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Structure and kinetics of disproportionation of GeO thin films

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The study object is thin films ($\sim 10-15$ nm) of germanium monoxide obtained by thermal evaporation in vacuum of composite GeO_2 layers containing Ge nanoclusters and deposition of GeO vapor on a cold substrate. Based on X-ray photoelectron spectroscopy data, it has been established that the short-range order structure of germanium monoxide films can be described by the random bonding model. The stoichiometric parameter x in GeO_x films was 1.07 ± 0.05. Raman spectroscopy and infrared spectroscopy data indicate different depths of the GeO disproportionation process during annealing from 5 to 30 minutes and a temperature of $200-400^\circ$C in vacuum. Annealing for 45 minutes or more at the same temperatures led to partial oxidation of amorphous Ge clusters in the oxide matrix.

Keywords: germanium monoxide, germanium nanoclusters, random bonding model, disproportionation reaction, X-ray photoelectron spectroscopy, Raman spectroscopy, IR spectroscopy.

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1. Introduction

In the scientific community, interest in germanium oxides does not disappear. In literature there are data on prospects for the use of GeO_2 and GeO_x films as anode layers in batteries [1,2] and anti-reflective coatings in solar cells [3]. Due to high density of defects (oxygen vacancies) in germanium oxides the memristor effect is observed [4,5]. It is known that amorphous germanium monoxide exists in a metastable state, and at $T > 200^\circ$C starts disproportionate into thermodynamically stable phases of germanium and germanium dioxide according to the reaction: $2GeO \rightarrow Ge + GeO_2$. The released germanium inclusions in GeO_x films form deep traps for charge carriers and demonstrate photo- and cathodoluminscescence at room temperature [6].

Structure of short-range order in amorphous germanium monoxide for long time remains the discussion issue. This is associated with GeO high sensitivity to external effects (thermal, beam of electrons, ions, photons), which can result in local disproportionation of germanium monoxide and introduce distortions in the results of structure study. Difference of synthesis of germanium monoxide films can also determine difference of structure in this material. Authors of paper [7–9] earlier suggested use of random bonding model (RB model) to describe structure of the amorphous germanium monoxide. RB model supposes statistical distribution of five types of tetrahedrons of GeO_vGe_{4-v} ($v = 0, 1, 2, 3, 4$) in GeO lattice. But there are no experimental confirmations of this supposition in these papers, and, generally, in publications.

The germanium monoxide at different stages of disproportionation is of great interest both due to fundamental point of view, and in practical terms. Control of disproportionation depth of GeO (for example, using oven annealings) provides the possibility to obtain a composite material with nanoclusters (NC) of germanium of controlled size. But kinetics of Ge nanoclusters formation in thin GeO films during annealing is studied insufficiently [10–13], especially at initial stage of disproportionation. In papers [10,11] the authors, using X-ray photoelectron spectroscopy (XPS), or ellipsometry, determined activation energy of disproportionation (E_a) of GeO_x films after series of annealings. For germanium monoxide of stoichiometric composition, grown on Si substrate, value E_a was 0.7 eV [10], and for heavily hydrated GeO_x on Ge — 0.8 eV [11]. F. Zhan et al. registered spectra of Raman scattering (RS) of GeO_x ($x = 1.1-1.2$) films on silicon or quartz substrate after series of annealings. It was determined that kinetics of Ge nanoclusters formation is described by Kolmogorov-Johnson-Mehl-Avrami model with activation energy in the range $0.9-1$ eV [12,13]. It is obvious that value E_a depends in composition and, may be, on thickness of germanium monoxide films, as well on type of substrate.

In present paper composition and structure of short-range order in thin GeO films are determined using X-ray photoelectron spectroscopy. Besides effect of temperature on kinetics of Ge nanoclusters formation in thin GeO films is studied also using RS and IR spectroscopy. Annealing parameters for the beginning of the disproportionation process of GeO film and beginning of process of crystallization of germanium nanoclusters in it were determined.

2. Experimental procedure

Germanium monoxide films were obtained by quick condensation of GeO vapors on cold Si substrate in vacuum (10^{-3} Pa) during thermal reduction of GeO_2 by germanium: $Ge + GeO_2 \rightarrow 2GeO\uparrow$. The sample evaporated due to resistive heating was Si substrate with composite film (100−500 nm), comprising mixture of germanium nanoclusters and germanium dioxide, with limit accurate ratio of components $Ge : GeO_2 = 1 : 1$ mol [6]. In experiments GeO films ∼ 10 and ∼ 15 nm thick were used.

The energy spectrum of electrons and stoichiometric composition of fresh deposited GeO film 10 nm thick were determined using XPS. Spectra were measured using SPECS photoelectron spectrometer equipped with FOCUS-500 X-ray monochromator and PHOIBOS-150-MCD-9 semi-spherical analyzer. Narrow spectral Ge3d region was registered using monochromatic radiation of AlKα-line ($h\nu = 1486.74$ eV), at that the transmittance energy of the analyzer was 10 eV. For calibration C1s line ($E_{\text{commun}} = 284.8$ eV) from carbon was used comprising hydrocarbons present on surface of samples. Note that surface of GeO film was not subjected to etching by argon ions to remove contaminants before XPS, as this can result to its disproportionation. The spectra were mathematically processed using XPS Peak 4.1 software. Using with Fityk 0.9.8 program Ge3d region was decomposed to individual spectral components, and contribution of each state of germanium into common spectrum was determined.

GeO films 15 nm thick were annealed in infrared cylindrical furnace MILA-5000-UHV at temperature of 200 to 400°C with step 50°C in vacuum (10^{-2} Pa). The annealing time varied of 5 to 120 min. Temperature range was selected considering that thin films of germanium monoxide start disproportionate at $T \geq 200^\circ$C and evaporate at temperature above 420°C [14].

Presence of Ge nanoclusters and their phase state in GeO films after series of annealings was registered using Raman scattering spectroscopy. RS spectra were registered using „T64000 Horiba Yobin Yvon“ spectrometer with micro-attachment, in back-scattering geometry at room temperature. The detector was cooled with liquid nitrogen. A Ar^+ laser with a wavelength of 514.5 nm was used for RS excitation. The laser beam was slightly unfocused so its diameter was ∼ 10 μm. This ensures avoidance of noticeable heating of samples and crystallization of Ge nanoclusters under action of laser beam. The spectral resolution was at least 1.5 cm^{-1}. The integral intensity of RS peak from vibrations of Ge-Ge bonds is proportional to the bulk portion of germanium nanoclusters. To study the kinetics of formation of amorphous germanium nanoclusters the dependence of integral intensity of RS peak on annealing time was plotted. The spectra were processed in Fityk 0.9.8 program: background (signal from silicon substrate) was substracted, spectrum was decomposed to Gaussian curves, integral intensity was taken as sum of areas of all Gaussian curves. Then integral intensities were normalized per unit by value of maximum peak for each annealing temperature. To avoid errors associated with fluctuations in the excitation laser power, RS signal from the sample was compared each time with the signal from the single-crystal Si substrate.

In paper using IR spectroscopy the evolution of GeO matrix before and after series of annealings was studied. Spectra of IR absorption were registered by Fourier transform spectrometer „Infralyum FT-801“ with a spectral resolution of 4 cm^{-1}. IR spectra were processed in ZaIR 3.5 and Fityk 0.9.8 program. Si substrate without film was used as reference sample.

3. Experimental results

3.1. Composition and short-range order structure in thin GeO films

Figure 1 presents XPS spectrum of 3d-electrons of germanium in fresh deposited GeO film 10 nm thick on Si substrate. Portion of germanium in GeGe4 state$_4$ („pure“ Ge) was 4% (maximum at 29.4 ± 0.1 eV). Value of the bond energy of most intense peak is 31.2 ± 0.1 eV and inherent to germanium in GeO_2Ge_2 state (stoichiometric GeO oxide) with portion 54%. Besides two specified peaks, there is maximum at 33 ± 0.1 eV in XPS spectrum, which can be assigned to germanium, associated with four oxygen atoms in GeO_2 composition (GeO_4 tetrahedron) with

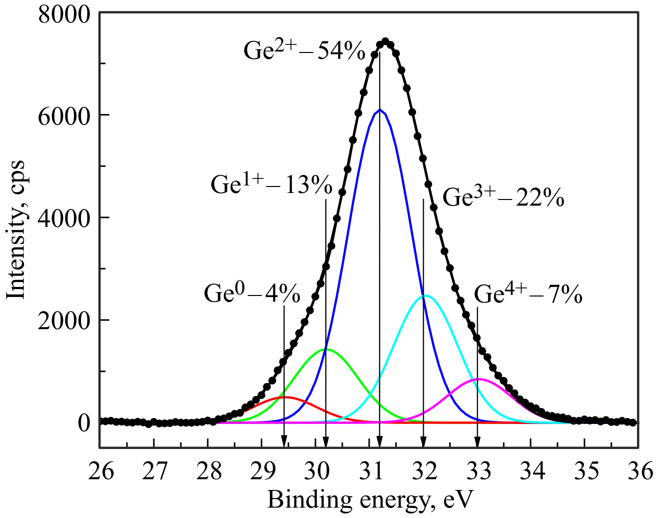

Figure 1. XPS spectrum of atomic Ge3d level in fresh prepared GeO film (10 nm)/Si. Spectrum deconvolution to components is shown.

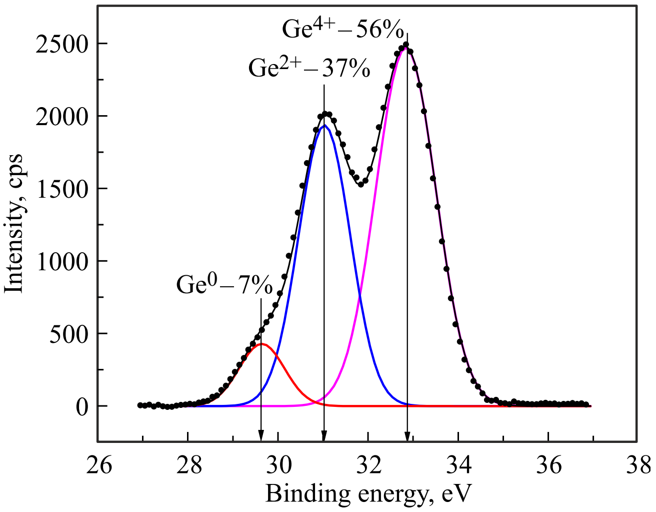

Figure 2. XPS spectrum of atomic Ge3d level in GeO film (10 nm)/Si after its storage in air for four years. Spectrum deconvolution to individual spectral components is shown.

portion 7%. Besides the spectrum comprises components corresponding to intermediate oxides: $GeOGe_3$ (13%) and GeO_3Ge (22%) tetrahedrons with maxima at 30.2 ± 0.1 and 32 ± 0.1 eV respectively [14]. Width of all peaks at half-height is 1.4 eV.

To determine composition of fresh prepared GeO_x films formula from paper [15] was used:

$$x = \frac{1}{2}\,\frac{\sum\limits_{\upsilon=1}^{4} \upsilon W_\upsilon}{\sum\limits_{\upsilon=0}^{4} W_\upsilon},$$

where $\upsilon = 0, 1, 2, 3, 4$, and W_υ — portion of tetrahedron in film (determined from XPS spectrum). In our case the x parameter was 1.07 ± 0.05, from this we can conclude that obtained GeO films are highly stoichiometric.

The experimental data indicate that atomic structure of the amorphous germanium monoxide with composition close to stoichiometric one can be described by random bonding (RB) model [16]. Under this model GeO structure comprises coupled tetrahedrons of $GeGe_4$, $GeOGe_3$, GeO_2Ge_2, GeO_3Ge, GeO_4 type, at that probability to identify tetrahedron of each composition corresponds to random distribution of excess (as compared to germanium dioxide) germanium atoms in the atomic mesh.

For comparison in Figure 2 XPS spectrum of Ge3d level in same GeO film (~ 10 nm) on Si substrate after its storage for 4 years is presented. Portion of GeO (GeO_2Ge_2 tetrahedrons) in film decreased from 53 to 37%, portion of germanium dioxide significantly increase from 7 to 56%, and portion of pure Ge changed from 4 to 7%. This can be explained by the fact that studied film GeO during long-term storage in air can oxidize to GeO_2 in near-surface layer (presumably, to 1–3 nm). It is known that XPS method collects signal from top layer of film ~ 3–5 nm thick, this can effect the obtained results.

3.2. Studies of kinetics of Ge nanoclusters formation in thin GeO films

Figure 3 presents XPS spectra of GeO film before and after annealings at temperature 400°C with duration of 5 to 120 min. XPS spectrum of the original GeO film did not contain signals from amorphous Ge clusters (Figure 3, black spectrum). After annealings in all spectra the weak wide band appears near 270–280 cm^{-1}, which corresponds to light scattering on local vibrations of Ge-Ge bonds in amorphous germanium. Note that annealing of GeO film at temperature 400°C for 2 h resulted in partial crystallization of Ge clusters, this is indicated by narrow peak near 301.4 cm^{-1} (Figure 3, orange spectrum). The temperature of beginning of crystallization process of germanium clusters in thin GeO film (400°C) was lower then it was described in publications (500–550°C) [17,18].

Analysis of dependence of normalized intensity of RS peak of amorphous Ge clusters on annealing time of GeO film showed that disproportionation process of GeO film

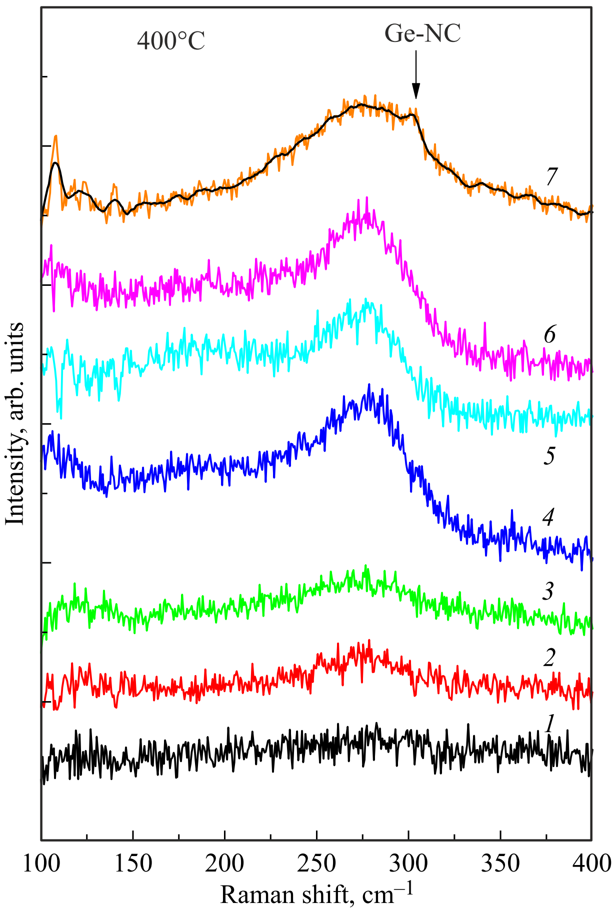

Figure 3. RS spectra of $GeO_{1.07}$ film before (*1*) and after series of annealings at $T = 400$°C: *2* — 5, *3* — 15, *4* — 30, *5* — 45, *6* — 60, *7* — 120 min.

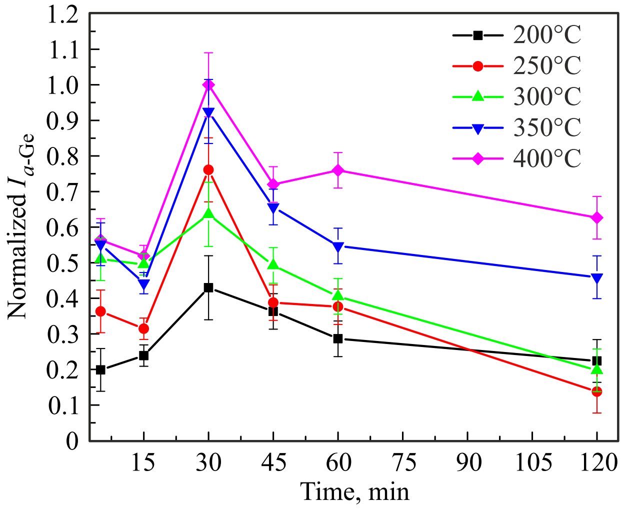

Figure 4. Normalized intensity of RS peak of amorphous Ge clusters vs. annealing time of GeO film at temperatures 200−400°C.

started from 200°C and annealing time 5 min (Figure 4). Upon temperature increasing from 200 to 400°C and annealing time from 5 to 30 min the intensity of RS signal increases, this indicates the increase in number of amorphous Ge clusters in GeO film (Figure 4). Annealings for 45 min at same temperatures resulted to noticeable decrease in RS signal from amorphous Ge clusters (Figure 4). This, probably, is associated with their partial oxidation in low vacuum (10^{-2} Pa). During further annealings of germanium monoxide films this tendency generally kept. Small rise of RS signal after annealing at temperature 400°C for 60 min, may be associated with device measurement error or competition of processes of GeO disproportionation and oxidation of Ge clusters in it.

Figure 5 presents IR absorption spectra of GeO film before and after annealings at temperature 400°C with duration of 5 to 120 min. In IR absorption spectrum of initial GeO film there is a band in region 770−780 cm^{-1} (Figure 5, curve *1*), which corresponds to stretching vibrations of Ge-O-Ge bridge of germanium monoxide. After annealings for 5−30 min intensity of this band significantly increased, and it monotonously offsets towards larger frequencies (Figure 5, curves *2*−*4*). Such trend was observed for all annealing temperatures (Figure 6). This is associated with the fact that frequency of stretching vibrations of Ge-O-Ge bonds depends on environment of Ge atoms, and environment depends on the stoichiometric parameter x. During disproportionation of germanium monoxide ($2GeO \rightarrow Ge + GeO_2$) there is total regrouping of its lattice by translation of broken bonds between neighboring atoms, this is inherent to GeO_2 and SiO_2 glasses at $T < 400$°C. With rise of time and temperature of annealing the oxygen concentration gradually in some regions shall approach to stoichiometry GeO_2 (these are nanoregions of matrix GeO_2), and in another regions — decrease to zero (these are Ge nanoclusters). In intermediate states the composition of the substance of nanoregions of both types is described by the formula shifts GeO_x, where $0 \leq x \leq 2$. With stoichiometric parameter x increasing IR absorption band gradually

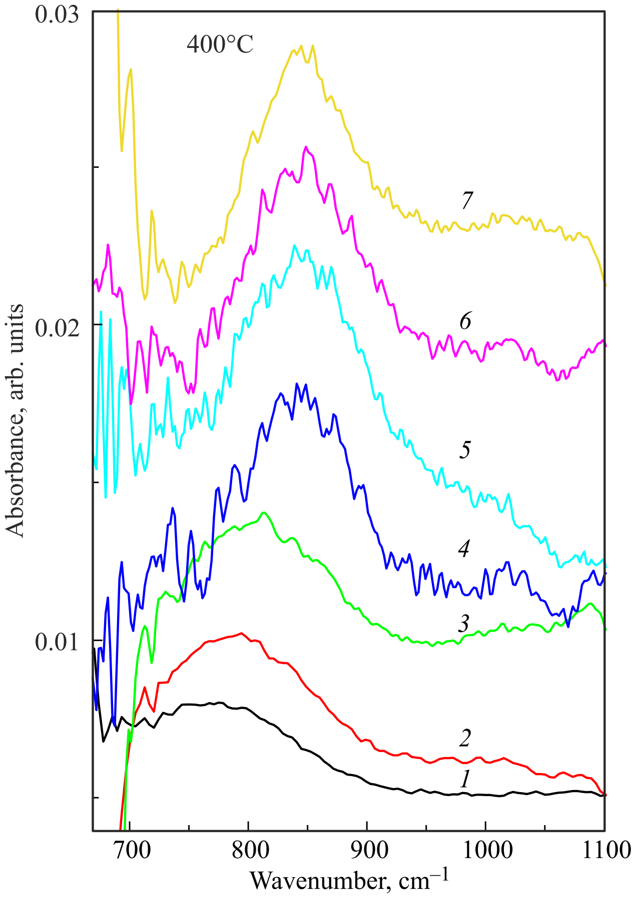

Figure 5. IR absorption spectra of GeO film before (*1*) and after series of annealings at $T = 400$°C: *2* — 5, *3* — 15, *4* — 30, *5* — 45, *6* — 60, *7* — 120 min.

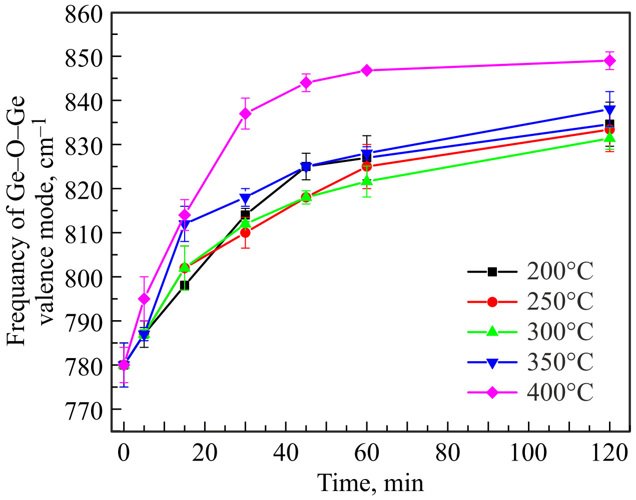

Figure 6. Peak position of IR absorption on stretching vibrations of Ge-O-Ge bond in GeO film vs. annealing time at temperatures 200−400°C.

shifts to region 870–880 cm^{-1} (frequency of stretching vibrations of Ge-O-Ge bridge in amorphous GeO_2). Note that none of the annealings resulted in the transformation of the GeO film matrix into stoichiometric germanium dioxide, i. e. complete disproportionation of germanium monoxide does not occur. Shift of discussed IR absorption band decelerates after annealing for 45 min and more for temperatures 200–350°C, and for $T = 400°\text{C}$ curve reaches saturation (Figure 6). This is determined by the fact that with time the process of release of excess Ge in the surrounding matrix and formation of nanoclusters decreases, and at temperature 400°C practically stops. Earlier it was determined that surface density of Ge nanoclusters in single-layer GeO_x coating can be from $\sim 10^{10}$ to $\sim 10^{14}$ NC/cm^2 depending on depth of disproportionation [19]. Probably, around Ge clusters some transition layer GeO_x is formed, which provides significant contribution to total IR absorption spectrum that differs from IR spectrum of amorphous GeO_2.

Data of RS spectroscopy correlate to data of IR spectroscopy and indicate about progress of the disproportionation process of GeO during annealing from 5 to 30 min and $T = 200{-}400°\text{C}$. Annealing for 45 min and more at same temperatures lead to that the process of oxidation of amorphous Ge clusters began to dominate above the process of disproportionation of germanium monoxide film. This excluded calculation of activation energy of reaction of GeO disproportionation based on RS data analysis. It is obvious that it is necessary to deposit the protective coating, for example, made of SiO_2 ($\sim$ 10–20 nm), to prevent oxidation of thin GeO films and Ge clusters during annealing.

4. Conclusion

Structure of $GeO_{1.07}$ film comprises 5 types of GeO_xGe tetrahedrons $_{4-\upsilon}$ ($\upsilon = 0, 1, 2, 3, 4$) and is described by RB model. Temperatures of beginning of disproportionation of thin $GeO_{1.07}$ films and beginning of crystallization process of germanium nanoclusters in them are determined. It is identified that $GeO_{1.07}$ films during long-term storage in air can oxidate to GeO_2 in near-surface layer. Depending on annealing time of $GeO_{1.07}$ films at temperatures from 200 to 400°C in low vacuum either process of germanium monoxide disproportionation (5–30 min) or oxidation of Ge clusters in matrix (45–120 min) dominates. By annealing depth of disproportionation of GeO films can be changed, and size of amorphous nanoclusters formed during release of excess germanium is varied. Study results can be applied to create memristors based on Ge oxides with required properties.

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Conflict of interest

The authors declare that they have no conflict of interest.

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