# Chalcogenide photonics

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The unique and striking material properties of chalcogenide glasses have been studied for decades, providing applications in the electronics industry, imaging and more recently in photonics. This Review summarizes progress in photonic devices that exploit the unique optical properties of chalcogenide glasses for a range of important applications, focusing on recent examples in mid-infrared sensing, integrated optics and ultrahigh-bandwidth signal processing.

halcogenide glasses (ChGs) are an important class of amorphous semiconductors used in phase-change memories, solar cells, sensors and photonics. ChGs contain as a major constituent one or more of the chalcogen elements from group 6a of the periodic table (sulphur, selenium and tellurium, but excluding oxygen), covalently bonded to network formers such as As, Ge, Sb, Ga, Si or P. The existence of a broad range of possible glassforming systems with large composition space and good resistance to crystallization yields glasses with optical properties such as nonlinearity, photosensitivity and infrared transparency, which can all be optimized for photonic applications.

#### **Basic material properties**

Research into the optical properties of ChGs started around sixty years ago<sup>1,2</sup>. ChGs are comprised of covalently bonded heavy elements, and this gives them some unique properties for infrared, nonlinear and waveguide optics. Because their inter-atomic bonds are weak relative to those in oxides, the bandgap of ChGs is redshifted to the visible or near-infrared region of the spectrum. The vibrational energies of the bonds are low because the constituent atoms are particularly heavy. This means that ChGs are transparent into the mid-infrared and, as a consequence, their low phonon energies make them interesting hosts for rare-earth dopants<sup>3,4</sup>. Typically, sulphides transmit to ~11 μm, selenides to ~15 μm and tellurides to beyond 20 µm. However, physical attributes such as the glass transition temperature  $(T_g)$ , glass hardness, strength and durability generally deteriorate with weaker bonding and therefore decrease with long-wave transparency. A low value of  $T_g$ means that precision glass moulding becomes a viable approach for fabricating low-cost optical components for applications such as thermal imaging<sup>2,5</sup>. Glass densities are also high relative to oxide glasses and, when combined with strong polarizability, this leads to a high refractive index of  $n \approx 2-3$ . A high linear refractive index implies, according to the empirical Miller's rule<sup>6</sup>, a high nonlinear refractive index,  $n_2$ . This has been confirmed by measurements<sup>7-9</sup> that reveal ultrafast third-order (Kerr) nonlinearities up to a thousand times that of silica, making chalcogenides attractive for alloptical signal processing10.

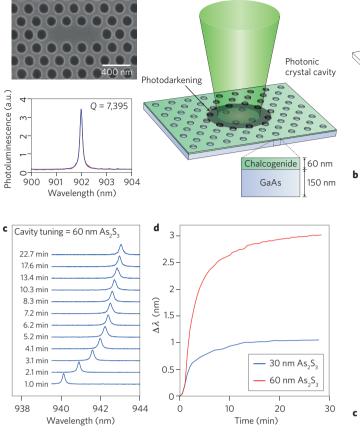
The structure of ChGs on the atomic scale is best described as a continuous random network, for which an important parameter is the mean coordination number (MCN) — the sum of the products of the individual abundance times the valency of the constituent atoms. For common binary chalcogenides such as arsenic triselenide ( $As_2Se_3$ ), the  $As_2Se_3$  network is locally two-dimensional

with weak van der Waals bonding between the layers. The addition of fourfold-coordinated atoms such as germanium makes the network three-dimensional by creating bonds between layers, increasing network rigidity,  $T_{\rm g}$ , strength and hardness. Covalent bonding leads to a high degree of short-range order, providing well-defined nearest neighbours, bond lengths and bond angles. The relationships between the MCN, network topology and the physical properties of these glasses have been explored by many authors; notably Phillips<sup>11</sup>, Thorpe et al. 12, Tanaka<sup>13</sup> and Boolchand et al. 14. Thorpe et al. 12 showed the existence of a phase transition at MCN = 2.4, providing a percolation threshold between an under-constrained 'floppy' network to an over-constrained 'rigid' phase. Tanaka<sup>13</sup> found that a second phase transition exists at MCN = 2.67, which represents a topological change from a twoto a three-dimensional 'stressed rigid' phase. Boolchand et al.14 suggested the existence of an 'intermediate' phase, representing a self-organized network characterized by zero non-reversing heat flow in measurements using temperature-modulated differential scanning calorimetry. These models are increasingly supported by experimental evidence. An example is the exceptionally large glass-forming range of the Ge-As-Se glass system, in which transitions have been observed in the material density, elastic moduli, index of refraction and bandgap<sup>11-13,15</sup>.

If atoms in a continuous random network have fewer or greater numbers of chemical bonds than expected from their valence, then the network will contain coordination defects<sup>16</sup>. The relatively high bond energy and delocalization of the valence and conduction band wavefunctions mean that these defects can exist as pairs with opposite electrical charge — one atom being over-coordinated and the other under-coordinated. These charged defects are 'frozen in' during glass production and are physically separated throughout the glass; if the charges were too close, they would annihilate and change the local chemical bonding. Such defects give rise to 'tail states' in the bandgap that can impact optical and electronic properties, with the number of defects depending on both the form of the material (bulk glass, thin film or fibre) and the preparation method.

One of the most striking properties of ChGs is their photosensitivity — a propensity for the chemical bonds to change when exposed to light with a wavelength near the bandedge<sup>17,18</sup>. Similar changes can also be produced by exposure to heat, X-rays or electron/ion beams. Understanding this phenomenon started with the pioneering work of Ovshinsky<sup>19</sup> and has led to one of the most important applications of chalcogenides: the phase-

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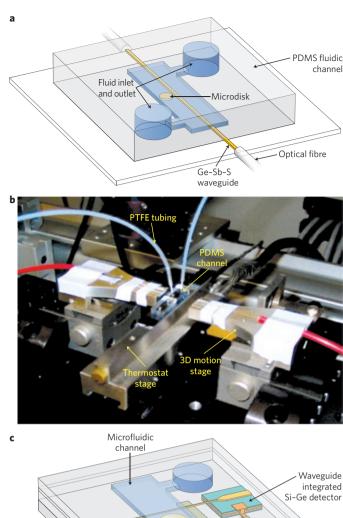
**b** Green (543 nm) laser

Figure 1 | Use of a photosensitive  $As_2S_3$  chalcogenide film to tune the resonant frequency of a photonic crystal cavity. **a**, An image of the photonic crystal cavity and its optical response. **b**, Schematic of the method used to tune the cavity. **c**, Cavity response as a function of illumination time for a 60 nm  $As_2S_3$  film. **d**, Tuning curves for two different thicknesses of the  $As_2S_3$  film. Figure reproduced with permission from ref. 32, © 2008 AIP.

change memories used in CD/DVD-RW discs and Numonyx memory chips.

The mechanism behind photosensitivity involves the creation of electron-hole pairs, which change the valence of neighbouring atoms and their chemical bonds, thereby creating coordination defects<sup>17</sup>. However, compared with the randomly placed coordination defects described above, these photo-induced states are physically close to each other and can therefore annihilate, restoring either the original bonding or, as a consequence of the steric flexibility of chalcogenides, a different bond configuration. Such bond switching by illumination can result in macroscopic changes in the physical properties of the material, providing a rich range of phenomena that includes photodarkening<sup>20</sup>, photodiffusion<sup>21</sup>, photofluidity<sup>22</sup> and photocrystallization<sup>23</sup>, as well as vectorial effects such as photoinduced birefringence<sup>24</sup>. Many of these effects, although still observable in bulk glasses, become particularly pronounced in thin films. The fabrication of thin films through vapour deposition onto a cold substrate is a non-equilibrium process. Films, therefore, can condense into amorphous states with a large number of defective bonds in molecular clusters, thereby creating a different topology from that of bulk glasses<sup>25</sup>. Photo-excitation creates coordination defects that provide a path through which the amorphous network can relax by bond switching towards a lower energy (bulk-like) state.

Photosensitivity can produce striking changes in the properties of chalcogenide films. For example, although as-deposited



**Figure 2 | Structure and testing of a chalcogenide microfluidic sensor. a**, Schematic of an integrated chalcogenide-based microfluidic sensor. **b**, Experimental realization of the device. **c**, Design of integrated onchip photonic sensor device. PDMS, polydimethylsiloxane; PTFE, polytetrafluoroethylene; CMOS, complementary metal-oxide-semiconductor. Figure reproduced with permission from ref. 84, © 2010 Wiley.

CMOS circuitry

thermally evaporated As–S thin films are soluble in amine-based developers, exposure to light near their bandedge or to electrons or high-intensity femtosecond pulses at 800 nm causes the network to polymerize, which strongly affects its solubility. This property has allowed chalcogenide films to be used as electron-beam resists<sup>26</sup> and for the creation of three-dimensional optical nanostructures by femtosecond laser direct writing<sup>27</sup>. Photodarkening is accompanied by a change in refractive index, and this has been used to write waveguides into evaporated films<sup>28</sup>, create Bragg gratings in fabricated waveguides<sup>29</sup>, tune the wavelength emitted by quantum cascade lasers<sup>30</sup>, create high-Q (125,000) cavities in chalcogenide photonic crystals<sup>31</sup>, and for post-tuning a photonic crystal cavity made from GaAs to match the emission from embedded quantum dots<sup>32</sup>. This last example is illustrated in Fig. 1, which shows that the photosensitivity of a 30–60-nm-thick As<sub>2</sub>S<sub>3</sub> layer could be used

Doped glass

Ultrahigh-Q ChG

ring laser

resonator

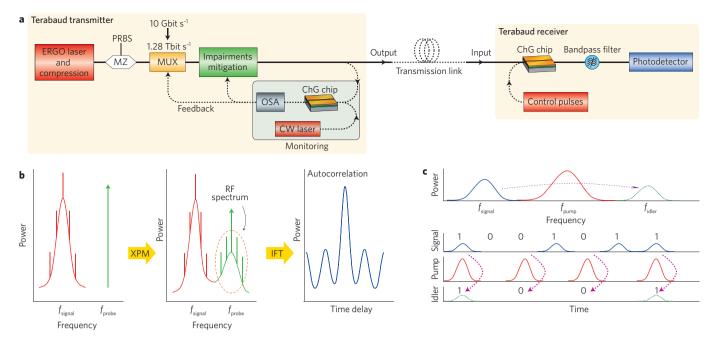


Figure 3 | Use of a chalcogenide photonic chip for transmitter optimization and demultiplexing at 1.28 Tb s<sup>-1</sup>. a, Diagram of terabaud transmitter optimization and terabaud receiver OTDM demultipexing. b,c, Schematics of cross-phase-modulation-based RF spectrum analyser for optimizing the optical performance monitor and multiplexer at the transmitter and all-optical terabaud demultiplexing (c). ERGO, erbium glass oscillator; MZ, Mach-Zehnder interferometer; PRBS, pseudo-random bit sequence; MUX, multiplexer; OSA, optical spectrum analyser; CW, continuous wave; XPM, cross-phase modulation; IFT, inverse Fourier transform. Figure reproduced with permission from ref. 96, © 2010 OSA.

to tune the resonant frequency of a GaAs photonic crystal cavity by up to 3 nm.

Although photostructural effects in ChGs are a fertile ground for research and applications, they are not necessarily desirable in optical devices exposed to high intensities of light. Photosensitivity has been observed at 1,550 nm in As<sub>2</sub>S<sub>3</sub> films<sup>33</sup> — a wavelength well away from the one- or two-photon absorption (TPA) edges. It therefore remains an important question as to whether chalcogenides are stable enough for demanding optical applications such as the delivery of high-power infrared light or all-optical signals processing. In this context, Yang et al.34 recently identified a photostable composition within the family of Ge<sub>x</sub>As<sub>45-x</sub>Se<sub>55</sub> glasses at  $x \approx 10$ , and in glass systems studied for high-power beam delivery compositional tuning has been used to identify glasses with combinations of good infrared transparency, adequate stability and resistance to laser damage. Zhang et al. 35 reported laser damage thresholds of 10-20 kW cm<sup>-2</sup> in low-loss (1-4 dB m<sup>-1</sup>) multicomponent (Te-As-Se-I and Ga-Sb-Ge-Se) fibres at 9.3 µm that were suitable for CO<sub>2</sub> laser delivery. Similar results have also been reported for CO laser systems<sup>36</sup> and pulsed Er:YAG applications in which damage thresholds of 350 J cm<sup>-2</sup> at an average power density of 0.5 kW cm<sup>-2</sup> were realized in low-loss, purified As-S fibres<sup>37</sup>. It is worth noting that in the experiments into all-optical processing summarized below, neither photosensitivity nor optical damage were impediments to achieving high performance.

# Chalcogenide fibres and waveguides

The intrinsic transparency window of ChGs, which includes much of the molecular fingerprint region of 2–25  $\mu m$ , makes them attractive for use in infrared-transmitting optical fibres, and as waveguides for optical sensors and telecommunications.

The first reports of chalcogenide optical fibres in the 1980s<sup>38,39</sup> confirmed that impurity absorption was a major limiting factor for achieving high transparency. Losses remain a general problem for chalcogenides and have limited their use to relatively short fibre lengths (metres). Although the estimated minimum loss in

As $_2S_3$  fibres resulting from Rayleigh scattering is only 4 dB km $^{-1}$  (ref. 40), the lowest value achieved in purified fibres is 23 dB km $^{-1}$  (at 2.3 µm) and more typically lies in the range of 100–200 dB km $^{-1}$  (ref. 41). These elevated values are due to impurity absorption as well as scattering from microscopic bubbles and fragments of silica that become dispersed in the glass during the melting process $^{42}$ .

Purity is of the utmost importance for maximizing the utility of ChGs, regardless of the final application. Undistilled 'high purity' elemental starting materials often contain finite levels of oxygen, carbon or hydrogen<sup>43,44</sup>, with the absorption peaks of these impurities occurring in the range of 1.4–14.9  $\mu$ m (ref. 45). Reducing impurity levels involves a number of diverse approaches, including heat treatment under vacuum to remove surface oxides<sup>46</sup>; chemical distillation with an oxygen getter<sup>47</sup>; treatment with tellurium halides<sup>48</sup> or reactive chlorine atmospheres<sup>49</sup>; vaporization through porous quartz frits<sup>50</sup>; dynamic pyrolysis<sup>44</sup>; and high-temperature oxidation for purifying sulphur<sup>51</sup>. These allow impurity levels to be reduced to ~10<sup>-5%</sup> by weight, thus markedly improving infrared transparency.

Several approaches have been used to fabricate optical fibres from ChGs. Step-index fibres can be drawn from 'rod-in-a-tube' preforms produced by core drilling or rotational casting. Core drilling<sup>52,53</sup> can result in increased scattering from interface roughness. Rotational casting can produce preforms with much smoother surfaces than core drilling, but it is a more complex technique, requiring a lathe-mounted mould into which the molten glass is poured and spun during cooling<sup>41,54</sup>. Although other mid-infrared (heavy metal oxide) fibres produced from rotational casting have demonstrated losses as low as 2 dB m<sup>-1</sup>, such low values have not yet been achieved in ChG fibres. Thus, the 'double crucible technique' is more widely used than rotational casting for production due to the higher resulting glass volatility, which can lead to changes in stoichiometry<sup>55</sup>. Preforms suitable for fabricating step-index fibres have also been produced by extrusion — this leads to low interface roughness and therefore lowers scattering losses<sup>56</sup>.

Chalcogenide photonic crystal fibres, which can be either endlessly single mode or provide large/small mode volumes, are an

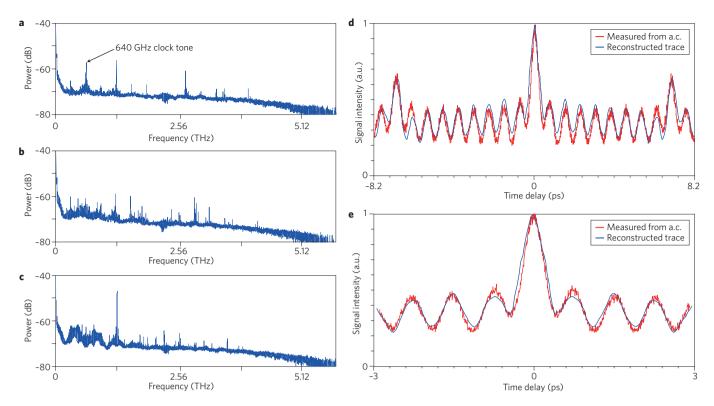


Figure 4 | RF spectra and recovered autocorrelation traces for the unoptimized and optimized transmitter. a-c, Captured RF spectra showing OTDM MUX misalignment (a), distortion due to dispersion (b) and optimization of the terabaud signal (c). d,e, Reconstructed a.c. waveforms of the unoptimized (d) and optimized (e) 1.28 Tbit s<sup>-1</sup> signals. Solid and dotted lines show the a.c. traces measured from the conventional autocorrelator and reconstructed from the captured RF spectra, respectively. Figure reproduced with permission from ref. 96, © 2010 OSA.

attractive alternative to traditional step-index structures because they can be made from a single glass composition. Preforms have been made using both the stack and draw process and through extrusion<sup>57,58</sup>. Hollow-core photonic bandgap omniguide fibres also use chalcogenides and are fabricated from concentric layers of As<sub>2</sub>Se<sub>3</sub> and polyethersulfone. They have proven particularly effective for transporting high-power CO<sub>2</sub> laser radiation for applications such as surgery<sup>59</sup>. Other applications of ChG fibres are summarized in ref. 60.

For many applications, optical circuits based on planar waveguides are often preferred over fibres. Chalcogenide glass films for waveguide fabrication have been produced by thermal evaporation<sup>61</sup>, sputtering<sup>62</sup>, chemical vapour deposition<sup>63</sup> and pulsed laser deposition<sup>64</sup>. For all of these methods, annealing post-deposition is required to relax the chemical bonds towards those of the bulk glass. Several methods for patterning rib or ridge waveguides have been demonstrated. The simplest is to exploit the photosensitivity of chalcogenides by illuminating them near their bandedge, thus photodarkening the material<sup>28,65</sup>. For example, illuminating As<sub>2</sub>S<sub>3</sub> films at fluences of around 100 J cm<sup>-2</sup> at 514 nm or 532 nm typically results in an index change of ~0.04 at 1,550 nm. This index change is sufficient for a single-mode waveguide with a core a few micrometres wide. However, photodefined waveguides can be unstable when heated or exposed to intense light, are difficult to realize in complex multicomponent glasses, and are not easily amenable to dispersion engineering.

A better approach, therefore, is to physically structure the film through lithography and etching to create a rib or ridge waveguide. Early work employed wet chemical etching with NH<sub>4</sub>OH to develop the resist patterns and etch the chalcogenide film<sup>28</sup>. However, this is unsatisfactory because the etching is isotropic, leading to poor dimensional control and large sidewall roughness. Anisotropic dry etching or lift-off techniques are therefore preferable. A problem

illustrated by the wet etching procedure, however, is that many ChGs are attacked by alkaline resist developers. This has the effect of increasing the roughness of the etched waveguide sidewalls at the nanometre-level, which increases scattering losses.

Lift-off methods, in which the chalcogenide film is deposited onto a pre-patterned resist, circumvent this problem <sup>66</sup>. Surface roughness still remains an issue, however, and methods based on reflow or the application of graded-index coatings have been employed to reduce losses from surface scattering. Losses at 1,550 nm in 800 nm  $\times$  400 nm  $As_2S_3$  nanowires were successfully reduced from ~6 dB cm $^{-1}$  to 3.2 dB cm $^{-1}$  by reflow, whereas values as low as 1.5 dB cm $^{-1}$  have been reported for  $As_{42}S_{58}$  1.6  $\mu$ m  $\times$  350 nm waveguides after the application of a graded-index coating — a twofold improvement over uncoated nanowires.

The sensitivity of chalcogenide surfaces to alkaline developers can be overcome by applying a protective coating beneath the resist prior to patterning. Several coatings have been employed so far, with the best results obtained using polymethylmethacrylate (PMMA) or SU-8, which is a chemically amplified epoxy-based negative photoresist. Careful choice of gas chemistry and annealing conditions prior to etching are essential to obtain smooth and vertical sidewalls. For As<sub>2</sub>S<sub>3</sub> films the use of CHF<sub>3</sub> gas chemistry for etching results in etched surfaces with a root-mean-squared roughness of ~1.5 nm. The annealing temperature must be limited to ~130 °C to avoid surface degradation and any associated increase in roughness. Standard photolithography and dry etching have been used to produce polymer-clad, dispersion-engineered As<sub>2</sub>S<sub>3</sub> rib waveguides measuring  $2 \mu m \times 850 \text{ nm}$  with losses as low as 0.35 dB cm<sup>-1</sup> (ref. 67). PMMA is also useful as an electron beam resist when producing chalcogenide nanowires, and was recently used to pattern 530-nm-thick films of highly nonlinear Ge<sub>1.5</sub>As<sub>24.5</sub>Se<sub>64</sub> for producing 630-nm-wide dispersion-engineered waveguides with transverse magnetic losses of ~2.5 dB cm<sup>-1</sup> (ref. 68).

Table 1 | Nonlinear optical parameters for nonlinear waveguides used for all-optical signal processing. **Nonlinear** Dispersion coefficient parameter y Loss Free Device and material (W<sup>-1</sup> km<sup>-1</sup>) (ps km<sup>-1</sup> nm<sup>-1</sup>) (dB m<sup>-1</sup>) TPA (m W-1) **FOM** carriers n2 (m2 W-1) Reference Highly nonlinear silica fibre  $3.2 \times 10^{-20}$ 21 0.03 10-3 Negligible Large Nο Bismuth oxide fibre  $1.1 \times 10^{-18}$ 1.360 100 -260 0.8 Negligible Large No  $2 \times 10^{-18}$ As<sub>2</sub>S<sub>3</sub> fibre 160 101 410 0.88 6.2 × 10<sup>-15</sup> 208 No As<sub>2</sub>Se<sub>3</sub> fibre  $9 \times 10^{-16}$ 1.200 102 -504  $2.5 \times 10^{-12}$ 2.3 Nο As<sub>2</sub>S<sub>3</sub> rib waveguide  $2.9 \times 10^{-18}$ 1,700 103 -342 5  $6.2 \times 10^{-15}$ 304 Nο  $1.1 \times 10^{-17}$ As<sub>2</sub>Se<sub>3</sub> fibre taper 93,400 99 282 <1  $2.5 \times 10^{-12}$ 2.84 No As<sub>2</sub>S<sub>3</sub> dispersion-engineered rib waveguide 9,900 92 29 60  $6.2 \times 10^{-15}$ 312 No  $9 \times 10^{-18}$ 136,000 70 10-13 60 Ge<sub>11.5</sub>As<sub>24</sub>Se<sub>64.5</sub> nanowire 68 250 No <4.1 × 10<sup>-12</sup> Photonic crystal Ag-As<sub>2</sub>Se<sub>3</sub> waveguide  $7 \times 10^{-17}$ 26 × 10<sup>6</sup> 104 Not provided 1,000 >11 No  $5 \times 10^{-12}$ Silicon nanowire waveguide  $6 \times 10^{-18}$  $1.5 \times 10^{5}$ 105 Engineered 400 0.77 Yes anomalous

#### **Applications**

Sensing. Crystalline chalcogenide materials have been explored as narrow-bandgap semiconductors for photovoltaic infrared imaging. The earliest work from the 1940s was based on PbS, but this quickly expanded to include InSb, PbSe and PbTe (ref. 69). One of the most attractive properties of lead-chalcogenides for infrared imaging — compared, for example, with HgCdTe — is the comparative ease of film deposition, as well as the higher tolerance for compositional inheterogeneities<sup>70</sup>. From a device standpoint, it is preferable to deposit the chalcogenide materials (crystalline detector materials and amorphous components) onto silicon substrates, which are physically robust and can be patterned using standard photolithographic techniques. To accomplish this, a variety of deposition techniques have been employed, including molecular beam epitaxy<sup>71</sup>, electrodeposition<sup>72</sup> and ion implantation<sup>73</sup>.

ChGs are commonly used in optical sensing platforms, either in fibre or planar form. Fibre-based systems generally operate by exposing a section of the fibre core to the environment to be sensed (liquid or vapour) and monitoring the fibre transmission that is altered by the interaction of the evanescent wave with the medium. This technique is known as fibre evanescent wave spectroscopy  $^{74,75}$ . Because analyte species are generally organic and so absorb in the mid-infrared, the high transparency of ChGs, along with its availability in fibre form, makes chalcogenide materials attractive for this technique  $^{76}$ . The hydrophobic surface of the glass itself, along with ease of surface functionalization, leads to high sensitivity. Additionally, it is possible to reduce the diameter of the chalcogenide fibre core, either thermally by heating to a temperature above  $T_{\rm g}$  and then tapering  $^{78}$ , or by chemical etching  $^{79}$ , to increase the system sensitivity.

Recent years have seen significant interest in the use of planar waveguides for chemical sensing. Such waveguides exploit either evanescent wave spectroscopy<sup>80</sup> or Raman spectroscopy<sup>81</sup>, and have the advantage of small size, greater reproducibility that fibre devices, and the ability to be monolithically integrated with sources/emitters, detectors and microfluidic analyte delivery systems<sup>61,66</sup>. Waveguide-coupled planar optical resonators have also been demonstrated<sup>82</sup>, which provide sensitivities similar to those of commercially available surface-plasmon devices<sup>83</sup>, but in a smaller footprint. Figure 2 is a schematic of an enlarged chalcogenide resonator and microfluidic system, showing the entire detection system and the experimental realization<sup>84</sup>. High infrared transparency is the key to achieving high sensitivity. Surface functionalization of

the resonator to the analyte(s) produces enhanced selectivity by allowing preferential binding of the species to the surface using, for instance, bacterial antibodies<sup>85</sup>. This flexibility of the sensing platform allows for the detection of multiple species on the same chip.

Devices based on ChGs are also being used in non-optical sensing applications. The detection of heavy metal ions in solution using an 'electronic tongue' is an example of a device that utilizes the solubility of metal ions in a vitreous chalcogenide matrix as its prime functionality, rather than any optical property of the material<sup>86</sup>.

Nonlinear effects and all-optical processing. The high material nonlinearity of ChGs, combined with the strong confinement and dispersion engineering achievable in fibre and waveguide devices, makes them attractive as fast nonlinear optical devices. This makes them a good platform for ultrafast nonlinear optics and a key technology for future ultrahigh-bandwidth optical communications systems. For an optical waveguide, the strength of the nonlinear response is characterized by the nonlinear parameter  $\gamma = \omega n_2/cA_{\text{eff}}$ where  $A_{\text{eff}}$  is the area of the propagating mode, c is the speed of light and  $\omega$  is its frequency. The nonlinear phase shift due to the Kerr effect is  $\Delta \phi = \gamma P L_{\text{eff}}$ , where *P* is the power and  $L_{\text{eff}}$  is the propagation length, which may be limited by losses, phase matching or pulse walk-off. An important material figure of merit, FOM =  $n_2$ /  $\beta\lambda$ , where  $\beta$  is the TPA coefficient, parameterizes the nonlinear phase shift achievable over one TPA length. Devices used for alloptical processing ideally require FOM > 1. Table 1 compares the parameters of ChG waveguides with those of highly nonlinear silica fibre and silicon nanowires. Chalcogenide devices now offer among the highest values of  $\gamma$  but also benefit from negligible TPA, compared with silicon. This leads to a large FOM and no free-carrier effects, making them an ideal platform for signal processing at ultrahigh bit-rates well beyond the speed of modern electronics. Chalcogenide nanowires can also be dispersion-engineered to provide zero or anomalous dispersion in the telecommunications bands. Such high values of  $\gamma$  allow short device lengths and, when combined with small dispersion, this leads to nonlinear devices with bandwidths of several terahertz87.

The first demonstrations of nonlinear ChG devices were reported in 1992<sup>88</sup> and used a Kerr shutter or loop mirror based on an  $As_2S_3$  fibre. Strong Kerr nonlinear effects were reported by Lenz *et al.*<sup>89</sup> in Se-based ChGs, and Spalter *et al.*<sup>65</sup> showed strong self-phase modulation in single-mode ChG planar waveguides. Thielen *et al.*<sup>90</sup>

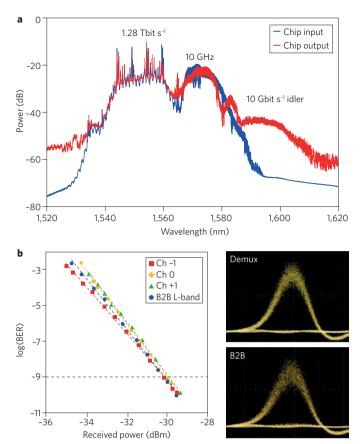


Figure 5 | Performance of the all-optical demultiplexer used to extract individual single data channels at a base rate of 10 Gbit s<sup>-1</sup> from a 1.28 Tbit s<sup>-1</sup> signal. a, Optical spectrum at the input and output of the chalcogenide chip. b, Bit-error-rate (BER) measurements for three adjacent channels after demultiplexing (demux) compared with back-to-back (B2B) measurements for a 10 Gbit s<sup>-1</sup> signal in the L-band. Output traces of the B2B and demultiplexed channels are shown on the right. Figure reproduced with permission from ref. 96, © 2010 OSA.

demonstrated 20 dB of Raman gain in a 1.1-m-long As–Se fibre, and Slusher *et al.*<sup>91</sup> measured Kerr nonlinearities nearly 1,000 times higher than those for silica fibres and Raman gains nearly 800 times that of silica. Recently, following the development of nanowires engineered to have anomalous dispersion, ChG waveguides have proven themselves to be efficient broadband generators of supercontinuum light<sup>92,93</sup>. The broad infrared transparency of chalcogenides should also allow the supercontinuum to be extended well into the mid-infrared, and this is now the subject of active research<sup>94</sup>.

The large instantaneous Kerr nonlinear response of ChG waveguides allows all-optical processing with large bandwidths. All-optical processors allow single-channel bit-rates in an optical communications system to far exceed the limits imposed by electronics, potentially allowing wavelength-division multiplexing networks to become simpler and more efficient. Over the past five years there have been reports of chalcogenide devices used for regeneration<sup>95</sup>, wavelength conversion<sup>10</sup>, demultiplexing<sup>96</sup>, four-wave-mixing gain<sup>97</sup>, optical sampling<sup>98</sup> and performance monitoring<sup>87</sup>.

Here we describe an example to illustrate the current state-of-the-art in ChG technology. This involves optical time-division multiplexing (OTDM) to create a single-wavelength data channel at 1.28 terabaud by interleaving 128 channels of 300 fs pulses at a base rate of 10 gigabaud. 1.28 terabaud is equivalent to 1.28 Tbit s<sup>-1</sup>, which is over 20 times faster than today's commonly available electronic processors. At the end of a link the OTDM signal must be

demultiplexed back to the base rate for detection using electronics. A schematic of the system is shown in Fig. 3a. The key signal processing device is a 7-cm-long dispersion-engineered  $\mathrm{As}_2\mathrm{S}_3$  rib planar waveguide with a nonlinear parameter of  $\gamma\approx 9,900~\mathrm{W}^{-1}~\mathrm{km}^{-1}$  and a zero-dispersion wavelength close to 1,550 nm. This device has two essential roles: at the transmitter it functions as an optical performance monitor and is used to optimize the multiplexing and compression of the ultrashort pulses; and at the receiver it is used to demultiplex the 1.28 terabaud signal back to the base rate.

The optical performance monitor continuously monitors the quality of the output signal from the transmitter and then generates an error signal that is fed back to optimize the multiplexer and mitigate signal impairments introduced by drift, for example, due to temperature fluctuations. Its working principle is shown in Fig. 3b. When the high-speed OTDM signal co-propagates with a continuous probe, new frequencies are generated around the probe due to cross-phase modulation in the ChG waveguide. These represent the radiofrequency (RF) spectrum of the signal, thus providing detailed information about the signal quality. Impairments may effectively be monitored by exploiting distinguishing features of the RF spectra. The bandwidth of this all-optical RF spectrum analyser is determined by the response time of the underlying nonlinearity (~femtosecond) and the group velocity walk-off between the signal and the probe. These short, dispersion-engineered ChG waveguides provide over a bandwidth of over 3 THz (ref. 87).

Figure 4a–c shows sample RF spectra obtained using this cross-phase-modulation-based RF spectrum analyser. The strong sub-harmonic peak at 640 GHz in Fig. 4a reveals a misalignment of the multiplexer stages, whereas the low 1.28 THz optical tone in Fig. 4b indicates signal distortion due to dispersion. Figure 4c presents the RF spectrum of a well-optimized 1.28 terabaud output signal.

The working principle of the all-optical demultiplexer is based on four-wave mixing (FWM), as shown in Fig. 3c. The high-bitrate signal is co-propagated with pump control pulses at the base rate. The pump pulses are adjusted in time to coincide with the desired channel of the high-bit-rate signal, generating a new idler wavelength through FWM that can be extracted from the output by spectral filtering. Figure 5a shows the optical spectra of the 1.28 terabaud source signal and 10 GHz control pulses at the input and output of the waveguide. The high FWM conversion efficiency (~60%) ensures the generation of a high-quality idler signal, as evidenced by the eye diagrams and bit-error-rate measurements shown in Fig. 5b. Although the idler signal seems significantly weaker in the optical spectrum, it should be noted that the duty cycle of the demultiplexed signal is 128 times lower than that of the input signal, corresponding to around a 25 dB reduction in spectral intensity. This highlights the excellent performance achievable with negligible degradation of signal quality and no indication of an error floor in bit-error-rate measurements. It is significant to note that these chalcogenide waveguides operate reliably with continuous power loadings in the 10-20 MW cm<sup>-2</sup> range.

#### **Conclusions**

ChGs offer a unique set of properties among optical glasses that make them an excellent choice for mid-infrared science and non-linear optics. The research outlined here has not only led to a much better understanding of the material properties that affect the optical performance of chalcogenides, but also illustrates the momentum in the field that has led to the development of high-performance chalcogenide waveguide devices. In this context, chalcogenide nanowires have proven particularly effective for the all-optical processing of high-speed data and low-threshold supercontinuum generation<sup>99</sup>. Following the development of the quantum cascade laser there is renewed interest in waveguide platforms for sensing illicit and dangerous materials through mid-infrared spectroscopy — an area ideally suited to chalcogenide devices. Chalcogenides also provide

an excellent platform for integrated interferometers for mid-infrared astronomy, promising to greatly simplifying existing optical systems based on bulk optics. The main challenge for all applications is to identify glasses that have the required stability at high optical fluence — together with adequate transparency and processability — from among the myriad of chalcogenide glass compositions currently available. If achieved, this intriguing range of optical glasses should have an extremely bright future.

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## **Additional information**

The authors declare no competing financial interests.