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Permittivity of Ge, Te and Se thin films in the 200–1500 nm spectral range. Predicting the segregation effects in silver

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ABSTRACT

Optical properties of well-known bulk materials can be significantly modified by decreasing dimensions to nm-size. Using Molecular Beam Epitaxy (MBE) and e-beam Physical Vapour Deposition (PVD) we have fabricated 20–30 nm-thick amorphous Ge, Te and Se films. The permittivities of investigated layers have been extracted from measurements of the Ψ and Δ ellipsometric azimuths. We found that for all of the investigated films, the intensity of all bands in the permittivity spectrum is smaller than for bulk materials or thick ($>$ 100 nm) films. Using the acquired optical constants along with the permittivity of a 20 nm-thick silver film, we have applied the Maxwell-Garnett equation to predict the permittivities of a silver film with Ge, Se or Te segregated in its structure. Implementing the parameters of 20 nm-thick Ge results in an 81 nm redshift of the segregation-induced band with respect to the experimental value, while implementing the parameters of 2 nm-thick Ge film results in a 95 nm blueshift of this band.

1. Introduction

Since the middle of the previous century, germanium, selenium and tellurium have attracted a growing interest because of their photoconductive properties. Such optical parameters as refractive indices and absorption profiles have been calculated [1,2] and measured for diverse samples like monocrystalline Ge, Se and Te [3–12], amorphous and polycrystalline evaporated films [13–21], Se-Te, Ge-Te or Ge-Se-Te alloys [12–25] or even liquid samples [26–31]. P. Vasko has compiled the data for selenium in the wavelength range of 0.13 Å − 150 µm [32]. However, all of these works either focus on the infrared range or investigate more than 300 nm-thick samples which already exhibit bulk-like properties. The thinnest Se film was measured by Soliemann and Abu-Sehly [33], yet it was still as thick as 100 nm. They have also shown, that there is a very strong dependence in the permittivity of the Se film on its thickness.

Modern technologies of evaporating multilayers of different materials and design of functional alloys has created interest in diffusion and segregation phenomena [34,35]. Recently, a number of works have been published on manipulation of the permittivity of the silver films due to controlled segregation of germanium [36–38]. Earlier works investigate the process of segregation of selenium [39] and tellurium [40] in silver. Since all three of those materials exhibit high energy gap in the band structure, silver layers with segregated Ge, Se and Te atoms should all exhibit an additional segregation-induced band in the permittivity spectrum, either in the visible or in the near-infrared. The existence of such band should be predicted by effective medium calculations [41], which require optical parameters of all mixed materials in their initial forms and volumes employed. Hence the need to investigate the optical parameter for ultra-thin films. In this work, we have fabricated 20–30 nm-thick Ge, Se and Te layers as well as an ultra-thin (2 nm) Ge film and determined their crystallinity using XRD measurements as well as optical parameters using ellipsometry. Then we used those optical parameters as an inclusion material in a Maxwell-Garnett effective medium approximation to determine the effective optical constants of silver systems with segregated Ge, Se and Te atoms, which allow to predict the position and intensity of the segregation-induced band in the permittivity spectrum.

2. Materials and methods

Ge films were deposited from fabmate crucibles using PVD75 Lesker e-beam evaporator, on fused silica substrates with RMS roughness equal to 0.3 nm. The purity of the material was 5 N. Before evaporation, substrates were cleaned with argon flow at 2 bar pressure. Ge was evaporated at an average deposition rate of 0.5 Å/s. The deposition rate and total film thickness were monitored by two quartz weights inside the deposition chamber. Then, film thicknesses were verified by Dektak

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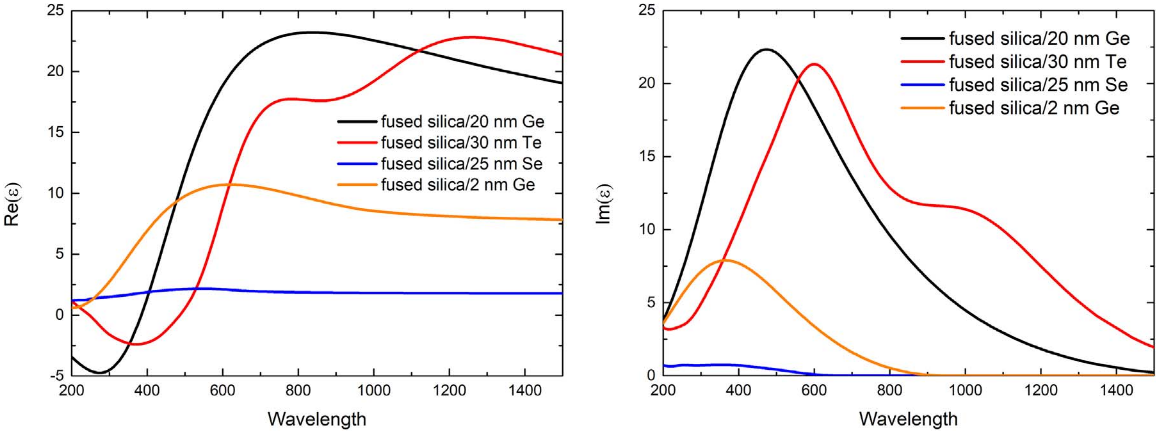

Fig. 1. Real (left) and imaginary (right) parts of permittivity of 20 nm-thick Ge, Te and Se films as well as 2 nm-thick Ge film.

6 M stylus profiler. The pressure in the vacuum chamber was kept below 5×10^{-5} Torr during the whole deposition process. The crucible-substrate distance was 40 cm.

Se and Te films were deposited on similar fused silica substrates using II-VI semiconductor growth chamber of dual chamber Molecular Beam Epitaxy (MBE) system delivered by SVT Associates. Substrates were kept at room temperature. Background pressure was below 5×10^{-10} Torr. The purity of sublimated ingots for both Te and Se was 7 N. To avoid cross-contamination during deposition of Te or Se only one Knudsen cell was kept at working temperature [42]. The nominal thickness of layers estimated from a typical growth rate of Se and Te compounds was set to 20 nm. However, further optical measurements proved that the deviation from the nominal thickness could be as large as 10 nm.

The wide-angle X-ray diffraction (XRD) measurements were performed in transmission mode using Bruker Discover D8 GADDS system. The system works with Cu Kα X-ray source. The X-ray patterns are recorded with 2D Vantec 2000 detector. For precise diffraction angle measurements, also Bruker Discover D8 system was used, but the measurements were performed in reflection geometry in $\theta - 2\theta$ scans. The X-ray signals were recorded with 1D Vantec-1 detector.

Ellipsometric azimuths Ψ and Δ of fabricated samples were measured in the UV–VIS–MIR spectral range (0.06–6.5 eV) for three angles of incidence (65°, 70° and 75°) by the use of two instruments: V-VASE (J.A.Woollam Co., Inc.) in the UV–VIS–NIR and Sendira (Sentech GmbH) in the MIR. The complex dielectric functions of the semiconductor layers were extracted using a layered model of the samples. We have achieved very good fits assuming perfectly smooth (roughness root-mean-square equal to 0) fused silica substrate/semiconductor and semiconductor/air interfaces, thus we can assume that the role of roughness is negligible. The fit quality was good enough, that no additional oxide layer was necessary to be considered in the model, thus we can assume that the role of oxidation is negligible. The permittivities were then interpreted in terms of the Gaussian oscillator model and the Tauc-Lorentz oscillator model developed by Jellison and Modine [43,44]. Permittivity curves presented in this work result from the combination of exactly one Tauc-Lorentz oscillator (which is essentially responsible for modeling the absorption on valence band to conduction band transitions) with a number of Gaussian oscillators, which are responsible for modeling the additional absorption on interband transitions.

The imaginary part of permittivity defined by the Tauc-Lorentz oscillator is given by

$$\varepsilon_{2\mathrm{TL}}(\mathrm{E}) = \left\{ \begin{matrix} \left[\dfrac{\mathrm{A_{TL}E_{TL}B_{TL}(E - E_g)^2}}{\mathrm{E((E^2 - E_{TL}^2)^2 + B_{TL}^2 E^2)}} \right] & \mathrm{E > E_g} \\ 0 & \mathrm{E \le E_g} \end{matrix} \right\} \tag{1}$$

where E_g is the semiconductor energy band gap, and A_{TL}, E_{TL} and B_{TL} denote the amplitude, position and broadening of the Tauc-Lorentz oscillator.

The imaginary part permittivity defined by the Gaussian oscillator is given by

$$\varepsilon_{2\mathrm{G}}(\mathrm{E}) = \mathrm{A_G} e^{-\left(\frac{2\sqrt{\ln 2}\,(\mathrm{E - E_G})}{\mathrm{B_G}}\right)^2} + \mathrm{A_G} e^{-\left(\frac{2\sqrt{\ln 2}\,(\mathrm{E + E_G})}{\mathrm{B_G}}\right)^2} \tag{2}$$

where A_G, E_G and B_G denote the amplitude, position and broadening of the oscillator.

The real parts of the dielectric function can be calculated using the Kramers-Kronig relation for both oscillators.

Complex permittivity values of silver films with Ge, Te or Se segregated in the silver structure were calculated using the Maxwell-Garnett formula [44,45]:

$$\varepsilon_{eff} = \frac{\varepsilon_m \left(2f \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m} + 1\right)}{1 - f \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m}} \tag{3}$$

where ε_{eff} is the effective permittivity of the system, ε_m the permittivity of the medium (in this case the Ag layer) ε_i the permittivity of the inclusion (in this case the Ge, Se or Te atoms) and f is the inclusion fill factor. For the medium, the permittivity values of the 20 nm-thick pure silver layer measured in work [37] were used, while for the inclusion material, the permittivities of Ge, Se and Te layers studied in this work were used.

3. Results and discussion

Fig. 1 presents the permittivity values of Te and Se films with nominal thickness of 20 nm fabricated using MBE as well as 20 nm-thick and 2 nm-thick Ge films fabricated using e-beam PVD. Since germanium forms continuous and smooth films even at thicknesses at the order of 2 nm, we have been able to measure optical constants of such a film. However, the same can not be said about Te or Se films, which at such small thicknesses grow in islands and thus are very hard to measure. It is also worth noting, that the 20 nm thickness is the nominal mass thickness and so in the ellipsometric experiment, the thickness was left as a fittable parameter. For germanium, the measured optical thickness is in agreement with the quartz weight indications after the deposition process, while it is larger for Se and Te films – 25 and 30 nm, respectively. The recorded XRD spectra show no distinct features, therefore we assume that our samples are amorphous or polycrystalline with a grain size at the order of 1 nm or less.

Unlike bulk Ge single crystals, which exhibit multiple resonances, with two dominant ones at about 290 and 535 nm [10,11], the permittivity of our Ge films exhibits only one band, which is centered at 475 nm for the thicker film and 365 nm for the thinner film. The