Peculiarities of the synthesis of GST films by magnetron sputtering for nonvolatile optical memory cells

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Abstract. The structure and optical properties of thin films of the chalcogenide semiconductor Ge²Sb²Te₅, deposited by magnetron sputtering, was studied. A significant change in the topology and optical properties of the films is demonstrated with varying deposition conditions. It is shown that an increase in the deposition time leads to an increase in the surface roughness. Doping with nitrogen during deposition leads to a smoothing of the film surface, and also provides a strong change in the band structure and optical properties.

1. Introduction
The development of technology for creating traditional devices of modern silicon electronics is currently faced with limitations associated with the problems of scaling devices to sizes of the order of a few nanometers [1]. It can be replaced by a dynamically developing field of silicon nanophotonics, which allows to increase the performance of integrated circuits due to a significant increase in the signal transmission speed. One of the important tasks required to implement fully photonic integrated circuits is the creation of nonvolatile optical memory elements. The implementation of such memory became possible due to the development of phase-change materials (PCM), which have the ability to quickly reversibly switch between amorphous and crystalline states with significantly different electrical and optical characteristics [2]. A well-established material for optical applications is the Ge-Sb-Te (GST) compound, which is used as an active material in PCM and optical disks. The advantage of using this material is in substantial contrast of the optical characteristics in different phase states of GST, and this contrast can be adjusted by changing the composition and stoichiometry of the compound [3]. However, the combination of such materials with silicon-based waveguides for the implementation of fully optical memory for use in radiophotonics devices has been clearly studied insufficiently. In this work, we present the results on the formation of GST layers by magnetron sputtering with a variation in the deposition parameters for use in nonvolatile optical memory cells.

2. Experimental
The experimental samples were 8-220 nm-thick films of the Ge²Sb²Te₅ compound deposited by RF magnetron sputtering at room and elevated (350 °C) temperature on n-Si (100) and fused silica substrates from the sintered target of high-purity Ge²Sb²Te₅ powder. The composition of the deposition atmosphere was used both 100% Ar, and a mixture of argon and nitrogen in various
proportions in order to dope the deposited films with nitrogen atoms. The optical characteristics of the samples were studied using optical transmission (Varian Cary 6000i) and spectroscopic ellipsometry (MicroPhotronics PhE-102), the morphology of the films was studied by atomic force microscopy (NT-MDT Solver Pro M), and the structure of the samples was studied by electron diffraction (EMR-102).

3. Results and discussion

Let us begin consideration with the results of studying the topology of GST films deposited by magnetron sputtering under varying deposition conditions - time, temperature, and also when nitrogen is added to the deposition atmosphere. According to the literature data [4], doping with nitrogen makes it possible to control such important parameters of the PCM material as the crystallization temperature, optical gap, and the range of possible states. An image of the surface topography of GST films synthesized in different regimes is shown in Figure 1.

![Figure 1. Surface topography of GST films deposited at room temperature with different thicknesses (a, b, c), deposited at 350 °C (d), as well as at room temperature, but with the addition of N₂ to the deposition atmosphere (e).](image)

The deposited films are distinguished by good uniformity of the relief over the sample surface. As the film thickness increases, its grain (columnar) structure becomes more pronounced, which is characteristic of the magnetron sputtering method. The average lateral grain size increases from 30 to 50 nm with an increase in thickness from 8 to 220 nm. At an elevated substrate temperature (350 °C), the grain structure is retained, but the relief becomes more diffuse, which is most likely associated with a large spread of grains in size. The addition of nitrogen to the gas mixture significantly affects the growth of the films and leads to a significant smoothing of the surface relief due to the growth of grains to a lateral size of about 100 nm and more with increasing nitrogen concentration. AFM data processing showed that an increase in the substrate temperature leads to a decrease in the surface roughness, and for nitrogen-doped samples, the surface roughness does not exceed 1 nm.

The study of the structure of the samples by electron diffraction showed that all deposited GST films (including those deposited at elevated temperatures) are amorphous (data not shown).

Investigation of the optical transmission spectra depending on the deposition time (thickness) of GST films on fused silica substrates revealed the following (Figure 2a). An increase in the film thickness leads to a decrease in the transmission in the visible region of the spectrum (almost to 0%). The absorption edge is in the near-IR region of the spectrum (0.7–0.8 eV), but its determination is complicated by distortion of the spectra due to interference. An increase in the nitrogen concentration
in the film (Figure 2b), on the contrary, leads to a significant bleaching of the film and a monotonic shift of the optical absorption edge to the visible region of the spectrum, which is apparently associated with a change in the band structure of the doped film material. An increase in the substrate temperature (Figure 2c) leads to an even greater decrease in transmission, which can be associated with both a change in the local structure of the semiconductor and a larger film thickness. Thus, by varying the deposition parameters, it is possible to control the optical parameters of the GST magnetron films. The shift of the optical absorption edge upon additional doping with nitrogen during the deposition process makes it possible to change the band structure of the films obtained by varying the amount of nitrogen in the deposition atmosphere.

Figure 2. Optical transmission spectra of GST films with different thicknesses (different deposition times) obtained at room temperature of a silica substrate (a), doped with nitrogen (b), as well as comparison with a sample deposited at 350 °C (c).

More accurate information on the optical parameters of films, which are important for use in optical memory elements, was obtained by spectroscopic ellipsometry. To approximate the experimental data, two models were used: the Cauchy – Urbach model, used to describe transparent dielectrics, and the Tauz – Lorentz model, used to describe amorphous semiconductors [5]. Data on the spectral dependences of the refractive index and extinction coefficient for GST films with various thicknesses, as well as those at elevated temperatures and the addition of nitrogen to the deposition atmosphere were obtained (Figure 3).
Figure 3. Spectral dependences of the refractive index (a) and extinction coefficient (b) of GST films.

The values of the band gap and refractive index (at a wavelength of 1550 nm), determined from the results of the approximation of experimental data, are given in Table 1.

| Sample       | Band gap $E_g$, eV | Refraction index $n@1550$ nm |
|--------------|-------------------|-----------------------------|
| 8 nm         | 0.6               | 3.32                        |
| 110 nm       | 0.59              | 3.43                        |
| 220 nm       | 0.46              | 3.42                        |
| 210 nm (350 °C) | 0.82           | 3.74                        |
| 120 nm (+N₂) | > 1.5             | 2.11                        |

To study the optical properties of samples with different GST film thicknesses and elevated deposition temperatures, we used the Tauz – Lorentz model. As can be seen from Figure 3, the refractive index values of ~ 3.5 in the visible and near-IR ranges weakly depend on the film thickness and correspond to the values for amorphous semiconductor GST films [6]. An increase in the refractive index by ~1 for a sample deposited at a temperature of 350 °C indicates partial crystallization of the film. A sample of a GST film doped with nitrogen was studied using the Cauchy – Urbach model. It is transparent in almost the entire optical range, while the refractive index ~ 2.1 corresponds to the optical characteristics of the dielectric. This suggests that doping with a high nitrogen concentration significantly changes the band structure of the material towards an increase in the band gap.

4. Conclusions
The structural and optical properties of Ge₂Sb₂Te₅ films obtained by magnetron deposition were investigated. Variations in deposition parameters such as deposition time, temperature, and composition of the gas mixture significantly affect the topology and optical properties of the deposited films. It is shown that the addition of nitrogen to the deposition atmosphere leads to a significant
change in the band structure of GST films. The obtained results will be used to create optical memory elements based on silicon waveguides with deposited GST film.

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