Amorphous chalcogenide thin films for nonlinear integrated optics in mid-infrared

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ABSTRACT

Some chalcogenide glasses (ChGs) are showing a large transparency window in the infrared coupled with outstanding optical nonlinearities offering tremendous opportunities for achievement of innovative mid-infrared (MIR) on-chip components. By means of industrial co-sputtering deposition technique, we study the amorphous structure and the nonlinear optical properties of As-free amorphous $GeSb_wS_xSe_yTe_z$ chalcogenide thin films. The nonlinear refractive Kerr index (n_2) of the films were evaluated by means of modelling of spectroscopic ellipsometry data validated experimentally for some compositions by means of advanced nonlinear optical characterizations in waveguides. State-of-the-art and higher n_2 values were obtained. Depending on the composition of the $GeSb_wS_xSe_yTe_z$, n_2 can vary of more than one order of magnitude. Finally, Fourier-Transform Infrared (FTIR), Raman and X-ray Absorption (XAS) spectroscopies analysis of the amorphous structure of some ChGs prototypical compositions in relation with their nonlinear optical properties was used as a basis for *ab initio* molecular dynamics (AIMD) simulations. Thus, the intimal link between local atomic configurations and optical nonlinearities is proposed giving unique clues to control optical nonlinearities of chalcogenide materials.

Keywords: chalcogenide glasses; mid infrared; nonlinear optics; co-sputtering; AIMD; photonics.

1. INTRODUCTION

Among their unique portfolio of properties, some chalcogenide glasses (ChGs) offer also unique opportunities for innovative mid-infrared (MIR) components thanks to their outstanding trade-off between a high transparency window and large optical nonlinearities in the infrared range. However, the REACH European recommendation and the World Health Organization have both identified Arsenic as one of the ten most harmful chemicals for human health. In that context, we study here how to tailor the linear and nonlinear optical properties of As-free amorphous $GeSb_wS_xSe_yTe_z$ chalcogenide thin films with a particular emphasis on their compatibility with CMOS technologies for future realization of on-chip MIR components.

2. EXPERIMENTS

The $GeSb_wS_xSe_yTe_z$ thin films were obtained by means of magnetron co-sputtering in an industrial 200 mm deposition cluster tool. Modelling of spectroscopic ellipsometry data acquired on the as-deposited films allowed to determine their optical constants (refractive index n, extinction coefficient k and optical bandgap E_g^{opt}) using Cody-Lorentz model as well as evaluating their nonlinear refractive Kerr indices (n_2). Experimental nonlinear coefficient (γ) link to Kerr index are obtained by analysing the nonlinear phase shift of waveguides using heterodyne detection setup. The good agreement between experimental and calculated Kerr indices of chosen prototypical ChGs allows to validate modelling of 3rd order nonlinear refractive indices. The link between amorphous structure and enhanced optical nonlinearities was probed by means of FTIR, Raman and XAS spectroscopies on some chosen compositions. On the basis of all experimental data, AIMD simulations permitted to calculate the local electronic polarizability depending on the local structural motifs in the different prototypical glasses evidencing the non-obvious link between some peculiar structural motifs and the material's enhanced macroscopic optical nonlinearity.

3. RESULTS & DISCUSSION

3.1 Experimental evaluation of Kerr index

In Fig. 1 are plotted the nonlinear coefficient γ of 4 $GeSb_wS_xSe_yTe_z$ chalcogenides and SiN_x reference material measured in waveguides using an experimental heterodyne detection setup at 1550 nm. The experimental n_2 Kerr refractive indices of the samples are derived from the nonlinear coefficient γ and compared to those calculated with the Sheik-Bahae model [1] using linear refractive index and optical band gap values evaluated in thin films.

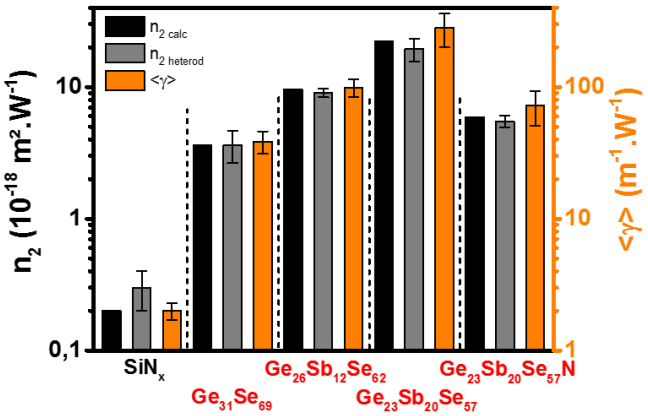

Figure 1: Experimental nonlinear coefficient γ of some chalcogenide thin films and SiN_x measured in waveguides at 1550 nm. The $n_{2\ heterod}$ Kerr index is deduced from nonlinear coefficient and compared to $n_{2\ calc}$ the Kerr index calculated using the Sheik-Bahae model.

One can note a good agreement between experimental and calculated Kerr indices of chalcogenide films. The obtained values are of one to two orders of magnitude higher than that of SiN_x samples. A huge variation of 3rd order nonlinearity is also observed depending on the composition of the chalcogenide film. The dramatic change of Kerr index depending on the chalcogenide composition can be related to modifications of the amorphous structure.

3.2 Study of the link between optical properties and local amorphous structure

In Fig. 2a are plotted the n_2 Kerr refractive indices as a function of the bandgap of the studied $GeSb_wS_xSe_yTe_z$ thin films. Depending on the composition, the amorphous $GeSb_wS_xSe_yTe_z$ films exhibit a wide range of n_2 values reaching up to 500 times that of silicon dioxide. We emphasize that these results are well supported by previous study of similar $GeSb_xSe_y$ compounds in the literature [2]. Kerr index shows strong dependence on the ChG's composition [3]. In order to relate optical nonlinearities and structure, four prototypical compositions differing by their n_2 values were selected and studied experimentally by means of optical and advanced structural characterization to be used as a basis to robust AIMD models for atomistic simulations.

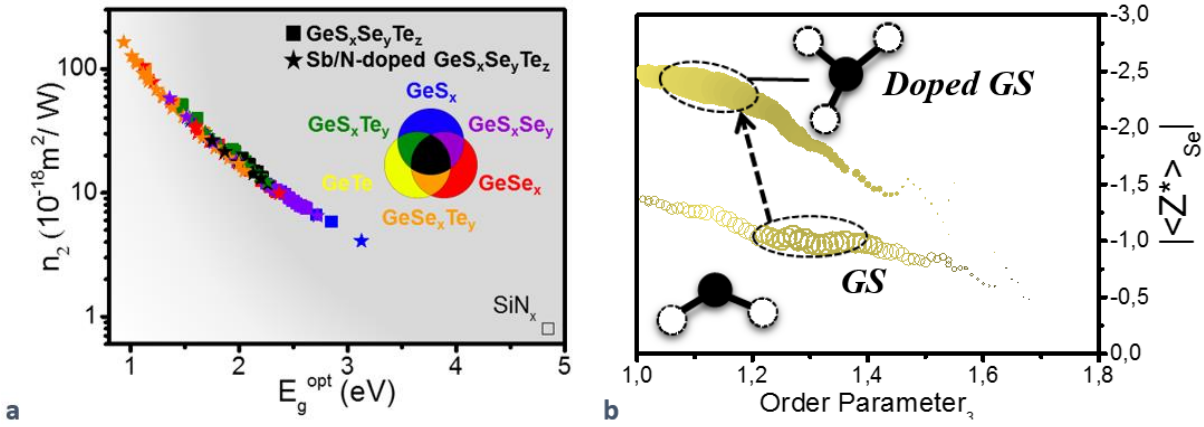

Figure 2: (a) calculated 3rd order nonlinear refractive indices at 0,534 x E_g^{opt} depending on optical band gap energy of (co-)sputtered $GeSb_wS_xSe_yTe_z$ films. (b) Born effective charges Z^* extracted from AIMD calculations for $Ge_{72}Se_{168}$ (GS) and $Ge_{66}Se_{127}Sb_{48}N_{12}$ (doped GS) materials (open and close symbols). Dots' size is proportional to number of Se-based structural motifs distinguished by means of the order parameter. A significant increase of Z and thus electronic polarizability is observed for GS upon doping.*

From the calculation of the atomic Born effective charges in Fig. 2b, one could relate the origin of the local very high electronic polarizability related to highly polarizable structural motifs in the amorphous network to the enhanced optical nonlinearities of the material. We show that these highly polarizable motifs result from a unique bonding configuration that is somehow reminiscent to the so called metavalent bonding (MVB), a unique bonding mechanism that is behind the huge optical and electrical contrast between amorphous and crystalline state of phase-change materials [4,5].

4. CONCLUSIONS

The outstanding linear and nonlinear optical properties of some chalcogenide glasses at origin of their promising potential of applications for MIR on-chip components is shown to result from formation of peculiar structural motifs leading to specific bonding mechanism at origin of their huge polarizability. In particular, some element increases dramatically the local electronic polarizability by inducing structural motifs supporting bonds similar to the newly introduced metavalent bonding mechanism arising in some local crystal-like motifs [6]. These results pave the way to control and improve further the unique optical properties of chalcogenide glasses in thin films.

REFERENCES

[1] M. Sheik-Bahae, *et al.*: Dispersion of Bound Electronic Nonlinear Refraction in Solids. *J. Quantum Electron.* 27, 1991.

[2] T. Kuriakose *et al.*: Measurement of ultrafast optical Kerr effect of Ge–Sb–Se chalcogenide slab waveguides by the beam self-trapping technique. *Opt. Commun.* **403**,352-357, 2017.

[3] J.-B. Dory, *et al.*: Ge-Sb-S-Se-Te amorphous chalcogenide thin films towards on-chip nonlinear photonic devices. *Under revision for publication* in *Scientific Reports* 2020.

[4] M. Wuttig *et al.*: Incipient Metals: Functional Materials with a Unique Bonding Mechanism. *Adv. Mater.* 30, 1803777, 2018.

[5] J.-Y. Raty *et al.*: A Quantum-Mechanical Map for Bonding and Properties in Solids. *Adv. Mater.* 31, 1806280, 2019.

[6] J.-B. Dory, J.-Y. Raty *et al.*: Revealing the role of amorphous structural motifs on the huge optical nonlinearities of chalcogenide glasses. *To be published* 2020.