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Ge–Sb–S–Se–Te amorphous chalcogenide thin films towards on-chip nonlinear photonic devices

J.-B. Dory1,2, C. Castro-Chavarria3, A. Verdy1,3, J.-B. Jager2, M. Bernard1, C. Sabbione1, M. Tessaire3, J.-M. Fédéli1, A. Coillet2, B. Cluzel3 & P. Noé1,*

Thanks to their unique optical properties, Ge–Sb–S–Se–Te amorphous chalcogenide materials and compounds offer tremendous opportunities of applications, in particular in near and mid-infrared range. This spectral range is for instance of high interest for photonics or optical sensors. Using co-sputtering technique of chalcogenide compound targets in a 200 mm industrial deposition tool, we show how by modifying the amorphous structure of GeSb₅SₓSe_yTe_z chalcogenide thin films one can significantly tailor their linear and nonlinear optical properties. Modelling of spectroscopic ellipsometry data collected on the as-deposited chalcogenide thin films is used to evaluate their linear and nonlinear properties. Moreover, Raman and Fourier-transform infrared spectroscopies permitted to get a description of their amorphous structure. For the purpose of applications, their thermal stability upon annealing is also evaluated. We demonstrate that depending on the GeSb₅SₓSe_yTe_z film composition a trade-off between a high transparency in near- or mid-infrared ranges, strong nonlinearity and good thermal stability can be found in order to use such materials for applications compatible with the standard CMOS integration processes of microelectronics and photonics.

Chalcogenides are commonly defined as non-oxide compounds containing at least one chalcogen element such as S, Se and/or Te (belonging to group 16 of O) alloyed with electropositive elements (more often elements of group 15 (As, Sb, Bi) and/or group 14 (Si, Ge, Sn, Pb)). Chalcogenide exhibit a unique portfolio of properties which has led to their wide use for non-volatile memory applications such as optical data storage (CD-RW and DVD-RAM), Conductive-Bridging Random Access Memory or Phase-Change Random Access Memory. More recently, thanks to the huge electronic nonlinearities and discontinuity [in particular the Ovonic Threshold Switching (OTS) mechanism] observed in some chalcogenide glasses (CGs) under electrical field application, the latter are considered as the most promising materials to be used as innovative selector element in 3D memory arrays. Besides, thanks to a high transparency window in the infrared range and large optical nonlinearities, chalcogenide glasses offer also opportunities for elaboration of innovative mid-infrared (MIR) components such as MIR super-continuum (SC) laser sources, optical sensors, IR micro-lens arrays and all-optical integrated circuits. The potential of amorphous semiconductors for optical applications is already demonstrated but the progresses in glass science is still behind crystal science due to inherent complexity of highly disordered systems hindering thus their structural description and theoretical modelling. Up to now, state-of-the-art of MIR SC generation have been achieved by using mainly chalcogenide compounds containing Arsenic such as As₂S₃ and As₂Se₃ fibres10 or GeAsSe rib waveguides11. However, the R.E.A.C.H. European recommendation (https://echa.europa.eu/regulations/reach) as well as a recent publication from the World Health Organization (https://www.who.int/ipcs/assessment/public_health/chemicals_phe/en/) have both identified Arsenic as one of the ten most harmful chemicals for human health. As a result, developing new materials using less and less harmful or rare element is a huge challenge for the materials science.

In that context, the aim of the present study is to develop As-free amorphous chalcogenide thin films compatible with CMOS technology of microelectronics and photonics. The ultimate purpose would be to give clear clues to select the most suitable chalcogenide compositions exhibiting the best trade-off between stability and optical properties in order to enable future achievement of passive and active on-chip MIR components such...
as MIR optical waveguides or portable SC laser sources. To this aim, a wide composition range of amorphous GeSb$_x$S$_{1-x}$Te$_{2}$ chalcogenide thin films were deposited on 200 mm Si-based substrates by means of magnetron co-sputtering technique. Despite the ability of such technique to permit a fast and easy study of a wide range of chalcogenide thin films’ compositions, only very few studies of the optical properties of co-sputtered chalcogenide films have been reported in literature yet\textsuperscript{12–14}. Since the local structure of glasses determines their physical properties, a first description of the amorphous structure of the (co-)sputtered chalcogenide films was probed by means of Raman and Fourier-transform infrared (FTIR) spectroscopies. Then, modelling of the spectroscopic ellipsometry data acquired on as-deposited thin films permits to determine their linear optical constants in the visible to near infrared range. From these experimental data and by using the well-known Sheik-Bahae model, a first evaluation of their $n_2$ Kerr refractive index is given in order to get better insight on their nonlinear optical properties. Moreover, the thermal stability of all deposited thin films was probed by monitoring their optical reflectivity during annealing under N$_2$ atmosphere. Finally, some of the GeSb$_x$S$_{1-x}$Te$_{2}$ compositions are shown to exhibit an optimized compromise between the good glass stability (but limited transparency window) of S-based chalcogenide and the high 3rd order nonlinear refractive index $n_2$ (but low thermal stability of the amorphous phase) of Te-based compositions\textsuperscript{15,16}. Besides, we reveal the major impact of Sb introduction in Ge$_x$S$_{1-x}$Te$_{2}$ binary as well as GeS$_x$Se$_{1-x}$ and GeSe$_x$Te$_{1-x}$ ternary compounds on the amorphous structure and therefore on the optical properties of chalcogenide thin films obtained by co-sputtering deposition technique.

**Methods**

**Chalcogenide thin films deposition and basic characterization.** The amorphous chalcogenide thin films were obtained by means of (co-)sputtering on 200 mm Si(001) substrates from either a single or up to simultaneously three targets of pure chalcogenide compounds. Before (co-)sputtering deposition, we did not perform any particular surface preparation of the Si substrates. Indeed, the substrates are standard high-quality microelectronic Si wafers with high purity and very low surface contamination and covered, as usual, by a few nm thick layer of native silicon oxide. The films’ thicknesses were either fixed to 100 nm or 200 nm. The compositions of sputtering targets were Ge$_{40}$Sb$_{60}$, Ge$_2$S$_{38}$, Ge$_x$S$_{74}$, Ge$_{50}$Se$_{50}$, Ge$_2$Se$_{80}$ pure Sb and pure Ge. The targets were sputtered by magnetron sputtering with an Ar plasma either achieved by using radio frequency (RF) at 13.56 MHz or direct current (DC) plasma discharges. It is well known that deposition parameters of magnetron sputtering technique, such as Argon gas flow, substrate temperature, deposition vessel geometry, RF or DC plasma, applied power on targets and deposition pressure especially can play a major role on the density, composition and structure of the thin films\textsuperscript{17–19}. In this study, all deposition were made using the same Ar flow and the deposition pressure was kept at 5.10$^{-3}$ mBar. Note that due to geometry and deposition conditions in our multi-cathode chamber, the substrate temperature was kept very close to room temperature during deposition of chalcogenide films.

The different compositions of the sputtered films were obtained by varying the power applied to the targets between 10 and 220 W (see Sect. 1 of the Supplementary Information). Note that a slight composition deviation between targets and deposited films can occur. This is the result of the different sputtering yields between chemical elements due to a selective atoms-ions interactions. This effect also depends on the deposition conditions such as applied power or aging of the targets. For instance, Ge$_{38}$Sb$_{62}$ and Ge$_{36}$S$_{64}$ thin film samples were obtained by means of sputtering of the same Ge$_2$S$_3$ target and in the same deposition conditions. The slight deviation of composition is probably due to aging of the target after a high number of deposition cycles. This variation is of the order of the accuracy level of characterization methods used to determine films’ compositions (\textapprox{} 1 at. %). However, this trend on compositions is also confirmed by changes of properties and amorphous structure of these films as shown in the following.

The different compositions of the films were adjusted by varying the deposition rates ratio in between the different sputtering targets during the co-sputtering deposition. Then, the obtained compositions were verified by means of Wavelength Dispersive X-Ray Fluorescence (WDXRF) and/or ion beam analysis (Rutherford Back Scattering (RBS) and Particle Induced X-Ray Emission (PIXE) measurements).

Immediately after deposition all films were transferred under high vacuum in a second deposition chamber in order to be capped by a 10 nm thick SiNx protective layer. This nitride layer deposited by reactive RF magnetron sputtering of a pure Si target under Ar/N$_2$ reactive atmosphere is shown to be highly efficient to protect chalcogenide thin films from surface oxidation since chalcogenides are particularly prone to oxidation\textsuperscript{16,20,21}. We must note that during Si$_N_4$ deposition the temperature of the chalcogenide thin film samples can reach up to 180 $^\circ$C due to thermal heating resulting from RF sputtering of the Si target. We note that since this temperature is below the glass transition temperature of our chalcogenide samples, it is expected to have no detrimental impact on the films, as already studied for similar chalcogenide bulk glasses and thin films\textsuperscript{12–27}.

In order to get a first evaluation of the limit of stability of the deposited amorphous chalcogenides upon annealing, the reflectivity of the films at 670 nm was monitored during an annealing under N$_2$ atmosphere. The heating ramp rate was fixed to 10 $^\circ$C/min. The limit temperature was defined as the temperature for which an irreversible change of sample reflectivity was detected indicating an irreversible structural modification of the amorphous material (phase crystallization, phase segregation, layer delamination \ldots{}).

**FTIR and Raman scattering measurements.** Fourier-Transform Infrared spectroscopy (FTIR) analysis of local order of the amorphous films was performed in transmission mode in the 100–500 cm$^{-1}$ range. All absorbance spectra were acquired in the same experimental conditions (average over 32 scans and spectral resolution of 2 cm$^{-1}$). A reference absorbance spectrum collected on a Si(100) substrate covered by a 10 nm SiN$_x$ capping layer was used as background subtraction for all FTIR spectra acquired on the chalcogenide thin
film samples. Then, all raw spectra were normalized to the chalcogenide film thicknesses in order to get a more accurate comparison between the different thin film samples.

Raman scattering spectra were acquired in a micro-Raman spectrometer in the range from 100 to 500 cm⁻¹ using a laser probe at 532 nm wavelength. The acquisition conditions (laser power, magnification and exposure time) were adjusted for each film in order to optimize the signal-to-noise ratio but with a particular emphasis to keep no or very limited impact on the material’s structure.

**Spectroscopic ellipsometry measurements.** Spectroscopic ellipsometry (SE) measurements were performed in the 400–1,700 nm range. Data were collected at three incidence angles (55, 65 and 75°). Analysis of the raw data was performed using WVASE 32® software. A 10 nm SiNx layer deposited on a Si substrate was also measured separately in order to take into account any possible influence of capping layer when modelling of chalcogenide films’ data. For chalcogenide thin film samples, the film thicknesses, dielectric functions, optical constants (refractive index n and extinction coefficient k) and absorption coefficient α as a function of the photon energy in the 0.73–3.1 eV range were obtained by means of modelling of the SE data with a Cody-Lorentz (CL) model (see also Sect. 3 of the Supplementary Information).

The optical bandgaps of the films were estimated by using the bandgap values obtained from the CL fitting model (Eg(CL)) as well as by considering the energy for which the absorption reaches 10⁴ cm⁻¹ (Eg04).

Using the M-line technique at two wavelengths (1,313 and 1,548 nm), the effective refractive indices of the films as well as their thicknesses (by prism coupling technic) were also accurately determined (not shown). The obtained values of n at 1,313 and 1,548 nm were compared with those obtained from SE modelling and were used to validate the accuracy of SE results.

In order to get an estimation of the optical nonlinearities of the studied glasses the well-known Sheik–Bahae model was used. This method allows to estimate nonlinear Kerr refractive index n² by means of an analytical approach using linear refractive index and optical band gap energy values. This model takes into account contributions from several physical origins: two-photon and Raman transitions, linear Stark and quadratic Stark effects. A divergent term is also added in order to subtract the unphysical behaviour resulting from the formula used to adjust these contributions. For these calculations, we used a Sellmeier fit of the refractive index in the material’s transparency range obtained by using the Cody-Lorentz modelling and the optical band gap energy Eg04. The results of Sellmeier fits were extrapolated to wavelengths beyond spectral range of the ellipsometry measurements.

**Results and discussion**

**As-deposited chalcogenide thin films’ composition map.** All compositions of the studied chalcogenide thin films are reported on the ternary diagrams of Fig. 1 (see also Sect. 1 of the Supplementary Information). As shown in Fig. 1 the wide composition range of amorphous chalcogenide thin films that can be obtained exhibits a minimal thermal stability of 250 °C and up to higher than 400 °C depending on film composition (see “Methods” and Sect. 2 of the Supplementary Information).

**Amorphous structure of chalcogenide thin films by FTIR and Raman spectroscopies.** A summary of the bonds nature and main structural motifs detected in the amorphous structure of chalcogenide thin films deposited by co-sputtering is listed hereafter. All the details are given in Sect. 3 of the Supplementary Information. Table 1 summarizes the main structural motifs for each type of chalcogenide thin film compounds of the present study deduced from analysis of the Raman and FTIR vibration modes as well as the references from literature supporting our conclusions. As follows, the main conclusions on the amorphous structure drawn from the analysis of the Raman and FTIR spectra of each film is summarized system by system based on the extended discussion of the Supplementary Information.

**Ge₁₋ₓSex, Ge₁₋ₓSₓ and [Ge₄₀S₆₀]₁₋ₓ[Ge₂₆Se₇₄]ₓ thin films.** In Fig. 2a are shown the FTIR and Raman spectra acquired on the Ge₁₋ₓSex thin films, with x varying in 0.63–0.74 range. Se enrichment in Ge₁₋ₓSex films leads to reduction of homopolar inter-tetrahedral Ge–Ge bonds (Ge-Ge ETH) in favour of Se–Se ones accompanied by an increase of the number of corner-sharing (CS) compared with edge-sharing (ES) GeSe₄/2 tetrahedra in excellent agreement with previous works.

The FTIR and Raman spectra of Ge₁₋ₓSₓ films are presented in Fig. 2b. In amorphous Ge₁₋ₓSₓ films, vibrational modes corresponding to GeS₄/2 tetrahedra are observed along with contributions attributed to Ge–Ge and S–S homopolar bonds. The decrease of disorder in the amorphous Ge₁₋ₓSₓ films evidenced by a hardening of the Raman modes is observed when going from Ge₄₀S₆₀ toward Ge₃₆S₆₄ composition as the amorphous network evolves toward composition being more and more close to that of the stoichiometric Ge₅₂ glass. The intensity of the visible contribution of the crystalline Si substrate (c-Si) depends on the thickness and transparency of the chalcogenide films at 532 nm.

In Fig. 2c, the FTIR and Raman spectra of the [Ge₄₀S₆₀]₁₋ₓ[Ge₂₆Se₇₄]ₓ thin films obtained by co-sputtering of Ge₄₀S₆₀ and Ge₂₆Se₇₄ targets exhibit the main modes related to Ge–S and Ge–Se bonds with broadening and a slight frequency shift of their intensity maxima compared with those detected in pure amorphous Ge₄₀S₆₀ and Ge₂₆Se₇₄ compounds. The relative intensities of these two main contributions depend on the Ge₄₀S₆₀/Ge₂₆Se₇₄ concentration ratio introduced in the film during co-sputtering. Besides, random incorporation of sulphur and selenium in mixed Ge₄₃S₃₇Se₇/Se₇ tetrahedra (with m = 1, 2 and 3) is observed as supported by previous experimental and simulation studies.

**Discussion**
Figure 1. Ternary and pseudo-ternary diagrams showing compositions of the chalcogenide thin films deposited by magnetron (co)-sputtering: (a) Ge$_{1-x-y}$S$_x$Se$_y$, (b) [Ge$_{37}$S$_{63}$]$_{1-x-y}$[Ge$_{30}$Se$_{70}$]$_x$Sb$_y$ and (c) [Ge$_{30}$Se$_{70}$]$_{1-x-y}$[Ge$_{52}$Te$_{48}$]$_x$Sb$_y$ films. The dots’ size denotes the error bars estimated on the compositions of the films and the dots’ colour corresponds to an estimation of their limit temperature of stability defined by means of the temperature-resolved reflectivity measurements (see “Methods” and the Supplementary Information). Compounds’ compositions indicated in square bracket correspond to those of the sputtering targets which may differ from those obtained for the deposited films.

Figure 3a shows the Raman and FTIR spectra acquired on the [Ge$_{30}$Se$_{70}$]$_{1-x}$Sbx films. Addition of Sb in Ge$_{30}$Se$_{70}$ films results in formation of SbSe$_{3/2}$ pyramids, which are reminiscent of the main structural units of amorphous Sb$_2$Se$_3$, connected to GeSe$_{4/2}$ tetrahedral units by the Se atoms, and a decreasing number of Se–Se homopolar bonds in favour of a more and more prominent amount of homopolar Sb–Sb and wrong Ge–Sb bonds. This observation is of a major importance since homopolar Sb–Sb and wrong Ge–Sb bonds are shown to play a major role on electronic and hence optical properties of chalcogenide glasses.$^{3,36,37}$ Apart the non-negligible amount of Sb–Sb and Ge–Sb bonds present in our films which are chalcogen-deficient compared with the GeSe$_2$ and Sb$_2$Se$_3$ stoichiometric compositions, a similar trend has been previously observed in [GeSe$_2$]$_{1-x}$[Sb$_2$Se$_3$]$_x$ bulk glasses.$^{38}$

The FTIR and Raman spectra of the [Ge$_{37}$S$_{63}$]$_{1-x}$Sbx thin films are shown in Fig. 3b. S-deficient [Ge$_{37}$S$_{63}$]$_{1-x}$Sbx films are mainly composed of GeS$_{4/2}$ tetrahedral units and, upon addition of pure Sb, Sb–Sb and Sb–Ge bonds are formed with appearance of a small amount of SbS$_{3/2}$ pyramids. Therefore, in other words the amorphous network of our S-poor glasses can be depicted as a mix of GeSb$_{4-m}$S$_m$ tetrahedral motifs (with $m = \{0, 1, 2, 3\}$) and few SbGe$_{3-m-n}$Sb$_m$S$_n$ pyramidal units (with $n + m = \{0, 1, 2, 3\}$) in favour of homopolar Sb–Sb and wrong Sb–Ge bonds.$^{39-42}$

In Fig. 3c, the FTIR and Raman spectra of the [Ge$_{37}$S$_{63}$]$_{1-x-y}$[Ge$_{30}$Se$_{70}$]$_x$Sb$_y$ thin films upon Sb incorporation show vanishing of the Raman modes of mixed GeS$_{4-m}$Se$_m$ tetrahedral units at least in favour of an increase number of GeSe$_{4/2}$ tetrahedra. This indicates differences between Ge and Sb atoms in chemical bonding affinity with S and Se chalcogen elements. This has a different impact on the amorphous structure depending on the S/Se ratio. Increasing Sb concentration in [Ge$_{37}$S$_{63}$]$_{1-x-y}$[Ge$_{30}$Se$_{70}$]$_x$Sb$_y$ films leads to preferential formation of Ge–Se and Sb–S bonds by detriment to Ge–S and Sb–Se ones in films exhibiting a lack of chalcogen element compared with the stoichiometric compositions in agreement with a previous study$^{41}$. Raman and in a less manner FTIR
spectra also evidences the presence of a significant amount of Ge–Ge, Sb–Sb and Ge–Sb bonds in our sputtered $[\text{Ge}_{37}\text{S}_{63}]_{1-x-y}[\text{Ge}_{30}\text{Se}_{70}]_{x}\text{Sb}_{y}$ films.

Figure 4 shows the FTIR and Raman spectra acquired on the $[\text{Ge}_{30}\text{Se}_{70}]_{1-x}[\text{Ge}_{52}\text{Te}_{48}]_{x}$ thin films obtained by co-sputtering of $\text{Ge}_{30}\text{Se}_{70}$ and $\text{Ge}_{52}\text{Te}_{48}$ targets. Ge–GeTe₃ tetrahedra and GeTe defective octahedral motifs present in a-GeTe phase⁴³,⁴⁴ are expected also in $[\text{Ge}_{30}\text{Se}_{70}]_{1-x}[\text{Ge}_{52}\text{Te}_{48}]_{x}$ thin films. The structure of our $[\text{Ge}_{30}\text{Se}_{70}]_{1-x}[\text{Ge}_{52}\text{Te}_{48}]_{x}$ thin films obtained by co-sputtering can be depicted as $\text{GeSe}_{4-n}\text{Te}_{n}$ tetrahedral motifs with $n = \{0, 1, 2, 3, 4\}$ forming a disordered network connected, for small $x$ values, by means of the chalcogen elements and, for higher $x$ values, coexisting with a non-negligible amount of Ge–Ge homopolar bonds and possibly some Te–Te bonds as proposed in a previous work²².

In Fig. 4b,c are shown the FTIR and Raman spectra of $[\text{Ge}_{30}\text{Se}_{70}]_{1-x-y}[\text{Ge}_{52}\text{Te}_{48}]_{x}\text{Sb}_{y}$ and $[\text{Ge}_{1-2x}\text{Se}_{x}\text{Te}_{x}]_{1-y}\text{Sb}_{y}$ thin films obtained by co-sputtering of $\text{Ge}_{30}\text{Se}_{70}$, $\text{Ge}_{52}\text{Te}_{48}$ and $\text{Sb}$ targets. The comparison between both figures tends to indicate that in our amorphous $[\text{Ge}_{30}\text{Se}_{70}]_{1-x}[\text{Ge}_{52}\text{Te}_{48}]_{x}$ films, which are getting more and more Ge-rich as $x$ value is increased, Ge–Ge homopolars are found and Ge–Se(Te) bonds represent the vast majority of

Table 1. List of bonds and their main vibration frequencies in the corresponding structural motifs as detected by Raman and FTIR analysis of chalcogenide thin films. The frequencies of the Raman and FTIR modes correspond to position of experimental peaks reported for stoichiometric glasses in the literature. The analysis of these peaks is extensively discussed in Sect. 3 of the Supplementary Information. CS, ES and ETH denotes respectively corner-sharing, edge-sharing and ethane-like motifs as commonly labelled in the literature.

| System Bond Main structural motifs | Raman modes (cm⁻¹) | References | IR modes (cm⁻¹) | References |
|-----------------------------------|--------------------|------------|----------------|------------|
| $\text{Ge}_{1-x}\text{S}_{x}$    |                   |            |                |            |
| Ge–Se                             | $\text{GeSe}_{4/2}$ tetrahedra | 115; 140 | 68,69 | 115; 260; 285; 310 | 69 |
| CS $\text{GeSe}_{3}$ tetrahedra   | 195                | 70        | –              | –          |
| ES $\text{GeSe}_{5}$ tetrahedra   | 218; 310           | 70        | –              | –          |
| ETH $\text{GeS}_{2}$ units       | –                  | –         | 220            | 80         |
| Ge–Ge                             | ETH $\text{GeSe}_{2}$ tetrahedra | 179; 270 | 74,75 | –              | –          |
| Ge tetrahedra in amorphous Ge phase | 275               | 71        | –              | –          |
| S–S                               | $\text{Se–Se}$ bridge between $\text{GeSe}_{2}$ tetrahedra | 265 | 14 | –              | –          |
| $\text{Ge}_{1-x-y}\text{S}_{x}\text{Sb}_{y}$ |                   |            |                |            |
| Ge–Se                             | $\text{GeSe}_{2}$ tetrahedra | 115; 150 | 72,73,74 | 147; 367; 388 | 75,76 |
| CS $\text{GeSe}_{2}$ tetrahedra   | 343; 425           | 70,72,76  | 343            | 75         |
| ETH $\text{GeSe}_{2}$ tetrahedra  | 370; 437           | 70,73,76  | 437            | 75         |
| $\text{Ge}_{1-x-y}\text{S}_{x}\text{Se}_{y}$ |                   |            |                |            |
| Ge–Se                             | $\text{GeSe}_{2}$ tetrahedra | 115; 150 | 72,73,74 | 147; 367; 388 | 75,76 |
| CS $\text{GeSe}_{2}$ tetrahedra   | 343; 425           | 70,72,76  | 343            | 75         |
| ETH $\text{GeSe}_{2}$ tetrahedra  | 370; 437           | 70,73,76  | 437            | 75         |
| S–S                               | $\text{Se–Se}$ bridge between $\text{GeSe}_{2}$ tetrahedra | 265 | 14 | –              | –          |
| $\text{Ge}_{1-x-y}\text{S}_{x}\text{Te}_{y}$ |                   |            |                |            |
| Ge–Se                             | $\text{GeTe}_{2}$ tetrahedra | –         | 150; 220 | 86         |
| Se–Te                             | $\text{Se–Te}$ bridge between $\text{GeSe}_{2}$ tetrahedra | 200 | 22,88 | –              | –          |
| Te–Te                             | $\text{Te}$ chains | 150 | 89 | –              | –          |
| $\text{Ge}_{1-x-y}\text{Sb}_{x}\text{Te}_{y}$ |                   |            |                |            |
| Sb–Se                             | $\text{SbSe}_{2}$ pyramids | 190 | 14 | 180; 200; 250 | 32,77 |
| Sb–S                              | $\text{SbSe}_{2}$ pyramids | 190 | 14 | 180; 200; 250 | 32,77 |
| Sb–S                              | ETH $\text{SbS}_{2}$ units | 159 | 14 | 156         | 79         |
| Ge–S                              | ETH $\text{SbS}_{2}$ units | 159 | 14 | 156         | 79         |
| Ge–S                              | ETH $\text{SbS}_{2}$ units | 159 | 14 | 156         | 79         |
| Ge–S                              | ETH $\text{SbS}_{2}$ units | 159 | 14 | 156         | 79         |
| Se–S                              | $\text{Se–Se}$ bridge between $\text{GeSe}_{2}$ tetrahedra | 200 | 22,88 | –              | –          |
| Te–Te                             | $\text{Te}$ chains | 150 | 89 | –              | –          |
| $\text{Ge}_{1-x-y}\text{S}_{x}\text{Se}_{y}$ |                   |            |                |            |
| Ge–Se                             | $\text{GeSe}_{2}$ tetrahedra or Ge–Te tetrahedral motifs | 120 | 87 | –              | –          |
| Se–Te                             | $\text{Se–Se}$ bridge between $\text{GeSe}_{2}$ tetrahedra | 200 | 22,88 | –              | –          |
| Te–Te                             | $\text{Te}$ chains | 150 | 89 | –              | –          |
| $\text{Ge}_{1-x-y}\text{S}_{x}\text{Se}_{y}$ |                   |            |                |            |
| $\text{Ge}_{1-x-y}\text{Sb}_{x}\text{Se}_{y}$ |                   |            |                |            |
| Sb–S                              | $\text{SbSe}_{2}$ pyramids | 145 | 92 | –              | –          |
| Sb–S                              | $\text{SbSe}_{2}$ pyramids | 145 | 92 | –              | –          |
| Si substrate                      | $\text{Si–Si}$ c–Si modes | 300; 520 | 93 | –              | –          |
bonds involving the chalcogen elements. Upon introduction of Sb in the \([\text{Ge}_{30}\text{Se}_{70}]_{1-x}[\text{Ge}_{52}\text{Te}_{48}]_x\) films, whereas the contribution of Sb–Se bonds to the Raman spectra is weak their presence in IR absorption is more visible in FTIR spectra probably thanks to the high IR cross section of such bonds compared with others. Sb doping of the \(\text{Ge}_{43}\text{Se}_{29}\text{Te}_{28}\) compound lead to formation of Sb-Sb homopolar bonds and probably Ge–Sb wrong bonds as already discussed above for Sb-doped \(\text{Ge}_{30}\text{Se}_{70}\) films. As a result, \([\text{Ge}_{30}\text{Se}_{70}]_{1-x-y}[\text{Ge}_{52}\text{Te}_{48}]_x\text{Sb}_y\) films obtained by co-sputtering appear to be a highly disordered system. It can be depicted as a mix of Ge–GeTe\(_3\) and GeSb\(_{4-m-n}\)SemE\(_n\) tetrahedra (with \(m + n = \{0, 1, 2, 3, 4\}\)) as well as SbGe\(_{3-m-n}\)SemE\(_n\) motifs (with \(m + n = \{0, 1, 2, 3\}\)). The relative fraction between these motifs varies as a function of the Ge/Se/Te atomic ratio of the films.

To conclude, the effect of Sb incorporation in the amorphous structure of \([\text{Ge}_{37}\text{Se}_{63}]_{1-x}[\text{Ge}_{30}\text{Se}_{70}]_x\) and \([\text{Ge}_{30}\text{Se}_{70}]_{1-x}[\text{Ge}_{52}\text{Te}_{48}]_x\) thin films is different depending on the nature of the chalcogen elements present in the film. A clear difference is observed between films containing S/Se compared with Se/Te as chalcogen elements. In particular, this is evidenced by formation of GeSb\(_{4-m-n}\)SemE\(_n\) tetrahedra (with \(m + n = \{0, 1, 2, 3, 4\}\) as well

Figure 2. FTIR and Raman spectra of as-deposited (a) Ge\(_{1-x}\)Se\(_{x}\) (b) Ge\(_{1-x}\)S\(_{x}\) and (c) \([\text{Ge}_{30}\text{Se}_{70}]_{1-x}[\text{Ge}_{52}\text{Te}_{48}]_x\) thin films. The different contribution of vibration modes related to GeSe\(_2\) and GeS\(_2\) amorphous phases are indicated by orange and green dash-lines, respectively. The contribution of the c-Si substrate to the Raman signal appearing on some spectra is also indicated by a red dash-line at 300 cm\(^{-1}\) as well as a shoulder visible after 450 cm\(^{-1}\) that corresponds to a c-Si phonon mode near 520 cm\(^{-1}\).
as SbGe_{3,m-n}Se_{m}Te_{n} motifs (with m + n = {0, 1, 2, 3}) in Sb-doped \([Ge_{30}Se_{70}]_{1-x}Sbx\), \([Ge_{37}S_{63}]_{1-x}Sbx\) and \([Ge_{37}S_{63}]_{1-x}–y[Ge_{30}Se_{70}]_{x}Sby\) thin films whereas no such mixed Ge tetrahedra nor mixed Sb pyramids can be observed in \([Ge_{37}S_{63}]_{1-x}Sbx\) compounds doped with Sb. Besides, in both case Sb addition \([Ge_{37}S_{63}]_{1-x}Sbx\) and \([Ge_{37}S_{63}]_{1-x}–y[Ge_{30}Se_{70}]_{x}Sby\) films does not lead to a random and homogeneous distribution of the chalcogen atoms in Ge-centered tetrahedra as observed in Ge-based chalcogenide films. From all the above FTIR and Raman study, one can conclude that the local order and the structure of the (co-)sputtered chalcogenide thin films are shown to largely vary with in particular a very different amount of homopolar bonds and the latter is shown to depend on thin films’ atomic composition. Since the properties of materials being intimately linked to their structure, probing the link between structure and optical properties is an invaluable clue in order to propose design rules aiming at fabricating chalcogenide compounds thin films with optimized properties for the applications in photonics. In the following, the linear and nonlinear optical constants of the films, such as the real and imaginary part of refractive index as well as Kerr nonlinear refractive index, are studied.

Figure 3. FTIR and Raman spectra of (a) \([Ge_{30}Se_{70}]_{1-x}Sbx\), (b) \([Ge_{37}S_{63}]_{1-x}Sbx\), and (c) \([Ge_{37}S_{63}]_{1-x}–y[Ge_{30}Se_{70}]_{x}Sby\) thin films. The position of the main vibration modes related to GeSe_{2} and GeS_{2} stoichiometric glasses are indicated by orange and green dash-lines, respectively. The contribution of the c-Si substrate to the Raman signal appearing on some spectra is also indicated by a red dash-line at 300 cm^{-1} as well as a shoulder visible after 450 cm^{-1} that corresponds to a c-Si phonon mode near 520 cm^{-1}.
Optical properties of the chalcogenide thin films. Linear optical constants. The optical constants (refractive index n and extinction coefficient k) of the films were deduced from the spectroscopic ellipsometry measurements from visible to near-IR (NIR) range (see "Methods"). The refractive indices n and Tauc’s plots of (α.E)1/2 vs energy (eV) obtained from the extinction coefficient k (see "Methods") are plotted in Figs. 5, 6, 7 for each composition of the chalcogenide films. First, Figs. 5, 6, 7 call for a general comment. For wavelength range located above inter band absorption range, which corresponds to energies lower than the bandgap energy (see the Tauc’s plots of Figs. 5, 6, 7), the refractive indices tend progressively to a kind of plateau. The latter gives therefore an estimation of the refractive indices in the MIR range up to multi-phonons absorption appearing at significantly higher wavelengths than NIR45,46. Therefore, the study of optical properties in the visible-NIR range is the best compromise in order to get an estimation of refractive indices from visible to MIR range as well as giving an estimation of the optical band gap energy from absorption measurements or ellipsometry data fitting models (see "Methods" and Sect. 4 of the Supplementary Information).
In Fig. 5a, the refractive index of the sputtered Ge$_{1-x}$Se$_x$ (0.63 < x < 0.74) thin films in the NIR range (above 850 nm) does not evolve linearly with composition but reaches a maximum for x = 0.63 as well as a minimum for x = 0.7. This effect can be related to the amorphous structure of Ge$_{37}$Se$_{63}$ film which exhibits the highest amount of Ge–Ge homopolar bonds in ethane-like structures among all Ge$_{1-x}$Se$_x$ (0.63 < x < 0.74) films (see the Raman of Fig. 2a). Besides, ab initio molecular dynamics simulations reported that the presence of numerous distorted Se–Ge–Se angles in Ge$_{1-x}$Se$_x$ (0.60 < x < 0.66) permits to reduce the stress induced by the increase of the Ge content and thus the mean atomic coordination number or network connectivity$^{47}$. By opposite, the Ge$_{30}$Se$_{70}$ film which has the lowest refractive index also presents the lowest amount of Ge–Ge and Se–Se homopolars and the narrowest and most well-defined modes corresponding to CS and ES GeSe$_{4/2}$ tetrahedra (195 and 212 cm$^{-1}$) as shown in Fig. 2a. This trend on the refractive index is in good agreement with previous literature for bulk glasses in which compositions with the highest Ge–Se/(Ge–Ge + Se–Se) bonding ratio exhibited the lowest refractive indices$^{26}$. The absorption of Ge$_{30}$Se$_{70}$...
film evidences its highest band gap value among all Ge$_{1-x}$Se$_x$ (0.63 < x < 0.74) films as seen on the Tauc's plots of Fig. 5a. Besides, the Ge$_{30}$Se$_{70}$ composition with the highest refractive index has the lowest band gap energy. The decreasing number of Ge–Ge bonds may be at origin of the strong increase of absorption between Ge$_{30}$Se$_{70}$ and Ge$_{37}$Se$_{63}$ films.

Ge$_{1-x}$S$_x$ thin films experience a significant increase of their refractive index in the NIR as the Ge fraction is slightly increased from x = 0.64 to x = 0.60 (Fig. 5b). This trend is consistent with previous literature studies. This could be attributed to an increasing number of distorted S–Ge–S bonds similarly to the previously mentioned presence of numerous distorted Se–Ge–Se angles in Ge$_{30}$Se$_{70}$ (0.60 < x < 0.66) related to the increase of the number of Ge–Ge homopolar bonds (see Fig. 2b) with the decrease of the S content. This leads to a reduction of the band gap energy in agreement with previous literature due to creation of new electronic states under the conduction band explaining the progressive shift of absorption toward lower energy (Fig. 5b). The absorption and refractive index change monotonously as x increases in our Ge$_{1-x}$S$_x$ films (Fig. 5b).

Figure 6. Refractive index n and Tauc's plots of (a) [Ge$_{30}$Se$_{70}$]$_{1-x}$S$_x$, (b) [Ge$_{27}$S$_{63}$]$_{1-x}$S$_x$, and (c) [Ge$_{27}$S$_{63}$]$_{1-x}$–y[Ge$_{30}$Se$_{70}$]$_x$S$_{by}$ thin films deposited by (co-)sputtering.
The refractive index of the \([\text{Ge}_{40}\text{S}_{60}]_{1-x}[\text{Ge}_{26}\text{Se}_{74}]_x\) films also exhibits a minimum for the \(\text{Ge}_{33}\text{S}_{37}\text{Se}_{30}\) composition (Fig. 5c). This is not surprising since, similarly to \(\text{Ge}_{1-x}\text{Se}_x\) and \(\text{Ge}_{1-x}\text{S}_x\) films, the amount of Ge–Ge homopolar bonds is expected to be minimum for this near-stoichiometric composition with a Ge/(S + Se) atomic ratio close to 1/2 (Fig. 2c). As a result, the general trends on refractive indices of studied Ge-based chalcogenide films are driven by the ratio between heteropolar and homopolar bonds.

Among the \([\text{Ge}_{40}\text{S}_{60}]_{1-x}[\text{Ge}_{26}\text{Se}_{74}]_x\) thin films, the band gap energy reaches a maximum for the \(\text{Ge}_{33}\text{S}_{37}\text{Se}_{30}\) composition as evidenced by the absorption curves in Fig. 5c. This results from the composition of \(\text{Ge}_{33}\text{S}_{37}\text{Se}_{30}\) film which is close to the GeCh2 stoichiometric compound (with Ch referring to S or Se chalcogen element) expected to exhibit almost no homopolar bonds. Note that for a same Ge concentration, replacing S by Se atoms results in a progressive decrease of band gap energy\(^{31}\).

The refractive index of the \([\text{Ge}_{40}\text{S}_{60}]_{1-x}[\text{Ge}_{26}\text{Se}_{74}]_x\) films also exhibits a minimum for the \(\text{Ge}_{23}\text{S}_{77}\) composition (Fig. 5c). This is not surprising since, similarly to \(\text{Ge}_{1-x}\text{Se}_x\) and \(\text{Ge}_{1-x}\text{S}_x\) films, the amount of Ge–Ge homopolar bonds is expected to be minimum for this near-stoichiometric composition with a Ge/(S + Se) atomic ratio close to 1/2 (Fig. 2c). As a result, the general trends on refractive indices of studied Ge-based chalcogenide films are driven by the ratio between heteropolar and homopolar bonds.

Among the \([\text{Ge}_{40}\text{S}_{60}]_{1-x}[\text{Ge}_{26}\text{Se}_{74}]_x\) thin films, the band gap energy reaches a maximum for the \(\text{Ge}_{33}\text{S}_{37}\text{Se}_{30}\) composition as evidenced by the absorption curves in Fig. 5c. This results from the composition of \(\text{Ge}_{33}\text{S}_{37}\text{Se}_{30}\) film which is close to the GeCh2 stoichiometric compound (with Ch referring to S or Se chalcogen element) expected to exhibit almost no homopolar bonds. Note that for a same Ge concentration, replacing S by Se atoms results in a progressive decrease of band gap energy\(^{31}\).
In Fig. 6, replacing tetravalent Ge atoms, as observed in structural motifs of stoichiometric GeSe₂ glass, by trivalent Sb atoms, as found in amorphous stoichiometric Sb₂Se₃ compound, within the Ge₅₆Se₄₄ films increases the non-chalcogen/chalcogen ratio required to keep the stoichiometric composition. This has been clearly evidenced for composition tie-lines crossing the stoichiometric Ge₅₆Se₄₄/Sb₂Se₃ pseudo-binary tie-line as Ge₅₆Sb₄Se₄₀, Ge₅₆Sb₆Se₃₈, Ge₅₆Sb₈Se₃₆, or Ge₅₆Sb₁₀Se₃₄ glasses. These compositions are again those with the smallest amount of homopolar bonds and corresponding to a limit of topological phase transition as reported in GeₓSb₁₀Se₉₀ glasses. Besides, in bulk glasses as well as in thin films, the decrease of the Ge₅₆Sb₄Se₄₀ ratio was shown to result in an increase of the refractive index and a decrease of the band gap energy since electronic polarizability of Sb–Se bonds is much higher than that of Ge–Se bonds.

In Fig. 6, are shown the change of optical constants upon Sb addition by means of co-sputtering in the Ge₅₆Sb₄Se₄₀, Ge₅₆Sb₆Se₃₈, and Ge₅₆Sb₈Se₃₆ thin films in order to increase films’ refractive indices by drifting away from compositions located on the Ge₇₄Sb₁₈Se₆₁ pseudo-binary tie-line. In Figs. 6a-c the incorporation of Sb in Ge₅₆Sb₄Se₄₀, Ge₅₆Sb₆Se₃₈, and Ge₅₆Sb₈Se₃₆ films significantly increases films’ refractive index and at the same time reducing the optical band gap energy of the material. This effect is attributed to the higher electronic polarizability of Sb atoms in particular when forming Sb–Ch bonds or Sb–Sb bonds. These highly polarizable bonds are revealed to appear in an increasing level as the incorporated Sb amount is increased in films (see amorphous structure analysis detailed in the Amorphous Structure section and in the Supplementary Information). One can also note that among all these compositions, some films exhibit compositions very close to that of well-studied commercial glasses such as for instance AMTIR-3 glass (also commercially called IGS-5 or IRG-5 or BD-2 or OPTIR-3) of Ge₅₆Sb₁₀Se₉₀ composition. Thus, this well-known glass is close to the Ge₅₆Sb₁₀Se₉₀ film of the present study and can be used as a point of comparison. In Fig. 6a, the optical constant values of our [Ge₅₆Sb₄Se₄₀] thin films are in good agreement with the literature.

In Fig. 7a, the increase of absorption of [Ge₅₆Sb₄Se₄₀] films upon increasing x can be related to the smallest bandgap of a-GeTe compared to that of Se-based compound. The absorption progressively decreases as the band gap of the film increases upon moving toward the Ge₇₄Sb₁₈Se₆₁ composition. By opposite, in Fig. 7b,c for [Ge₅₆Sb₄Se₄₀] films, a more complex trend is observed. First, in Fig. 7b an increase of the (Sb + Te)/Se ratio in [Ge₅₆Sb₄Se₄₀] films leads to a shift of the absorption curve toward lower energy due to a decrease of band gap energy. More surprising, in Fig. 7c the absorption curves and optical band gap of [Ge₅₆Sb₄Se₄₀] films remain almost constant for the three compounds containing Sb concentration ranging from 15 to 30 at.%. Increasing the concentration of homopolar bonds, mainly Sb-Sb bonds, and Te-related bonds due to an increase of the (Sb + Te)/Se ratio in [Ge₅₆Sb₄Se₄₀] films result in an increase of band tails as well as creation of electronic states in the bandgap, and hence to a reduction of the optical bandgap energy.

However, in Fig. 7c upon incorporation of Sb in the ternary Ge₁₋₂ₖSbxTeₙ compound, the refractive index of the films significantly increases while the decrease in bandgap energy is negligible. The incorporation of Sb is related to the changes in the amorphous structure. First, the increasing concentration of Sb leads to an increase of the material polarizability and thus that of the refractive index. However, at the same time the amount of Te–Ge heteropolars bonds decreases leading to an increase of band gap energy of the material hence counterbalancing the effect of Sb. Therefore in [Ge₁₋₂ₖSbxTeₙ] films, the incorporation of highly polarizable Sb bonds leads to an increase of the refractive index but does not significantly affect the optical band gap energy value. Indeed, the replacement of Ge–Te homopolars by Sb–Sb bonds upon Sb introduction is expected to impact mostly the density and nature of localized electronic defect states in the material band gap but with no or limited effect on the bandgap energy.

To summarize, the observed trend of refractive indices as a function of chalcogenide thin films’ compositions can be reasonably correlated to changes in films’ amorphous structure as extensively described in the FTIR/Raman experiments of the Amorphous Structure section and in Sect. 3 of the Supplementary Information. The electronic polarizability of local chemical environments and bonding configurations in the amorphous is shown to play key role aiming at controlling the refractive indices of the films. In particular, introduction of highly polarizable bonds such as Sb–Sb homopolars, Sb–Ch (with Ch = Te or Se) or Te–X (with X = Sb or Ge) in a less extent amount of homopolar bonds and corresponding to a limit of topological phase transition as reported in GeₓSb₁₀Se₉₀ glasses. Besides, in bulk glasses as well as in thin films, the decrease of the Ge₅₆Sb₄Se₄₀ ratio was shown to result in an increase of the refractive index and a decrease of the band gap energy since electronic polarizability of Sb–Se bonds is much higher than that of Ge–Se bonds.

In order to evaluate the potential interest for applications of such chalcogenide thin films in the emerging field of on-chip nonlinear photonics, determining the Kerr refractive indices, which quantify the nonlinear frequency conversion efficiencies, can give a first interesting insight. For that purpose, in the following the Kerr
refractive indices of the films are estimated by means of their linear optical constants as well as using estimated values of the band gap energy.

**Kerr nonlinear refractive indices $n_2$.** The $n_2$ Kerr nonlinear refractive indices were evaluated mainly using the Sheik–Bahae model. We considered this model as enough accurate in order to get qualitative trends on $n_2$ values (see Sect. 5 of the Supplementary Information). It has to be emphasized that a systematic error of about 20% exists in the experimental determination of non-linear optical coefficients.

The $n_2$ Kerr nonlinear refractive index is strongly correlated with the linear refractive index and the optical band gap energy value. Using the Sheik–Bahae model, the maximum of the third order nonlinear parameter is found for an energy close to $0.534 \times E_g^{opt}$. Therefore, the values of $n_2$ can vary considerably depending on the wavelength and must be taken into consideration depending on the value of the wavelength that will be used in the application. However, previous experimental work reported a maximum of Kerr index for photon energy values higher than that corresponding to $0.534 \times E_g^{opt}$. Table 2 shows the maximum values of the $n_2$ Kerr refractive indices for all the films studied in this work and their corresponding wavelengths, as well as the values obtained at 1,550 nm, the standard wavelength for telecommunications. In order to validate the Sheik–Bahae model, this method was also applied to samples of silica and silicon nitride thin film. The $n_2$ values at 1,550 nm for these two reference materials have been calculated to be $3 \times 10^{-20}$ and $2 \times 10^{-19}$ m$^2$/W, respectively. These values are in excellent agreement with those experimentally measured in the literature. Therefore, one can conclude that in our (co-)sputtered amorphous chalcogenide thin films, the Kerr indices are of two to three orders of magnitude higher than those obtained for silica or silicon nitride materials. These values are also in excellent agreement with previous experimental results reported for similar Ge$_{1-x-y}$Sb$_x$Se$_y$, Ge$_{1-x-y}$Sb$_x$S$_y$ compounds, as well as those deduced using the Sheik–Bahae model for Ge$_{1-x}$S$_x$ and Ge$_{1-x}$Sb$_x$Se$_y$ glasses.

For some of the chalcogenide thin films, the Sheik–Bahae model gives negative Kerr indices at 1,550 nm. In previous works, only positive experimental $n_2$ values were observed in the transparency window of chalcogenide glasses. Nevertheless, negative Kerr indices values were reported in Ge$_{1-x-y}$Sb$_x$Se$_y$ glasses at 800 nm where absorption starts to be non-negligible. Therefore, we can emphasize that the negative Kerr indices values at 1.55 µm (~0.8 eV) are found for co-sputtered films for which the optical band gap energy is below 1.6 eV and as a result when TPA becomes significant.

In literature, $n_2$ values have been related to the amorphous structure. In particular, a clear correlation was found between $n_2$ values and the concentration of highly polarizable heteropolar bonds. Herein, one observe a clear correlation between material polarizability, which is proportional to the linear refractive index, and the nonlinearities evidenced by the $n_2$ values calculated by using the Sheik-Bahae model. Thus, one can relate the enhancement of electronic polarizability and the resulting increase of $n_2$ values to presence of peculiar local atomic motifs and bonding configurations found in the amorphous structure of films. For instance, the amount of homopolar bonds play a key role in the increase of linear and nonlinear refractive indices as described above.

Finally, in Table 2 are also reported for each films the limit of temperature after which a degradation of the material could be observed by monitoring optical reflectivity at 670 nm upon annealing (see “Methods” and Sect. 2 of the Supplementary Information). This is also very instructive since temperature limit in between 250 and 400 °C were obtained. This emphasizes that a compromise between optical properties and thermal stability has to be found for selection of a particular composition depending on final application as well as taking into account the thermal budget required for integration process flow in devices. Indeed, an annealing after deposition is also expected to significantly affect the optical properties of these Ge-based amorphous chalcogenide thin films due to the structural relaxation. Thus, aging of these metastable amorphous materials will have to be studied in the future aiming at ensuring durability of MIR components that would integrate some of these compounds.

**Conclusion**

To conclude, industrial co-sputtering deposition method is a powerful tool in order to fastly study a wide compositions range of amorphous chalcogenide thin films aiming at ultimately achieving highly nonlinear on-chip MIR components. By means of a systematic study of the amorphous structure correlated with the trend on optical properties (linear optical constants, optical band gap and Kerr nonlinear refractive index) of the as-deposited chalcogenide thin films one can get invaluable clues in order to optimize the materials optical properties towards future applications. The materials’ polarizability and thus linear and nonlinear refractive indices increase significantly when moving from light to heavier chalcogen element such as S to Se and toward Te-based chalcogenide compounds but accompanied with a decrease of the thermal stability. The ratio of homopolar/wrong on heteropolar bonds in the amorphous chalcogenide is shown to play a main role on the electronic and thus optical properties of the films. For instance, the introduction of Sb atoms deeply modifies the amorphous structure as well as introducing Sb–Sb homopolar bonds. As a result, the electronic polarizability of the glass is significantly enhanced as evidenced by the significant increase of the material refractive indices. However, this also leads to a detrimental decrease of the material’s thermal stability and bandgap. Moreover, we show that the outstanding and state-of-the-art Kerr refractive indices in the MIR range are found for chalcogenide thin films deposited by means of industrial sputtering technique enabling fast transfer to applications. Finally, we demonstrate that a good trade-off between high nonlinearity, good thermal stability and optimized working wavelength in the IR can be found opening wide range of opportunities for future on-chip photonic applications fully compatible with CMOS large-scale integration technologies.
| Groups          | Co-sputtered Targets | Compositions | $E_g^{\text{opt}}$ (eV) | $E_g^{\text{cl}}$ (eV) | $n$ | $n_2$ (10^{-18} m²·W⁻¹) | $n_2^{\text{max}}$ (10^{-18} m²·W⁻¹) | Limit of thermal stability (°C) |
|----------------|----------------------|--------------|-------------------------|------------------------|-----|--------------------------|---------------------------------|-----------------------------|
| [Ge₃₀Se₇₀]₁ₓSbₓ |                      | Ge₂₉Sb₃₅S₅₄ | 1.94                    | 1.61                   | 2.53 | 8.3                      | 19.5 (λ = 1200 nm)              | 300                          |
|                |                      | Ge₂₅Sb₈₀S₅₁ | 1.76                    | 1.46                   | 2.67 | 13.6                     | 25.9 (λ = 1320 nm)              | 300                          |
|                |                      | Ge₂₇Sb₅₄S₄₈ | 1.61                    | 1.34                   | 2.79 | 25.2                     | 33.9 (λ = 1450 nm)              | 300                          |
| Ge₁₋ₓSₓ        |                      | Ge₃₈S₆₄     | 2.82                    | 2.46                   | 2.12 | 1.8                      | 6.1 (λ = 820 nm)               | 400                          |
|                |                      | Ge₃₈S₆₂     | 2.7                    | 2.37                   | 2.19 | 2.1                      | 6.8 (λ = 860 nm)               | 400                          |
|                |                      | Ge₄₀S₅₀     | 2.39                    | 1.98                   | 2.29 | 3.4                      | 10.2 (λ = 970 nm)              | 400                          |
| Ge₁₋ₓSₓSₓSe₀₋₇₀ |                      | Ge₃₈S₅₂S₄₀ | 2.43                    | 2.03                   | 2.27 | 3.2                      | 9.7 (λ = 960 nm)               | 400                          |
|                |                      | Ge₃₈S₅₀S₃₀ | 2.57                    | 2.3                    | 2.24 | 2.5                      | 8.0 (λ = 900 nm)               | 400                          |
|                |                      | Ge₃₈S₄₈S₄₀ | 2.5                    | 2.26                   | 2.26 | 2.8                      | 8.7 (λ = 930 nm)               | 400                          |
| Ge₁₋ₓSₓSe₀₋₇₀  |                      | Ge₃₈S₅₈S₅₇ | 2.35                    | 2.15                   | 2.33 | 3.6                      | 10.5 (λ = 990 nm)              | 400                          |
|                |                      | Ge₃₈Se₇₄     | 2.22                    | 2.11                   | 2.42 | 4.4                      | 12.3 (λ = 1050 nm)             | 300                          |
|                |                      | Ge₃₈Se₇₀     | 2.29                    | 2.19                   | 2.39 | 3.8                      | 11.1 (λ = 1010 nm)             | 350                          |
| Ge₁₋ₓSₓSe₀₋₇₀  |                      | Ge₃₈Se₆₆     | 2.13                    | 2.05                   | 2.42 | 5.3                      | 14.4 (λ = 1090 nm)             | 350                          |
|                |                      | Ge₃₈Se₆₃     | 1.88                    | 1.64                   | 2.55 | 9.9                      | 21.8 (λ = 1240 nm)             | 350                          |
| [Ge₃₇Se₅₀]₁₋ₓSbₓ |                      | Ge₃₈Se₆₀Te₆ | 2.01                    | 1.71                   | 2.48 | 7.1                      | 17.6 (λ = 1160 nm)             | 400                          |
|                |                      | Ge₃₈Se₅₀Te₁₃ | 1.73                    | 1.46                   | 2.67 | 15.2                     | 27.7 (λ = 1350 nm)             | 300                          |
| Ge₁₋ₓSₓSe₀₋₇₀  |                      | Ge₄₀Se₅₉Te₂₁ | 1.47                    | 1.26                   | 2.92 | 43.7                     | 44.4 (λ = 1580 nm)             | 300                          |
|                |                      | Ge₄₀Se₅₉Te₂₃ | 1.23                    | 1.12                   | 3.21 | 19.4                     | 75.7 (λ = 1890 nm)             | 250                          |
| [Ge₃₇Se₅₀]₁₋ₓSbₓ |                      | Ge₃₈Se₅₈Te₅ | 1.54                    | 1.29                   | 2.94 | 35.6                     | 36.6 (λ = 1510 nm)             | 250                          |
|                |                      | Ge₃₈Se₅₈Te₁₁ | 1.3                    | 1.14                   | 3.28 | 30.1                     | 58.6 (λ = 1790 nm)             | 250                          |
| Ge₁₋ₓSₓSe₀₋₇₀  |                      | Ge₃₈Se₅₈Te₁₅ | 1.13                    | 0.97                   | 3.6  | -10.2                    | 85.7 (λ = 2060 nm)             | 250                          |
|                |                      | Ge₃₈Se₅₈Te₂₄ | 1.12                    | 0.95                   | 3.6  | -13.7                    | 88.7 (λ = 2080 nm)             | 250                          |
| Ge₁₋ₓSₓSe₀₋₇₀  |                      | Ge₃₈Se₅₈Te₂₃ | 1.09                    | 0.93                   | 3.6  | -26.0                    | 95.0 (λ = 2140 nm)             | 250                          |
|                |                      | Ge₃₈Se₅₈Te₂₁ | 1.06                    | 0.92                   | 3.8  | -35.1                    | 98.9 (λ = 2190 nm)             | 250                          |
| [Ge₃₇Se₅₀]₁₋ₓSbₓ |                      | Ge₃₈Se₅₈Se₆ | 1.77                    | 1.54                   | 2.77 | 12.2                     | 23.5 (λ = 1320 nm)             | 300                          |
|                |                      | Ge₃₈Se₅₈Se₅₅ | 1.44                    | 1.27                   | 3.03 | 42.5                     | 45.4 (λ = 1620 nm)             | 250                          |
| Ge₁₋ₓSₓSe₀₋₇₀  |                      | Ge₂₃Sb₅₀Se₄₀ | 1.2                    | 1.03                   | 3.3  | 11.7                     | 78.8 (λ = 1930 nm)             | 250                          |
| [Ge₂₉Se₃₃]₁₋ₓSbₓ |                      | Ge₃₈Se₅₈Se₂₆ | 2.02                    | 1.79                   | 2.53 | 6.7                      | 16.6 (λ = 1150 nm)             | 300                          |
|                |                      | Ge₃₈Se₅₈Se₂₅ | 1.82                    | 1.59                   | 2.67 | 10.7                     | 22.4 (λ = 1270 nm)             | 300                          |
| Ge₁₋ₓSₓSe₀₋₇₀  |                      | Ge₂₉Sb₂₉Se₂₃ | 1.61                    | 1.46                   | 2.83 | 24.7                     | 33.1 (λ = 1450 nm)             | 250                          |
|                |                      | Ge₂₉Sb₂₉Se₂₁ | 1.42                    | 1.37                   | 2.96 | 45.3                     | 50.6 (λ = 1640 nm)             | 250                          |
| SiNₓ |                      | SiNₓ | 4.85 | 2.07 | 0.2 | 0.8 (λ = 480 nm) | >>400 |

Table 2. Summary of chalcogenide thin films obtained by (co-)sputtering deposition: composition, nature of the sputtering targets used for (co-)sputtering deposition, refractive index at 1.55 µm, band gap energy $E_g^{\text{opt}}$ and $E_g^{\text{cl}}$, $n_2$ Kerr nonlinear refractive index calculated either by means of the Sheik-Bahae model at 1.55 µm ($n_2$) and maximal $n_2$ values ($n_2^{\text{max}}$) at energy near 0.534×$E_g^{\text{opt}}$ eV (the corresponding wavelength value is also indicated into brackets) and a first evaluation of the limit temperature for material’s stability (see text for details as well as “Methods” and Sect. 2 of the Supplementary Information).

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**Author contributions**
PN. conceptualized and managed the project with help of C.S., B.C. and J.-B. J.-B. D. performed all experiments and treated all experimental data under supervision of P.N. and B.C. J.-B. D., C. C.-C., C.S., M.T. and M.B. prepared all the thin film samples in LETI clean rooms. J.-M. F. supported J.-B. D. for the supervision of the technological lots in LETI 200 mm technological platform. J.-B. D. performed spectroscopic ellipsometry data modelling under supervision of P.N., B.C. and A.C. J.-B.D. performed all Raman and FTIR experiments with invaluable help of A.V. The paper was written by J.-B. D. and P.N. with help of B.C. and A.V. All authors have given their approval to the final version of the manuscript.

**Competing interests**
The authors declare no competing interests.

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Correspondence and requests for materials should be addressed to P.N.

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