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Compositional dependencies in the vibrational properties of amorphous Ge-As-Se and Ge-Sb-Te chalcogenide alloys studied by Raman spectroscopy

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ABSTRACT

This work is focused on the compositional dependencies in the Raman spectra of amorphous Ge-As-Se and Ge-Sb-Te chalcogenides with the systematic increase of the Ge-content. Studied Ge-As-Se and Ge-Sb-Te chalcogenides are promising for applications in the photonics, optical, and electronic data storages. Gaussians used to fit the obtained Raman spectra were attributed to the vibrations of the structural units in Ge-Sb-Te and Ge-As-Se samples. Systematic compositional dependencies of the intensities of the characteristic Raman bands correlate with evolution of concentration of the different structural units in Ge-Sb-Te and Ge-As-Se alloys along the studied compositional lines. Obtained compositional trends in the intensities of Raman bands may enable one to predict vibrational properties of other amorphous Ge-Sb-Te and Ge-As-Se chalcogenides.

1. Introduction

Amorphous chalcogenides attract much attention due to their properties. Chalcogenide glasses (CG) are widely used in versatile technological applications such as infrared optical elements, acousto-optic and all-optical switching devices, holography recording media *etc*. Chalcogenide alloys that exhibit remarkable difference of their electrical and optical properties in the amorphous and crystalline states (Ge-Sb-Te alloys) belong to the class of the phase-change materials [1]. These chalcogenide alloys are promising for data storage, display and data visualization applications [2,3], their crystalline phase utilizes resonant bonding [4].

Information on the short-range order structure of chalcogenide glasses is particularly valuable in order to establish useful correlations between their structural and macroscopic properties [5]. Moreover, the nature of amorphous state is one of the most interesting and contradictory problem in solid state physics till now. When studying amorphous materials one faces with two principal difficulties. One is the absence of the only theory of a non-crystalline state and the other is that the every traditional experimental probes of structure study “by itself does not yield a unique interpretation” [5]. As a consequence of this situation the variety of structure models [6] were proposed for amorphous chalcogenides. Chalcogenide glassy alloys are attractive for both theoretical and experimental studies. Being essentially covalent materials [7] they are close to the model objects. This feature of chalcogenide glasses made possible the development of the topological concepts of their structure [8,9]. For example, the theoretical approach based on valence-force field approximation [9] was enough fruitful in the description of the elastic properties of amorphous chalcogenides. From the industrial point of view, a fundamental understanding of the structure, properties and stability of the amorphous chalcogenide alloys has important impact on the employment of the Ge-Sb-Te alloys in the next generation of storage media [2], as well as Ge-As-Se alloys for the fabrication of optical elements [10,11].

Optical spectroscopy has shown to be a powerful tool in studying the structure of amorphous and crystalline materials in the wide temperature range [12–15]. Recently, the analysis of Raman spectra of binary arsenic sulfide chalcogenide glasses, As_xS_{1-x}, evidenced the presence of phase separation effects for $x < 0.25$ [16] and the occurrence of intrinsic nanoscale phase separation for $x = 0.4$ [17]. Previous studies of $Ge_xAs_ySe_{1-x-y}$ glasses employing

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Raman spectroscopy have been performed in Refs. [18–20]. Authors [18] measured Raman spectra of amorphous Ge-As-Se and classified two distinct regimes based on the dominant peaks in the Raman spectra: low Ge (0% ≤ Ge ≤ 15%) and high Ge (22% ≤ Ge ≤ 39%). Raman spectra of Ge-As-Se glasses with a similar concentrations of germanium were presented in Ref. [19]. Quantitative analysis of these spectra based on their decompositions and relative ratio of the different chemical bonds derived from the decomposed Raman spectra. Authors confirmed that, while the glass network mainly consists of chemical-ordered $GeSe_{4/2}$ and $AsSe_{3/2}$ structural units, the concentrations of the structural units evolve with a change in Ge and As concentrations. In Ref. [20] authors focused on alloys $Ge_xAs_ySe_{100-x-y}$ with $33 < x < 39$. The structure of these glasses is dominated by tetrahedral units of germanium. Homo-polar and semi-polar 'defect' bonds, such as Ge—Ge, Ge—As, and As—As bonds, also occurred in the structural units.

It is interesting to study amorphous Ge-As-Se samples that lie within the nanophase separation region. It is well known that the appearance of phase separation can damage the back-bone of the network and consequently cause a decrease in the glass transition temperature T_g, which is one of the important parameters for the characterization of photosensitive media. Better understanding of the mechanism of compositional nanophase evolution in Ge-As-Se system can help in the optimization of the sensitivity and relief formation processes of composite nanomultilayer structures based on Ge-As-Se alloys. Such composite nanomultilayer structures are perspective for the direct recording of optical elements [10,11,21,22].

In the recent years significant progress in studying the structure of chalcogenide phase-change alloys by employing the Raman spectroscopy has been achieved by a number of authors [23–27]. In Ref. [28] authors focused on the compositional dependencies in the Raman spectra of several crystalline Ge-Sb-Te alloys without much focusing on those in the amorphous phase. Raman spectroscopy was employed to study the local structure of amorphous and crystalline Ge-Sb-Te thin films in Ref. [25]. Here authors present Raman spectra Ge-Sb-Te alloys along the pseudo-binary line between GeTe and Sb_2Te_3 in the 100-300 cm^{-1} spectral range, that does not cover all Raman active modes in these alloys and leaves out modes below 100 cm^{-1} already reported in Ref. [29]. Finally, authors [25] presented the assignment of Raman bands based on the qualitative analysis of their spectra. Quantitative analysis of the spectra that might point on all compositional trends (peaks positions and intensities) and therefore yield the unambiguous understanding the nature of observed Raman bands, has not been fully performed. Raman and far-infrared spectroscopy have been employed to study the temperature impact on the phonon modes of two Ge-Sb-Te alloys ($Ge_2Sb_2Te_5$ and $Ge_3Sb_2Te_6$) in Ref. [30]. Authors [30] represent Raman spectra of $Ge_2Sb_2Te_5$ and $Ge_3Sb_2Te_6$ in much wider range than in Ref. [25], however the band below 100 cm^{-1} has been attributed only to the characteristic Bose peak. By considering only two alloys it was not possible to draw conclusions regarding compositional evolution of Raman bands in the amorphous state. To evaluate the impact of GeTe content on the properties of Ge-Sb-Te alloys authors [31] used Raman spectroscopy together with other methods. For this purpose several GeTe-rich Ge-Sb-Te alloys have been studied. On one hand authors [31] mentioned the band below 100 cm^{-1} and discuss its assignment, but on other hand there is no corresponding experimental data were shown. To trace the trend in the influence of GeTe content on the properties of Ge-Sb-Te, the alloys along whole pseudo-binary line (not only GeTe-rich ones) should have been considered. To summarize, the approaches used in studies [25,28,30,31] provide some space for imprecise description of the compositional dependencies in the Raman spectra of amorphous Ge-Sb-Te alloys that in turn may lead to the ambiguous description of their structure.

The aim of this study is to perform the analysis of the compositional evolution of Raman spectra of the amorphous chalcogenide alloys upon systematic increase of the Ge-content (Fig. 1). In our study we have chosen two groups of chalcogenide alloys. The first group includes non-phase-change Ge-As-Se alloys: As_2Se_3, $Ge_{0.1}As_2Se_{2.9}$ (Ge 2 at.%), $Ge_{0.3}As_{1.9}Se_{2.8}$ (Ge 6 at.%), $Ge_{0.4}As_{1.8}Se_{2.7}$ (Ge 8 at.%), $Ge_{0.5}As_{1.8}Se_{2.7}$ (Ge 10 at.%). As the second group we chose phase-change Ge-Sb-Te alloys along the pseudo-binary line between GeTe and Sb_2Te_3 (i.e. $(GeTe)_x(Sb_2Te_3)_{1-x}$): $GeSb_4Te_7$ ($x = 0.33$), $GeSb_2Te_4$ ($x = 0.5$), $Ge_2Sb_2Te_5$ ($x = 0.66$), $Ge_3Sb_2Te_6$ ($x = 0.75$) and GeTe ($x = 1$). Results of the detailed qualitative and quantitative analysis of the compositional evolution of Raman spectra might yield the better understanding the structure of amorphous samples by establishing the interpretation and assignment of the Raman bands to the vibration of the structure units. Latter will also enable one to predict the vibrational properties of many other amorphous alloys along the Ge-As_2Se_3 and GeTe-Sb_2Te_3 lines.

2. Experimental

2.1. Sample preparation

Chalcogenide Ge-As-Se with systematic increase of Ge doping (As_2Se_3, $Ge_{0.1}As_2Se_{2.9}$, $Ge_{0.3}As_{1.9}Se_{2.8}$, $Ge_{0.4}As_{1.8}Se_{2.7}$, $Ge_{0.5}As_{1.8}Se_{2.7}$) samples were obtained in the form of glass. Component elements (Ge, As, Se) of 6N purity were melted in evacuated ($p\sim10^{-5}$ Torr) and sealed in silica ampoules at 800–850 °C for 8 h and subsequently quenched in air.

The phase-change chalcogenide Ge-Sb-Te films of $GeSb_4Te_7$, $GeSb_2Te_4$, $Ge_2Sb_2Te_5$, $Ge_3Sb_2Te_6$ and GeTe were d.c. sputter-deposited with an LS 320 von Ardenne system (background pressure of 4×10^{-7} mbar, 20 s.c.c.m. Ar flow, deposition rates 0.1–0.2 nms^{-1}, operating in constant power mode using 20–25 W) using stoichiometric targets of 99.99% purity. The phase-change films with the thickness of 500 nm were sputtered onto a glass substrate. As deposited samples were amorphous, their structure was checked by X-ray diffraction.

2.2. Raman measurements

Raman spectra of Ge-As-Se samples were measured in the spectral range from 50 to 400 cm^{-1} at room temperature using a FRA-106 Raman attachment to Bruker IFS 88 applying the diode pump Nd:YAG laser of ca. 100 mW power and using the liquid nitrogen-cooled Ge detector with the resolution set to 1 cm^{-1} with 256 scans collected in each experiment.

Raman spectra of Ge-Sb-Te samples were obtained in the spectral range from 40 to 300 cm^{-1} with backscattering configuration using a TriVista® Raman spectrometer employing a laser radiation with the spot size of 0.25 mm in the diameter, with 532.1 nm wavelength and 9 mW power with SPECAC® grid polarizer with the resolution of 1 cm^{-1}. Each spectrum was measured for 1000 s.

2.3. Analysis of Raman spectra

Obtained Raman spectra were analyzed in the home-made software CoRa [32]. To describe the bands in the reduced Raman spectra we used Gauss oscillators. One Lorentz oscillator has been employed to fit the main line at zero wavenumber in the spectra of Ge-Sb-Te samples. The quality of the fit of Raman spectra in CoRa