Dielectric Relaxation and Photo-electromotive Force in Ge-Sb-Te/Si Structures

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Abstract: The dielectric properties and photovoltaic effect spectra in the compositions of amorphous layers $GeSb_2Te_4$ (GST 124), $Ge_2Sb_2Te_5$ (GST 225) и $GeSb_4Te_7$ (GST 147) applied on the monocrystallic silicon surface are investigated. It is shown that with a change in the GST composition, both the dielectric capacitivity and the frequency at which the maximum dielectric loss is observed change. It was found that the value of the change in photo-electromotive force is different for different layers: on samples with GST 124, the influence of amorphous layers is by an order of magnitude greater than for GST 225, and by 3 orders of magnitude greater than for GST 147.

1 INTRODUCTION

Complex blend chalcogenide glassy semiconductors (CGSs) attract the attention of researchers in connection with their use in numerous devices of micro- and optoelectronics. For example, chalcogenide glassy semiconductors are currently used in the manufacture of thermal imaging systems (Cha, et al, 2012), fibers and transparent flat waveguides in the IR range (Snopatin, et al, 2009), in optical sensors (Charrier, et al, 2012) and nonlinear optics (Zhang, et al, 2015).

Electrophysical and structural properties of chalcogenide semiconductors have been intensively studied recently (Siegrist, et al, 2011, Zhang, et al, 2012, Gabardi, et al, 2015), which is associated with their successful application in non-volatile memory devices (fiscal memory, phase-change memory). The principle of operation of such devices is based on a sharp change in the electrophysical properties of the material during a reversible phase transition between crystalline and amorphous states. Complex chalcogenides of the Ge-Sb-Te (GST) system are some of the most popular materials of fiscal memory (Kozyukhin, et al, 2014).

The aim of this work is to establish the features of the dielectric relaxation spectra and photo-electromotive (photo-EMF) force in Ge-Sb-Te/Si structures based on GST layers obtained by HF magnetron sputtering.

The study of the features of polarization processes in structures based on silver halides and chalcogenide glassy semiconductors, including photostimulated ones, allows to determine at what energy level the transport of charge carriers is carried out, distinguishing between zone and hopping mechanisms, and what is the nature of charge carriers, and also to evaluate a number of microscopic parameters of the studied compounds (Goryaev, 1997, 1998, Bordovskii, et al, 2001, Castro, et al, 2006, Anisimova, et al, 2010).

2 EXPERIMENTAL

Thin films of the Ge-Sb-Te system ($GeSb_2Te_4$ (GST 124), $Ge_2Sb_2Te_5$ (GST 225) и $GeSb_4Te_7$ (GST 147)) with a thickness of the order of 50 nanometers were obtained by HF magnetron sputtering at room temperature on silicon substrates. The structural features of the samples were studied on a DRON-7 X-ray diffractometer. The obtained diffractograms (figure 1) measured at large 2θ scattering angles of X-rays in the range from 10° to 80° indicate the amorphous nature of the films under study. The elemental composition of the samples was studied

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using a Carl Zeiss EVO 40 scanning electron microscope (SEM).

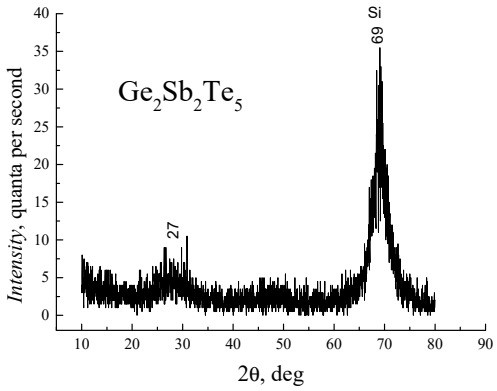

Figure 1: Diffractogram of the samples of Ge-Sb-Te/Si structure with 2θ angles indication.

The dielectric spectra of the studied layers were measured on a Concept-81 spectrometer (Novocontrol Technologies GmbH) designed to study the dielectric and conductive properties of a wide variety of materials. The measurements were carried out in the frequency range $f = 10^2$Hz…10^7Hz at room temperature. The voltage applied to the samples was $U = 10^{-1}$B. The relative experimental error did not exceed ± 3%.

The experimental data were the values of the imaginary and real part of the impedance of the cell with the measured sample:

$$Z^*(\omega) = R + \frac{1}{i\omega C} = Z' + iZ'' = \frac{U_0}{I^*(\omega)}.$$

The spectra of complex dielectric constant and conductivity were calculated from the impedance spectra according to the following formulas:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \frac{-i}{\omega Z^*(\omega)} \frac{1}{C_0},$$

where $C_0 = \frac{\varepsilon_0 S}{d}$ is empty cell capacity.

The photo-EMF of the samples was measured by the capacitor method (Akimov, 1966) under modulated illumination on the installation, the block diagram of which is shown in figure 2. To evaluate the efficiency of the internal photoelectric effect, the measured signals ΔU were normalized to the same number of light quanta incident on the sample.

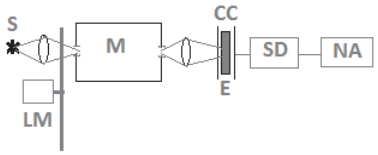

Figure 2: Installation diagram for measuring the spectra of the photo-EMF by the capacitor method. S – the light source, LM – the light modulator, M – the monochromator, CC – the capacitor cell, E – the sample, SD – the synchronous detector, NA – the narrow-band amplifier.

3 RESULTS AND DISCUSSION

3.1 Dielectric Properties

The frequency dependence of the dielectric constant ε' at room temperature of the layers of the Ge-Sb-Te system is shown in figure. 3. It is clear from the figure that ε' decreases with increasing frequency, approaching a constant value at high frequencies, due to the contribution of only electron polarization and space charge polarization (Anisimova, et al, 2010). In the low-frequency region, the manifestation of dipole-relaxation and interfacial polarization can be assumed.

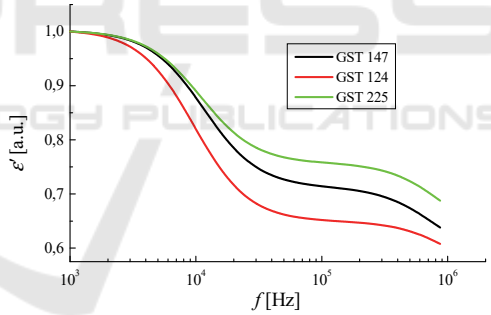

Figure 3: The frequency dependence of the dielectric capacitivity of the layers of the Ge-Sb-Te system.

Measurement of quantity of the dielectric loss $\mathrm{tg}\delta = \varepsilon''/\varepsilon'$ in the studied layers (Fig. 4) revealed the existence of a maximum of losses in the medium-frequency region. The presence of a maximum on the curves $\mathrm{tg}\delta = f(\omega)$ at room temperature indicates the existence of relaxation processes that cause relaxation losses in the studied samples. With a change in the GST composition, both the dielectric capacitivity and the frequency at which the maximum dielectric loss is observed (see table 1) change.

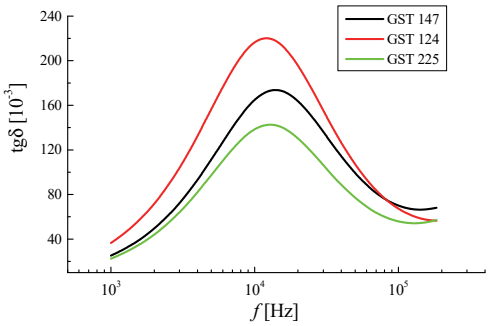

Figure 4: The frequency dependence of the dielectric loss factor of the layers of the Ge-Sb-Te system.

Table 1: The value of structural and relaxation HN parameters of samples of the glassy Ge-Sb-Te system.

Состав	$2\theta_{гало}$°	S (Å)	τ_{max} (c)	$\Delta\varepsilon$	α_{HN}	β_{HN}
$GeSb_4Te_7$	27.00	4.05	$1.34*10^{-5}$	$6.03*10^{-1}$	0.91	0.67
$GeSb_2Te_4$	28.38	3.86	$1.76*10^{-5}$	$6.18*10^{-1}$	0.88	0.90
$Ge_2Sb_2Te_5$	27.75	3.95	$1.62*10^{-5}$	$4.20*10^{-1}$	0.95	0.68

An analysis of the nature of the distribution of relaxators by relaxation times in the Ge-Sb-Te system within the framework of the Havriliak-Negami (HN) function model (Kremer and Schonhals, 2003) revealed the existence of a non-Debye oscillatory process with a distribution of relaxation times according to the Cole-Davidson model for the case of an asymmetric distribution of relaxators by relaxation times ($\beta \neq 1.00$) (see table 1):

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{\left[1+(i\omega\tau)^{\alpha_{HN}}\right]^{\beta_{HN}}},$$

where ε_∞ is the high frequency limit of the real part of the dielectric capacitivity, $\Delta\varepsilon$ is the dielectric increment (the difference between the low-frequency and high-frequency limits), $\omega=2\pi f$, α_{HN} and β_{HN} are shape parameters describing respectively the symmetric (β=1.00 is the Cole-Cole distribution) and asymmetric (α=1.00 is the Cole-Davidson distribution) expansion of the relaxation function.

3.2 Photovoltaic Effect

Figure 5 shows the spectra of the capacitor of the photo-electromotive force of the initial silicon samples and samples with amorphous layers of the Ge-Sb-Te system deposited on the semiconductor surface.

The above-cite results show that the value of photo-EMF of the initial samples (curves 1) in the entire studied region of the spectrum decreases with increasing wavelength in accordance with a change in

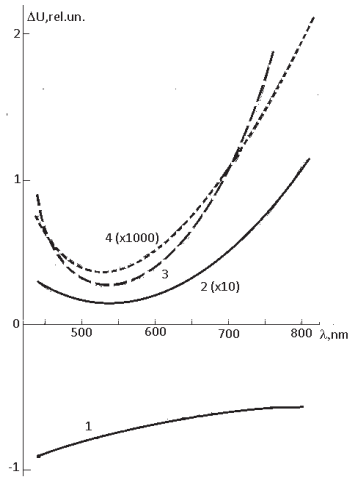

Figure 5: Spectra of the photo-EMF of initial silicon (1) and samples with amorphous layers GST 124 (2), GST 225 (3), and GST 147 (4) deposited on the semiconductor surface.

the absorption coefficient of the silicon. When amorphous GST layers are deposited on the semiconductor surface, the sign of the recorded signal changes (curves 2–4). This may be due to the fact that the photo-electromotive force has diffusion and drift components.

The diffusion component (Dember electromotive force) is the result of diffusion of photocurrent carriers in a semiconductor due to their concentration gradient created by absorbed light (Akimov, 1966):

$$V = \frac{kT}{e}\frac{\mu_n - \mu_p}{\mu_n + \mu_p} ln\frac{\sigma_i}{\sigma_d},$$

where μ_n and μ_p are mobility of electrons and holes, σ_i and σ_d are conductivity at the front (illuminated) and rear surfaces of the sample. The sign of Dember electromotive force should be opposite to the sign of the main carriers of the semiconductor. This is fully confirmed by the sign of the photo-EMF of the initial silicon samples having hole conductivity (curves 1).

The drift component is determined by the drift of light-generated carriers in the field of a surface charge. In case of locking bending of zones, when diffusion and drift currents add up, photo-electromotive force increases. In the case of anti-locking bending, the direction of the drift current is opposite to the diffusion, therefore, the resulting photo-electromotive force can not only decrease, but also change its sign.

The results of the effect of GST layers deposited on the silicon surface indicate that in this case an anti-locking bending of zones is formed in the semiconductor. In such heterojunctions, a

predominance of the drift component of the photo-EMF with a corresponding change in polarity is observed (figure 2, curves 2-4). At the same time, a change in the photoelectric effect spectra occurs, which may be due to the spectral dependence of the magnitude of the resulting band bending upon excitation. So, on the deposition of dyes on a silicon surface, the effect of a change in the sign of the photopotential was revealed under illumination in different spectral regions (Komolov, et al, 2006), as well as a sensitized photovoltaic effect (Goryaev, 2017, 2019, Goryaev and Castro, 2018).

Figure 5 also shows that the magnitude of the change in photoelectromotive force is different for different layers: for GST 124 samples, the influence of amorphous layers is by an order of magnitude greater than for GST 225, and by 3 orders of magnitude greater than for GST 147.

The difference in the nature of the change in photo-electromotive force for different GST compositions and the specific features of the dielectric spectra can be explained by the specific features of the energy spectrum of the amorphous phase of the Ge-Sb-Te system. Fluctuations in the composition should lead to the fluctuations in the electrophysical properties of materials, and, accordingly, to fluctuations in the edges of the bands and energy levels of localized states in accordance with the model proposed in (Voronklov, et al, 1974). Changes in the energy spectrum reflect changes in the structure that the amorphous system undergoes with an increase in the concentration fraction of germanium and a decrease in the concentration fraction of antimony. According to the presented data of X-ray spectral analysis (figure 1), with a change in composition, a change in the distance S between the most frequently encountered pairs of atoms is observed. Decrease or increase in S causes a change in polarization due to a change in the resulting dipole moment of the system. A change in the polarization of the system, in turn, is expressed in a change in the dielectric capacitivity. These changes determine the different contribution to the development of the observed relaxation and photostimulated processes in the Ge-Sb-Te/Si structures.

4 CONCLUSIONS

The dielectric relaxation and photo-electromotive force spectra in Ge-Sb-Te/Si structures were experimentally studied. It was found that the value of the change in photo-EMF is different for different layers: on samples with GST 124, the influence of amorphous layers is by an order of magnitude greater than for GST 225, and by 3 orders of magnitude greater than for GST 147. This difference in the nature of the change in photoelectromotive force and the features of the dielectric spectra for different GST compositions can be explained by the structural features of the amorphous phase of the Ge-Sb-Te system.

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