger than the (220) regions, confirming the grain size differences obtained from the XRD analysis. Moreover, note that the (111)-oriented crystallites are more abundant than the (220) and (311) ones, which is in agreement with the XRD analysis. The sample annealed at 500 °C consists of a polycrystalline Ge film covered by a relatively thick ( $\sim$ 70 nm) GeO<sub>2</sub> layer. This means that around 50% of the film has oxidized at this annealing temperature. The amount of oxidation with temperature is discussed in more detail below. An image taken at the edge of the sample revels the granular nature of this oxide layer. The sample annealed at 550 °C shows that most of the Ge film is now oxidized leaving only a thin remaining polycrystalline Ge film.

Complete oxidation of the Ge into  $\text{GeO}_2$  is achieved after annealing the sample at 600 °C, in agreement with the XRD analysis. At higher annealing temperatures the GeO<sub>2</sub> layer improves its crystal structure. Eventually the sample annealed at 900 °C consists of a granular polycrystalline GeO<sub>2</sub> film as detected by XRD and observed in the corresponding crosssectional TEM image.

Figure 3 shows the synchrotron GIWAXS pictures, where prominent Bragg peaks at positions which correspond to the *d*-spacing within the crystalline structure of the Ge film are visible. Thus upon using a wide *q*-range the structural characteristics of the samples are studied. The two scattering rings at  $q_z \sim 1.5$  and  $1.8 \text{ Å}^{-1}$ , as indicated by the red arrows within the image corresponding to the sample annealed at 300 °C, are due to the crystal structure of the Si/SiO<sub>2</sub> substrate. These also appear in the other images and can be ignored for the analysis of the Ge and GeO<sub>2</sub> films. Regarding these, the sample annealed at 300 °C shows a low crystallinity with only some crystallites diagonally oriented with respect to the substrate, as shown by the scattering ring at  $q_z \sim 2 \text{ Å}^{-1}$  which is related to the crystal structure of the Ge film.

With the sample annealed at 450 °C, the crystallization changes its orientation from diagonal to a random powderlike orientation. Due to their small number and size, these crystallites have not been detected by XRD, but they confirm the observation of previous authors that during the initial stage of thermal crystallization of *a*-Ge coalescence and growth of crystallites occur [7]. This annealing temperature is not sufficient to crystallize the amorphous film. In contrast, the sample annealed at 475 °C shows a clear dominant crystal plane, indicating an ordered crystallization. This plane, with a crystal spacing of around 3.2 Å, corresponds to the {111} family of planes of the crystalline Ge film. This result agrees very well with the XRD data presented above, as it confirms

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**Figure 3.** 2D GIWAXS map, as a function of the scattering vector q, of amorphous Ge films after annealing between 300 and 900 °C. The incident angle ( $\alpha_i$ ) = 0.4°.

**Table 1.** Thicknesses of the GeO<sub>2</sub> layers obtained by cross-sectional TEM and XRR, respectively and binding energy values of the Ge 3d, Ge  $2P_{3/2}$  and O 1 s peaks obtained by XPS measurements.

			Electronic states (eV)		
T (°C)	$d_{\text{GeO2-TEM}}$ (nm)	$d_{\text{GeO2-XRR}}$ (nm)	Ge 3d	Ge 2P <sub>3/2</sub>	O 1 s
300	$19.30\pm2$	21.2	$32.80\pm0.15$	$1221.18\pm0.1$	$532.48\pm0.05$
400	$15.70\pm2$	21.9	$32.88\pm0.1$	$1221.08 \pm 0.1$	$532.48\pm0.1$
425	$22.20\pm1$	27.9	$32.98\pm0.1$	$1220.98 \pm 0.1$	$532.38\pm0.1$
450	$30.70\pm2$	33.9	$32.88\pm0.05$	$1220.98\pm0.05$	$532.38\pm0.05$
475	$32.4 \pm 1$	39.7	$32.88\pm0.2$	$1220.98\pm0.05$	$532.18 \pm 0.15$
500	$71.50\pm2$	64.3	$31.18\pm0.15$	$1219.28 \pm 0.3$	$530.48\pm0.1$
550	$101.70\pm2$	102.00	$30.68\pm0.05$	$1218.38 \pm 0.05$	$529.88\pm0.05$
600			$34.88\pm0.05$	$1223.38 \pm 0.05$	$534.48  \pm  0.05$
700			$34.78\pm0.05$	$1223.18 \pm 0.15$	$534.28\pm0.1$
800			$34.98\pm0.05$	$1223.48 \pm 0.05$	$534.48\pm0.05$

that the *a*-Ge abruptly crystallizes at this annealing temperature.

The 2D scattering map for the sample annealed at 500 °C is identical to the sample annealed at 475 °C but it shows a lower degree of crystallinity. This apparent low crystallinity is caused by the abrupt growth of the top GeO<sub>2</sub> layer as observed by the TEM above, suggesting that the oxidation rate increases with crystallization. This observation is discussed in more detail below. Similarly, the crystallinity signal of the sample annealed at 550 °C weakens since the GeO<sub>2</sub> top layer is much thicker than the buried Ge layer (see TEM above).

For the sample annealed at 600 °C, in which there is no more pure Ge to oxidize (see TEM analysis above), a phase transition to GeO<sub>2</sub> is deduced by the orientation of the crystallites from random to a strongly preferential perpendicular orientation with respect to the substrate. The samples annealed above 600 °C improve crystallization: the rings at q = 1.8 and  $1.45 \text{ Å}^{-1}$  indicate interplanar distances of 3.42and 4.32 Å corresponding to the {101} and {100} family of planes as detected in the XRD analysis above. Thus in the samples annealed above 600 °C the crystal domain size increases and the dominant GeO<sub>2</sub> crystal plane becomes more pronounced. This confirms that the improvement in crystallization of the GeO<sub>2</sub> layers is accompanied by crystallite growth as previously suggested in the XRD analysis above.

Since cross-sectional TEM images provide information about the oxide thicknesses only from very small areas, x-ray reflectivity measurements have been performed. Figure 4 shows the experimental and simulated XRR curves of the amorphous Ge samples obtained after annealing at different temperatures between 300 to 500 °C. The XRR curve for the as-grown sample shows clear fringes meaning a smooth surface, as expected since most of the sample is a-Ge with no annealed oxide layer. In contrast, for the annealed samples, the XRR scans show wide-angle fringes due to the presence of GeO<sub>2</sub>. For the sample annealed at 300 °C, the computed thickness of the oxide layer from the simulated XRR loop is  $\sim$ 21 nm, which is quite similar to the value obtained by crosssectional TEM above. The computed values of the GeO<sub>2</sub> thickness are listed in table 1. A complete list of the roughness and densities for the refined model is given in table S2.

The XRR scans of the annealed samples show the coexistence of two profile fringes. The ones with a small  $\Delta\theta$  arise from the *a*-Ge layer, while those ones with a wide  $\Delta\theta$  come from the GeO<sub>2</sub> top layer. Note from table 1 that there is a pronounced difference in the oxide thickness obtained by XRR and cross-sectional TEM for most annealed samples, which might be caused by surface diffusion and not be detected by TEM since it is limited to local inspection from the cross-sections. Remarkably, the intensity of the fringe profile with small  $\Delta\theta$  decreases for the sample annealed at 475 °C. This might be caused because the amount of *a*-Ge has decreased, as discussed in the crystallographic and TEM analysis above, together with the increase in the GeO<sub>2</sub> thickness. The XRR scans for the sample annealed at 500 °C and those annealed above (not shown here) showed similar



**Figure 4.** Experimental and simulated XRR curves of Ge films on SiO<sub>2</sub> substrates obtained after annealing at different temperatures between 300 and 500 °C. Samples annealed above 500 °C (not shown here) showed similar loops to that annealed at 500 °C and were without fringes due to the increase in roughness.

curves with no fringes, meaning very rough surfaces which produce a large uncertainty in the fitting.

Figures 5(a) and (b) show the Ge 3d and Ge  $2P_{3/2}$  XPS spectra for the amorphous Ge films annealed at different temperatures. The signals correspond to the top layer which in all the samples is GeO<sub>2</sub>. The positions of the peaks are listed in table 1. For the samples annealed below 475 °C, the peaks in the Ge 3d and Ge  $2p_{3/2}$  spectra are centered around 33 and 1221 eV, respectively, and they correspond to Ge<sup>4+</sup> [12]. Increasing the annealing temperature to 500 and 550 °C, the corresponding peaks shift to lower binding energy levels. Considering that the Ge reduction leads to a chemical shift of about 0.8 eV per Ge–O bond [30, 31], then the XPS peaks obtained at 500 and 550 °C are identified as corresponding to Ge<sup>2+</sup> and Ge<sup>1+</sup>, respectively [32]. This suggests that these annealing temperatures promote an increase in the kinetic energy of the electrons in the 3d and  $2p_{3/2}$  levels, and,



**Figure 5.** Al K $\alpha$  XPS of amorphous Ge thin films after annealing at different temperatures: (a) Ge 3d, (b) Ge  $2P_{3/2}$  and (c) O 1 s. (d) Ultraviolet photoelectron spectroscopy excited by He-I.

depending on the annealing temperature, the  $Ge^{4+}$  atoms reduce to  $Ge^{2+}$  and  $Ge^{1+}$ .

The chemical shifts detected in the 3d and  $2p_{3/2}$  levels of the samples annealed at 500 and 550 °C also suggest a phase transition to GeO<sub>x</sub> (where x < 2) [15], which has also been studied by other techniques [33]. However, for the samples annealed at higher temperatures than 550 °C (in which there is no further pure Ge to oxidize and the GeO<sub>2</sub> formed is stable), both the 3d and  $2p_{3/2}$  spectra increase in binding energy to values of around 34.8 and 1223 eV, respectively. These shifts originate from the band bending caused by the occupancy of the band gap states, indicating an increase in the proportion of highly ionized atoms on the GeO<sub>2</sub> surface.

In order to better elucidate the phase transition from  $GeO_2$  to  $GeO_x$ , O 1 s level XPS was performed (see figure 5(c)). In this case the binding energy for the samples annealed below 475 °C is around 532.5 eV and it is assigned to GeO<sub>2</sub> [10]. However, after annealing at higher temperatures it presents a similar chemical shift when compared with the Ge 3d and Ge  $2p_{3/2}$  spectra. The corresponding binding energy values are listed in table 1. Remarkably, annealing at 500 and 550 °C causes the peak to shift to 529.88 and 530.48 eV, respectively. This confirms the phase transition from  $\text{GeO}_2$  (containing  $\text{Ge}^{4+}$ ) to  $\text{GeO}_r$  (containing  $\text{Ge}^{2+}$  and Ge<sup>+</sup>, respectively) [15]. In the case of the sample annealed at 550 °C, the corresponding binding energy is similar to GeO (x = 1) [15], which has also been detected at this temperature by ellipsometry, Auger electron spectroscopy [34] and thermal desorption spectroscopy [17]. In this sense, the direct formation of GeO from the underlying Ge (reaction: Ge+(1/ $2)O_2 \rightarrow GeO)$  can be discarded since none of the respective Ge 3d, Ge  $2p_{3/2}$  and O 1 s spectra show the coexisting signals of GeO and GeO<sub>2</sub>. Therefore the phase transition originates from the reduction of the GeO<sub>2</sub> layer instead, as also suggested by other authors [10, 34]. Hence, this originates from the  $GeO_2/Ge$  interface reaction following [15]:

$$Ge^{4+}O_2^{2-} + Ge \xrightarrow{\Delta} 2GeO.$$
 (1)

Therefore, annealing at 500 and 550 °C promotes the reduction of the GeO<sub>2</sub> layer. In contrast, for the sample annealed at 600 °C and higher, the O 1 s binding energy shifts to larger values. This is reasonable since the consumption of Ge is by now complete (see XRD and TEM above) and there is no further GeO<sub>2</sub>/Ge interface to react, leading to a highly ionized GeO<sub>2</sub> layer due to the high-temperature annealing.

Figure 5(d) shows the He-I UPS measurements of the *a*-Ge films after annealing at different temperatures. The data correspond to the top oxide layer and are better resolved with annealing temperature suggesting that the valence band resolution depends on the crystallinity of the GeO<sub>2</sub> layer. In particular, the spectra of the samples annealed below 450 °C show broad peaks centered around 9–10 eV. These broad peaks can be fitted with multiple peaks, which might indicate either random adsorption sites or multiple highly reactive species such as Ge, GeO and GeO<sub>2</sub>. If GeO was present it was

below the detection level of core XPS, presented above, due to its small amount.

The UPS spectrum of the sample annealed at 475 °C shows a clear valence band maximum around 9 eV suggesting a wide valence band offset between the GeO<sub>2</sub> and the polycrystalline Ge layers. Above 475 °C the main UPS peaks shift to lower values with annealing temperature, which is a signal of GeO formation as suggested by Pabhakaran [10, 15], and confirms the GeO<sub>2</sub> decomposition as described above. At annealing temperatures above 600 °C, when most of the film is oxidized, the UPS spectra are better resolved. The samples annealed at 700 and 800 °C show that the main peak in the UPS shifts to around 5.6 eV which corresponds well to the bandgap of 5.7 eV for GeO<sub>2</sub> [15, 35], whereas a secondary peak appears at around 9.3 eV. These values are assigned as originating from non-bonding or  $\pi$ -bonding O 2p orbitals and from the  $\sigma$ -bonding O 2p orbital, respectively [15, 35].

In general, the difference between the UPS features in the figure should be related to differences in the oxygen chemisorption and/or dimerization energy between the surfaces. For the lower annealing temperatures, the wide peaks represent the difficulty in localizing the respective hybrid O 2p orbital (due to the presence of volatile GeO), whereas for higher annealing temperatures this orbital is better resolved. This effect is accompanied by an increase in the oxidation rate, oxide thickness and crystallization for annealing temperatures above 475 °C.

In this work, the growth of the oxide layer is related to the remaining thickness of the *a*-Ge film and can be estimated by:

oxidation(%) = 
$$\left(\frac{d_{\text{GeO}_2}}{d_{\text{Ge}} + d_{\text{GeO}_2}}\right) \times 100\%$$
 (2)

where  $d_{\text{Ge}}$  and  $d_{\text{GeO2}}$  are the thicknesses of the Ge and GeO<sub>2</sub> layers, respectively. Figures 6(a) and (b) show the growth of the oxide layer as a function of the annealing temperature *T* obtained from the TEM images and XRR, respectively. After fitting the oxidation curves (in %) we obtain the following oxidation growth equations:

oxidation(%)<sub>TEM</sub> = 
$$d_0 + 0.04e^{\left(\frac{T}{75}\right)}$$
 (3)

oxidation(%)<sub>XRR</sub> = 
$$d_0 + 0.006e\left(\frac{T}{60}\right)$$
 (4)

where  $d_0$  is the smallest proportion of the measured thickness made up of the GeO<sub>2</sub> layer at room temperature (~3% from the TEM data and 7% from the XRR). The different results might be caused by the different information scales obtained by both techniques. The cross-sectional TEM images provide oxide thicknesses from smaller areas than those obtained by XRR.

The oxidation rate, obtained from the derivative of these curves, strongly depends on annealing temperature and it presents Arrhenius-like behavior at temperatures below 500 °C. For both cases, the oxidation rate increases at 400 °C and reaches a maximum (of around  $1.1 \text{ nm K}^{-1}$ ) at 500 °C after which it decreases, suggesting a change in the oxidation mechanism. Remarkably, annealing at 475 °C enhances the



**Figure 6.** Ge consumption after annealing in air at different temperatures computed by cross-sectional TEM (a) and XRR (b). The oxidation rate was obtained from the first derivative of the oxidation. Insets: Arrhenius plots of the oxidation rate below 500  $^{\circ}$ C (see text for details).

simultaneous crystallization and oxidation of the *a*-Ge film, suggesting that the oxidation rate may increase with the crystallization. This has also been concluded by Mastail *et al* by means of density functional theory (DFT) calculations [36]. Moreover, by means of XPS analysis, a recent work performed by Sahari *et al* on native oxidation of Ge(111) and (100) substrates also suggests that the oxidation rate depends on the crystallization of the surface [33]. This effect is also observed in the present work.

The Arrhenius plots obtained by fitting the oxidation rates with equation (5) are shown in the insets of figure 6:

$$k = A e^{\frac{-|E_a|}{k_B T}}$$
(5)

where k is the Arrhenius rate constant, A is the pre-factor,  $E_a$  is the activation energy, T is the temperature (in K) and  $k_B$  is the Boltzmann constant. After fitting the data measured by both techniques, we obtained:  $A_{\text{TEM}} = 2 \times 10^5 \text{ nm K}^{-1}$ ,  $A_{\text{XRR}} = 1.6 \times 10^4 \text{ nm K}^{-1}$ ,  $E_{a\text{-TEM}} = 0.82 \pm 0.09 \text{ eV}$  and

 $E_{\text{a-XRR}} = 0.6 \text{ eV}$ . Despite the fact that the cross-sectional TEM images provide thicknesses from smaller areas than XRR, the value of the activation energy obtained by this technique is quite similar to that obtained for the diffusion of Ge atoms on Ge(111) ( $E_{\text{Ge-Ge}(111)} = 0.83 \pm 0.02 \text{ eV}$  [37]), confirming that during the thermal oxidation transport of Ge ions from the Ge underlayer matrix occurs.

The assumption of a stressed interface does not apply for the samples annealed at 500 and 550 °C because of the high GeO desorption caused by the Ge/GeO<sub>2</sub> reaction, resulting in a decrease of the oxidation rate. Eventually, after annealing at 600 °C there is no further Ge to consume and the film is completely oxidized.

The process during the initial stages in the oxidation of the *a*-Ge film is complicated since it usually depends on many factors such as the thickness of the film, annealing temperature, oxygen partial pressure, annealing rate, annealing time, etc. In the present work, annealing was performed in air and thus the oxygen partial pressure can be considered constant (0.21 bar). Oxidation starts immediately after deposition, as a natural process, due to the exposure of the *a*-Ge surface to air. Following the oxidation process model for metal films proposed by Cabrera and Mott [14], we suggest here a model for the oxidation of a-Ge films. The oxidation of a-Ge might occur by free electron transfer through the solid-gas interface to form a monolayer of adsorbed oxygen  $O^{2-}$  ions on the surface, as schematically represented in figure 7. The resulting separation of charges at the interface induces a potential difference V across this initial layer, which is assumed to be independent of temperature [13]. Assuming  $\Delta x$  is the thickness of this initial layer, then an electric field  $E(V/\Delta x)$  is set up at the interface promoting the transfer of more anions [38, 39]. The predominant oxidation state of the non-reacted *a*-Ge film is  $Ge^{0+}$ ; however, the transfer of electrons should leave behind Ge cations at the metal-oxide interface. Since the XPS results above reveal that they are Ge<sup>4+</sup> and considering  $n_i$  as their concentration, then a current of:

$$I = n_i v_i V / \Delta x \,(\text{ions cm}^{-2} \,\text{s}^{-1}) \tag{6}$$

where  $v_i$  is the ion velocity, should flow through the oxide to form a new oxide layer.

In addition, when the *a*-Ge surface interacts with air there should be a continuous redistribution of oxide nucleation to preferred sites. The preferred sites for oxide nucleation might be surface defects such as vacancies in the terrace, adatoms on the terrace, monoatomic steps in the surface, ledges or kinks. Thus, during oxidation the nucleation sites expand laterally forming the natural GeO<sub>2</sub> film. It has been reported that this natural oxide film grows in a stepwise trend of about 0.2–0.3 nm, which is similar to the Ge–O bond length of 0.2 nm [40] and it stops at a thickness of 1.2 nm [32].

Annealing provides more energy to the  $Ge^{4+}$  cations and  $O^{2-}$  ions to diffuse, diminishing the impact of the initial electric field for continuing growth. The oxidation reaction is then thermally controlled by:

$$\operatorname{Ge}^{4+} + \operatorname{O}_2^{2-} \xrightarrow{\Delta} \operatorname{GeO}_2.$$
 (7)



**Figure 7.** Proposed model for the initial stages of the oxidation of a-Ge surfaces. Left: oxidation occurs by transfer of electrons through the solid–gas interface to form a monolayer of adsorbed oxygen ions on the surface. Right: the resulting separation of charges induces a potential difference V across this initial oxide layer promoting the transfer of more anions (see text for more details).

In this way, one molecule of  $\text{GeO}_2$  results from the reaction between one molecule of oxygen and one  $\text{Ge}^{4+}$ . Since in this work oxidation occurs from the top, then the  $\text{Ge}^{4+}$  cations diffuse faster and they reach the oxygen atoms first, incorporating an additional  $\text{GeO}_2$  into the oxide network and thus resulting in an increase in the oxide layer thickness. Note that no  $\text{GeO}_2$  grains have been detected by TEM embedded deep into the *a*-Ge layer, indicating that the growth of  $\text{GeO}_2$  occurs layer by layer.

### 4. Conclusions

In summary, the oxidation of a-Ge thin films by annealing in air has been studied. From the XRD and GIWAS analysis we observed that despite the presence of a top GeO<sub>2</sub> layer the underlying a-Ge crystallizes over a relatively short range of annealing temperatures (475 °C-500 °C) into a (111) textured Ge film. From the cross-sectional TEM, XRR, XPS and UPS analysis, we found that the thickness of the oxide layer grows in a layer-by-layer fashion with the annealing temperature and following an Arrhenius law behavior. The activation energies obtained by fitting the oxidation rate from cross-sectional TEM measurements and from XRR are  $0.82\pm0.097$  and 0.6 eV, respectively. Remarkably, it has been observed in this work that the rate of oxidation and crystallization of the *a*-Ge film simultaneously increase at annealing temperatures of 475 and 500 °C. The oxidation rate reaches a maximum of around  $0.8 \text{ nm} \circ \text{C}^{-1}$  at around 500 °C. At 500 and 550 °C desorption of  $\text{GeO}_x$  (containing  $\text{Ge}^{2+}$  and  $\text{Ge}^+$ ) occurs due to  $\text{Ge}/\text{GeO}_2$  reaction and resulting in a decrease in the oxidation rate. After annealing at 600 °C there is no further Ge to oxidize, upon which the crystallization of the GeO<sub>2</sub> improves with temperature. Eventually, at very high annealing temperatures, such as 1000 °C, the film melts and laterally diffuses over the surface of the substrate.

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