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Study of relaxers distribution in thin layers of amorphous $MoTe_2$

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Recently, transition metal dichalcogenides have come into the spotlight after they have been found to become direct semiconductor in the monolayer level. The paper presents the results of the study of the relaxers distribution in layers of amorphous molybdenum ditelluride obtained by high-frequency magnetron sputtering. According to the obtained values of relaxation parameters α and β, the transition from an asymmetric distribution to a symmetric distribution of relaxators at temperature $T = 283$ K can be stated. The existence of maxima on the temperature dependence of relaxation times $\tau_{\max} = f(T)$ was found, which can be associated with phase transitions in the studied system.

Keywords: molybdenum ditelluride, relaxers distribution, thin layers, phase transitions.

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1. Introduction

In many chalcogenide systems relaxation processes are associated with the existence of not one relaxation time, but with a set of relaxation times [1–3]. In this case we are dealing with the distribution of the relaxation time, and, consequently, the activation energy. This distribution can be associated with the manifestation of relaxation processes of different nature or with the distribution in concentration of dipoles in the structure. In case of ionic jumping processes it is assumed, that after each jump, the potential energy changes and it takes some time to return to the minimum potential energy. If we consider the contribution of a large number of mobile defects, then we obtain a set of relaxation times [4]. From a statistical point of view, it can be expected, that for each of these groups of dipoles, the relaxation time will deviate by some value from the most probable value. The system will have a distribution of relaxers (molecules, groups of molecules) over the relaxation times, that can be described using a certain function, which we denote by $G(\tau)$ — the relaxation time distribution function (RTDF). The value $G(\tau)d\tau$ characterizes the contribution to the polarizability of the system of groups (polar structures — dipoles) with characteristic relaxation times within the range from τ to $\tau + d\tau$.

In recent years such a class of chalcogenide materials as transition metals dichalcogenides (TMDs), with the general formula MX_2 ($M = Mo, W$; $X = S, Se, Te$), has come to the forefront of science. The TMDs, indirect-gap semiconductors in bulk, became the focus of interest after it was discovered that within the monolayer limit they become direct-gap semiconductors [5]. In addition, other unique properties of these materials were discovered, such as strong spin-valley interaction, which opened a new direction in spintronics called valleytronics [6,7]. TMD-based devices have also been demonstrated, from field-effect transistors to lasers, as well as in transparent and flexible electronic devices [8–10].

In this regard it is extremely interesting to study the distribution of relaxers in thin layers of the systems based on transition metal dichalcogenides. We are talking about a new mechanism of identifying the relationship between system data structure and the properties that determine the areas of their practical application. The purpose of this study was to reveal the features of relaxers spectrum in thin films of amorphous molybdenum ditelluride $MoTe_2$, obtained using the method of high-frequency magnetron sputtering.

2. Experimental procedure

Thin films of molybdenum ditelluride with a thickness of about 50 nm were obtained using HF magnetron sputtering method at room temperature on silicon substrates at the Nanoelectronics Research Institute, National Institute of Advanced Industrial Science & Technology (Tsukuba, Japan).

The features of the relaxers spectrum in thin films $MoTe_2$ were studied using dielectric spectroscopy method on the unit „Concept-81“ (Novocontrol Technologies GmbH). This method is successfully applied in the study of electronic processes in the systems with varying degrees of structural disorder [11–13]. The measuring unit includes a PC interface board and data acquisition software. As experimental data, the values of the imaginary and real parts of the impedance of the cell with the measured sample were collected. The complex permittivity and complex conductivity spectra were calculated from the impedance spectra using the following formula:

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

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

The temperature-frequency dependences of the dielectric parameters of $MoTe_2$ samples were measured in a wide frequency range (10^{-1} Hz–10^5 Hz) and temperature interval from 223 to 373 K. The error in measuring physical quantities and calculating the parameters of the system did not exceed 5%.

3. Results and discussions

To study the distribution of relaxers in thin layers of $MoTe_2$ the frequency dependences of complex permittivity $\varepsilon^*(\omega, T)$ were approximated with Gavriliak–Negami (HN) function (HN) [14]. The results of measuring dielectric spectra were approximated using software Winfit 3.3 (Novocontrol Technologies GmbH). On the basis of this approximation, the positions of the maxima of dielectric losses were found and the parameters (HN) for the studied polarization processes were determined according to the expression

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{[1 + (i\omega\tau)^{\alpha_{HN}}]^{\beta_{HN}}}, \qquad (2)$$

where ε_∞ — high-frequency limit of the real part of permittivity, $\Delta\varepsilon$ — dielectric increment (the difference between low-frequency and high-frequency limits), $\omega = 2\pi f$, α_{HN} and β_{HN} — shape parameters describing, respectively, symmetric ($\beta = 1.00$ — Cole–Cole distribution) and asymmetric ($\alpha = 1.00$ — Cole–Davidson distribution) extension of the relaxation function. The values of the relaxation parameters obtained by approximating the experimental curves within the HN model are presented in the Table.

Relaxation parameters of films $MoTe_2$ at different temperatures

T, K	$\tau_{\max}$, s	$\Delta\varepsilon$	α	β
223	0.441	10.100	0.858	1.000
233	0.244	9.879	0.851	0.952
243	0.293	9.299	0.918	0.791
253	0.230	9.900	0.920	0.707
263	0.233	9.446	0.849	1.000
273	0.135	9.294	0.864	0.922
283	0.818	8.936	0.903	1.000
293	0.036	8.513	0.906	0.978
303	0.019	8.282	0.916	1.000
313	0.010	8.155	0.925	1.000
323	0.006	7.960	0.938	1.000
333	$0.137 \cdot 10^{-2}$	8.153	0.918	1.000
343	$0.344 \cdot 10^{-2}$	8.454	0.920	1.000
353	$0.235 \cdot 10^{-2}$	8.402	0.923	1.000
363	$0.159 \cdot 10^{-2}$	7.912	0.946	1.000
373	$0.055 \cdot 10^{-2}$	8.055	0.936	1.000

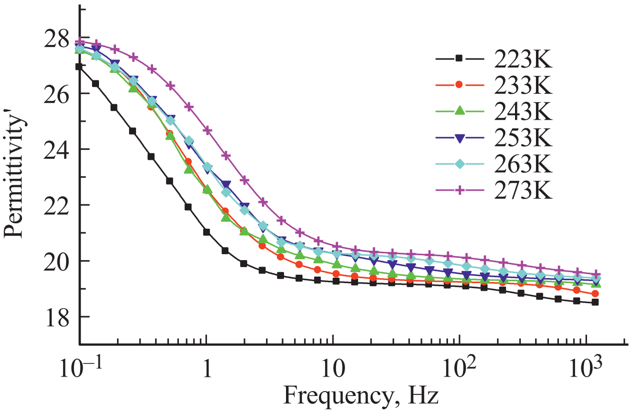

Figure 1. Frequency permittivity dependence ε' at various temperatures.

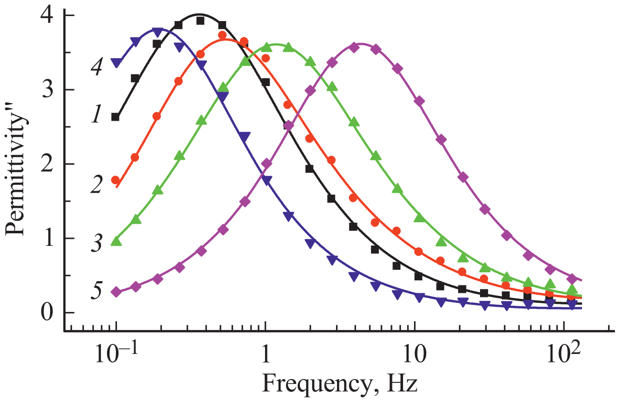

Figure 2. Frequency loss factor dependence ε'' at various temperatures. *1* — 223, *2* — 243, *3* — 273, *4* — 283, *5* — 293 K.

The found dispersion of permittivity (Fig. 1) and the existence of a maximum of dielectric losses in the low frequency area (Fig. 2) can be explained within the framework of the model proposed by the authors [15].

According to this model, the chalcogenide system structure can be a set of the dipoles formed by charged defects. Each dipole has its own relaxation time, which depends on the activation energy required to overcome the potential barrier by charge carriers. The existence of the potential barrier is based on the Coulombic interaction between neighboring defect states forming a dipole.

The distribution of relaxation times $G(\tau)$ is calculated as the inverse problem. For example, for Debye relaxation $G(\tau)$ is defined as

$$\varepsilon^*(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)\int\limits_0^\infty \frac{G(\tau)}{1 + i\omega\tau}\,d\tau, \qquad (3)$$

where ε_s — permittivity at extremely low frequencies, τ — relaxation time.

Fig. 3 demonstrates the relaxation time distribution function (RTDF) for thin layers of $MoTe_2$. From the obtained values of relaxation parameters α and β (see table), one can state the transition from a predominantly asymmetric distribution to a symmetric distribution of relaxers over relaxation times at a temperature of $T = 293$ K.

The temperature dependence of the most probable relaxation time $\tau_{\max}$ is shown in Fig. 4. The observed maxima on the dependence $\tau_{\max} = f(T)$ indicate the existence in this temperature range of two areas, probably associated with phase transitions, that the system under study undergoes.

The authors [16], when measuring the temperature dependence of specific resistivity in β-$MoTe_2$ monocrystals, a temperature anomaly $T = 247$ K was found in the area. Later the use of this system with high-resolution X-ray diffraction method [17,18] allowed to conclude, that this anomaly is associated with a first-order structural phase transition characterized by the existence of a two-phase area in the temperature range from 233 up to 290 K. The observed thermal hysteresis and blurring of the transition area confirmed the assumption, that two phases coexist in an unusually wide temperature range. It was also assumed that the presence of two phases is accompanied by a significant lattice deformation, and the existence of a large energy barrier between the two structures.

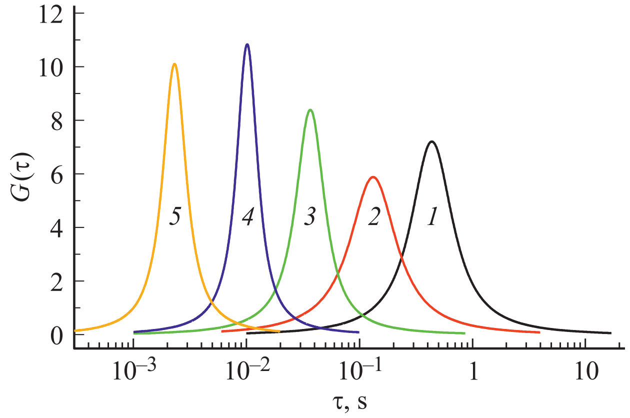

Figure 3. Calculated function values $G(\tau)$ for layers $MoTe_2$ at various temperatures. *1* — 223, *2* — 273, *3* — 293, *4* — 313, *5* — 353 K.

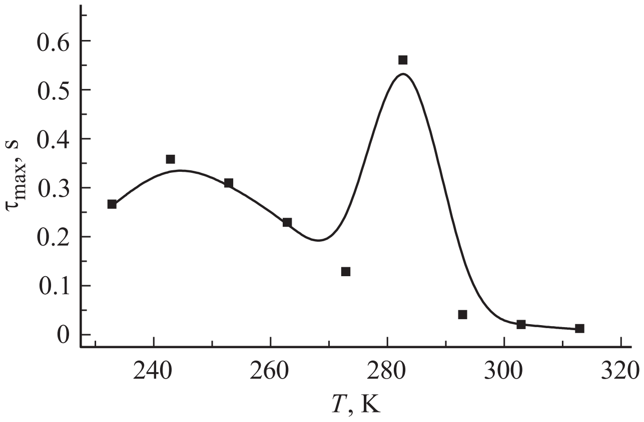

Figure 4. Temperature dependence of the most probable relaxation time for layers of amorphous $MoTe_2$.

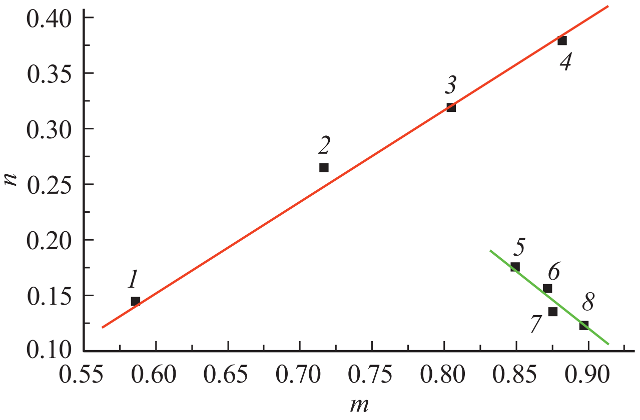

Figure 5. Function $n = f(m)$ for thin layers of the amorphous system $MoTe_2$ at various temperatures. *1* — 223, *2* — 233, *3* — 243, *4* — 253, *5* — 293, *6* — 303, *7* — 313, *8* — 323 K.

If we assume that the electronic structure is retained during the transition from the crystalline state to the amorphous state, then we can conclude that the observed regularities in the dependence $\tau_{\max} = f(T)$ for amorphous layers $MoTe_2$ can also be associated with a first-order phase transition and coexistence of two phases up to temperature $T = 285$ K. Here we can talk about monoclinic $1T'$ and low-temperature orthorhombic phases T_d [19,20]. This conclusion is supported by the change in nature of relaxers spectrum (see Table) and in width of the function $G(\tau)$ at this temperature (Fig. 1).

To analyze the dielectric spectra, in order to confirm the existence of changes in the materials structure, one can use the two-level Dissado–Hill model (DH) [21], which establishes a connection between HN equation parameters and two parameters of microstructure restructuring cooperative processes correlation n and m:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{F_{01}(1+i\omega\tau)^{n-1}} \times {}_2F_1\left(1-n, 1-m; 2-n; \frac{1}{1+i\omega\tau}\right), \qquad (4)$$

where ${}_2F_1$ — hypergeometric function Gaussian, F_{01} — is determined by the gamma function. The condition $n \to 0$, $m \to 1$ corresponds to real fluids. The DH diagram, from which the change in the behavior of the function $n = f(m)$ follows after the transition from the two-phase state into the single-phase state of the amorphous system $MoTe_2$, is shown in Fig. 5.

4. Conclusion

Thus, we have investigated the distribution of relaxers in thin layers of $MoTe_2$, obtained using high-frequency magnetron sputtering method.

The frequency dependences of complex permittivity $\varepsilon^*(\omega, T)$ were approximated by Gavriliak-Negami function. The obtained values of the relaxation parameters α and β, allow to state the transition from an asymmetric distribution to a symmetric distribution of relaxers over relaxation times at a temperature $T = 293\,\mathrm{K}$. The existence of maxima on the dependence $\tau_{\max} = f(T)$ was found, that is probably associated with phase transitions, which the system under study undergoes within this temperature range.

Analysis of DH diagram, i.e. the dependence $n = f(m)$ reveals the transition from the two-phase state (coexistence of the monoclinic $1T'$ and orthorhombic T_d phases) to the single-phase state of the amorphous system $\mathrm{MoTe_2}$.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] R.A. Castro, G.A. Bordovsky, V.A. Bordovsky, N.I. Anisimova. J. Non-Crystall. Solids **352**, *9–20*, 1560 (2006).

[2] V.A. Bordovskii, R.A. Kastro, G.I. Grabko, T.V. Taturevich. Glass Phys. Chem. **32**, *2*, 178 (2006).

[3] R.A. Castro, V.A. Bordovsky, N.I. Anisimova, G.I. Grabko. Semiconductors **43**, *3*, 365 (2009).

[4] K. Kremer, A. Schonhals A. Broadband dielectric spectroscopy. Springer, Berlin Heidelberg (2003). 729 p.

[5] K.F. Mak, C. Lee, J. Hone, J. Shan, T.F. Heinz. Phys. Rev. Lett. **105**, *13*, 136805 (2012).

[6] X. Xu, W. Yao, D. Xiao, T.F. Heinz. Nature Phys. **10**, *5*, 343 (2014).

[7] K.F. Mak, K. He, J. Shan, T.F. Heinz. Nature Nanotechnology **7**, *8*, 494 (2012).

[8] W. Chen, R. Liang, J. Wang, S. Zhang, J. Xu. Sci. Bull. **63**, *15*, 997 (2018).

[9] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis. Nature Nanotechnology **6**, *3*, 147 (2011).

[10] B. Radisavljevic, M.B. Whitwick, A. Kis. ACS Nano **5**, *12*, 9934 (2011).

[11] N.A. Nikonorova, M.Y. Balakina, O.D. Fominykh, A.V. Sharipova, T.A. Vakhonina, G.N. Nazmieva, R.A. Castro, A.V. Yakimansky. Mater. Chem. Phys. **181**, 217 (2016).

[12] R.A. Castro, A.I. Ignatiev, N.V. Nikonorov, A.I. Sidorov, M.V. Stolyarchuk. J. Non-Crystalline Solids **461**, 72 (2017).

[13] R.A. Castro, N.I. Anisimova, A.A. Kononov. Semiconductors **52**, *8*, 1043 (2018).

[14] S. Havriliak, S. Negami. Polymer **8**, 161 (1967).

[15] J.C. Giuntini, J.V. Zanchetta, D. Jullien, R. Eholie, P. Houenou. J. Non-Crystalline Solids **45**, 57 (1981).

[16] H.P. Hughes, R.H. Friend. J. Physics C **11**, *3*, L103 (1978).

[17] R. Clarke, R.E. Morley. J. Appl. Crystallography **9**, *6*, 481 (1976).

[18] A.M. Glazer. J. Appl. Crystallography **5**, *6*, 420 (1972).

[19] S. Dissanayake, C. Duan, J. Yang, J. Liu, M. Matsuda, C. Yue, J.A. Schneeloch, J.C.Y. Teo, D. Louca. npj Quantum Mater. **4**, *1*, 45 (2019).

[20] J. Yang, J. Colen, J. Liu, M.C. Nguyen, G.W. Chern, D. Louca. Sci. Adv. **3**, *12*, 4949 (2017).

[21] L.A. Dissado, R.M. Hill. J. Appl. Phys. **66**, *6*, 2511 (1989).