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Recent progress in germanium-core optical fibers for mid-infrared optics

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ABSTRACT

The search for low-loss and robust optical fibers in the infrared spectrum has always been an important research topic for many investigators. Over the years, fibers of various materials groups have been proposed to obtain 'the ultimate infrared fiber'. Recently, a new competitive alternative has emerged: the semiconductor-core glass-cladded optical fibers. The excellent bulk materials properties and integrated circuit applications reveals the potential of semiconductors as fiber materials. One of the important photonic materials that has been proposed as a fiber-core material is germanium. In this paper, the development of Ge-based fibers and their optical properties in the mid-infrared spectrum are discussed. The performance of Ge-based fibers has been compared with other semiconductor-core fibers. Recent developments in the area of semiconductor fibers and the future prospects of semiconductors as infrared fiber materials are also discussed.

1. Introduction

The emergence of the mid-infrared (IR) fibers coincides with the early period of silica-based optical fibers, when chalcogenide-glass optical fibers were proposed by Kapany and co-workers [1]. These chalcogenide fiber materials, comprised of various combinations of As, Se, and S with Ge, Te and several other elements, showed promising transmission properties in the mid-IR spectrum. The demonstration of new processing techniques for silica glass preform fabrication accelerated the development of the low-loss silica optical fibers, and silica optical fibers with transmission losses below 20 dB/km were fabricated in the early 1970s [2]. Since then, silica optical fibers have become the backbone of the global telecommunication industry by transmitting data in the visible and near-IR spectra. However, the sharply increasing transmission losses in silica glasses for wavelengths beyond $\sim 3~\mu m$ require different materials for effective mid-IR transmission.

Transmission in the mid-IR spectrum has many potential applications, including detection of environmentally hazardous greenhouse gases, remote laser delivery for surgery, and defense countermeasures, among others [3]. Although different communities define the internal boundaries of the IR region differently, it is generally accepted that the near-IR, mid-IR and far-IR regions for the photonics community are defined as wavelengths being in the 0.7–2 μ m, 2–15 μ m and 15–1000 μ m ranges, respectively. Materials such as chalcogenides,

fluorides, heavy metal oxides and photonic crystal fibers (PCFs) have been proposed for mid-IR transmission to create the ultimate low-loss optical fibers [4-7]. Although fibers made of these materials have shown unique transmission abilities in the mid-IR spectrum, the unsolved mechanical and chemical issues still preventing their widespread usage. On the other hand, semiconductors, known for their IR transmission properties in integrated photonic devices, have excellent bulk mechanical and chemical stability, and promising low-loss transmission in the mid-IR spectrum [8]. The promise of integrating mid-IR photonic circuits with fibers made of the same material is another motivation for the increased interest in semiconductors as fiber materials. Among the semiconductors, Ge has particular advantages in the mid-IR region due to its wide transmission window and strong nonlinear properties. Although the Ge transmission window does not include the telecommunication window (0.8-1.7 µm), it does include the entire mid-IR spectrum. The nonlinearity of Ge is known to be several orders of magnitude greater than silica glasses, a property widely exploited in Ge waveguides [9]. For instance, Ge's third order susceptibility ($\chi^{(3)}$) and Kerr coefficient (n₂) are 1.5×10^{-18} m²/V² and 2.6×10^{-17} m²/W, respectively, around 4 µm wavelength [10]. Ge has been used in photonic circuits for a variety of applications such as waveguides, lasers, multiplexers, and phase shifters [11-14]. Although low-loss transmission has been previously demonstrated in on-chip Ge waveguides, waveguides have complex fabrication processes, limited lengths and

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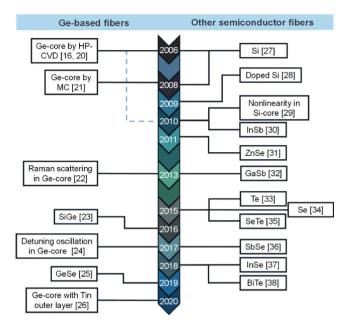


Fig. 1. Historical overview of semiconductor-core glass-cladded optical fibers. The major advances of Ge-based fibers (The left hand-side) and other semiconductor fibers (the right hand-side) are shown with their respective publication dates listed [16,20–38] (HP-CVD: High Pressure-Chemical Vapor Deposition; MC: Molten Core).

dependency on the design of circuits [13,15].

Ge-based optical fibers do not suffer from these limitations. The first demonstration of Ge-core fibers was achieved in 2006 by modifying the well-known chemical vapor deposition technique [16]. In this study, silica PCFs were filled with Si and Ge, forming rods, tubes and heterostructures of these materials. This seminal development led to a variety of unary-core and alloy-core semiconductor fibers. Alloy-core semiconductors fibers have additional advantages over their unary counterparts, such as tuning the transmission window and forming a graded-index (GRIN) structure. Fig. 1 provides a historical overview of the major achievements in semiconductor-core fibers, with Ge-based fibers highlighted on the left-hand side and other semiconductor-core fibers highlighted on the right-hand side. The blue-dashed line indicates the first demonstration of successful optical transmission through a Ge-core glass-cladded fiber.

It has been nearly fifteen years since the semiconductor-core fibers were proposed, and to date, several review papers on these fibers have been published [17,18]. Most of these reviews have been focused on silicon-core fibers which have been researched more extensively [8,19].

However, to the best of our knowledge, a review focused on Ge-based fibers is absent in the literature. This work aims to draw attention to the fibers with Ge and Ge alloy cores and the current trends in the semi-conductor-core fiber research.

This paper discusses the fabrication methods for different types of Ge-based fibers. The optical properties of Ge-based fibers are then discussed and compared with other semiconductor fibers. Finally, a discussion on the applications of Ge-core fibers and future trends in the semiconductor fibers are presented.

2. Fabrication methods

To date, there are two primary fabrication methods for semi-conductor-core fibers; high-pressure chemical vapor deposition (HP-CVD), and molten core (MC). Initially, the MC method involved two forms of the starting fiber core material, rods (rod-in-tube), and powders (powder-in-tube) [21,39]. Although both methods have been utilized for more than 10 years for the fabrication of semiconductor-core fibers, the rod-in-tube has become the dominant starting configuration of MC fabrication. The pros and cons of each method are discussed below.

2.1. High-pressure chemical vapor deposition

The HP-CVD was the first proposed method to fabricate semi-conductor-core fibers, and involves filling the inside of glass capillaries or PCFs with highly pressurized mixtures of precursors and carrier gases at the elevated temperatures [16,40]. A generalized schematic of the HP-CVD method is shown in Fig. 2a. The growth of semiconductor thin films and coatings on non-planar substrates by the chemical vapor deposition (CVD) is a well-developed process. The novelty of HP-CVD lies in the use of higher pressures, extending up to 100 MPa. This high pressure can assist with the filling of very high aspect ratio cavities. The mechanical strength of capillary glasses and PCFs allows for such high-pressure deposition to occur, without mechanical failures. The process temperature and pressure varies with the core material. To date, fibers with Si, Ge, ZnSe and SiGe cores have been fabricated by the HP-CVD [16,31,41]. For the deposition of compound or alloy semiconductor cores, the individual precursors are mixed in the appropriate ratio.

There are several advantages of the HP-CVD method. First, a wide selection of cores can be deposited, allowing for the deposition of materials such as ZnSe and ZnS, whose high vapor pressures make their fabrication by the MC method challenging [31]. Second, the process allows for the deposition of multi-layered core structures for optoelectronic junctions [42]. Finally, the ability to manipulate the processing conditions to form amorphous or polycrystalline cores allows for flexibility in fabricating fibers with different core microstructures [43]. On

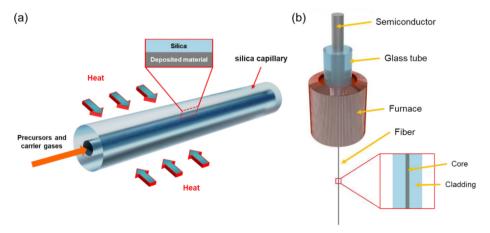


Fig. 2. Schematics of semiconductor-core fiber fabrication methods, depicting: (a) HP-CVD and (b) MC fabrication.

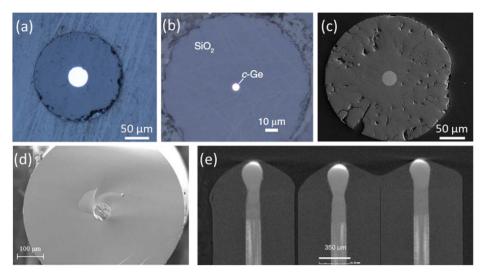


Fig. 3. SEM images of radial cross-sections of a) Gecore borosilicate glass-cladded fiber, b) Ge-core silica glass-cladded fiber, [Adapted] with permission from [48], © 2016, Wiley. c) SiGe alloy-core silica glass-cladded fiber and d) GeSe alloy-core K9 glass-cladded fiber. [Adapted] with permission from [25], © 2015, Elsevier. e) SEM image of longitudinal cross-sections of Ge-capped SiGe fiberarray. [Adapted] with permission from [49], © 2019, The Optical Society. Fibers a), c), d) and e) were drawn by the MC method, and fiber b) were fabricated by the HP-CVD method.

the other hand, the important disadvantages of this technique are the limited fiber length (on the order of a few meters) over which deposition can be achieved, as well as difficulty in achieving complete filling of the hollow core [31]. Slowing down the deposition rates can assist with better core filling, but that can lead to unrealistically long fabrication times. Finally, precursor gases like silane (SiH₄) for Si cores and germane (GeH₄) for Ge cores are highly flammable and toxic, requiring special care during deposition.

2.2. Molten core fabrication

The molten-core (MC) method was originally proposed in the 1990s to draw fibers whose core materials that were unstable (e.g., amenable to oxidation) to the drawing atmosphere, with the initial starting core materials being in the form of powders [44]. Although the preforms for the MC method are different from the preforms of conventional solidcore silica optical fibers or PCFs, the drawing technique itself is similar. In the MC method, the core material, that is in the form of a rod, powders, pieces or the combination of these, is placed into a glass tube. The lower end of the tube is sealed to hold the core in place by either collapsing the preform tube with a flame torch or by insertion of tightly fitting glass rods. The upper end of the core material is also sealed off with a glass rod to prevent oxidation at the elevated drawing temperatures. Fibers with core diameters from tens to hundreds of micrometers are drawn in conventional fiber draw towers at the temperatures that are above both the melting point of the core and softening point of the glass cladding. Additional glass tubes with increasing diameters can be added concentrically to control core/cladding diameter ratio of the fibers. The MC method is shown schematically in Fig. 2b.

There are several advantages of the MC method. First, this method is amenable to kilometer-long fiber drawing with a high degree of uniformity of core and cladding diameters. Second, it does not require any specific modification of fiber draw towers designed for drawing fibers of the cladding glass. Finally, the preform fabrication for this method is relatively simple. A disadvantage of the MC method is the diffusion of impurities from cladding to the core, especially where borosilicate cladding is used [21]. A variety of techniques have been used to combat the diffusion problem. Using alkaline oxide modifiers at the interface of the core and cladding was found to limit impurity diffusion into the core [45]. Placement of the core material just above the necking point, can minimize the time the core remains molten before being drawn, thereby reducing impurity diffusion [46].

In spite of the diffusion issue, the MC method is the preferable technique for fabricating semiconductor core fibers, and is widely accepted as the fabrication method for semiconductor core fibers. However, MC fabrication is not amenable for drawing fibers whose core

materials have a high vapor pressure, or when composition changes in the radial direction of the core are required. For these cases, the HP-CVD method is preferred for the fabrication of such fibers [18].

3. Fiber types

As shown in Fig. 1, various semiconductors have been used as the core material IR optical fibers. The HP-CVD filled PCFs were first processed with pure Ge and SiGe heterostructure cores, and this work was a significant milestone for Ge-core fibers [16]. In this section, the Gebased fibers with various cladding glasses are reviewed. This section discusses both unary core (Ge only) and Ge alloy/compound core fibers.

3.1. Ge-core fibers

Pure Ge-core fibers have been successfully processed by both HP-CVD and MC methods [16,20,21]. For HP-CVD, silica capillaries were filled with Ge, and both amorphous and polycrystalline core fibers were deposited [20]. For the MC method, two different glass types were selected as the cladding material: silica and borosilicate glasses [21,47]. Borosilicate glasses have a better coefficient of thermal expansion (CTE) match with Ge, which reduces the propensity of crack formation during fiber cool down. Also, the drawing temperature range of borosilicate glasses (850 °C to 1150 °C), overlaps with the melting point of Ge (938 °C), allowing the fibers to be drawn at relatively lower temperatures, not significantly above the melting temperature of Ge. This reduces the kinetics of diffusion of impurities from the cladding to the core [46]. Silica glasses have much higher drawing temperatures (1850-2200 °C), but do not have the network modifiers present in borosilicate glasses. The lower drawing temperatures for borosilicate claddings limit the impurity diffusion of oxygen into the core. A crosssectional image of a polycrystalline Ge-core borosilicate glass-cladded fiber drawn by the MC method is shown in Fig. 3a. A monocrystalline Ge core was achieved recently by post-deposition laser recrystallization processing of a HP-CVD fiber. The cross-section of the fiber is shown in Fig. 3b [48]. A continuous-wave 488 nm argon ion laser was used to heat the semiconductor core by exploiting the absorption of Ge at the emission wavelength. Ge-core fibers have been processed with amorphous, monocrystalline and polycrystalline cores.

Another technique that has been reported to form Ge cores, is using pressure assisted filling of the hollow cores of silica-air photonic crystal fibers by molten Ge [50]. This method was successful in filling channels as small as 600 nm in diameter. This structure has potential usage for in-fiber thermometer and sensing applications.

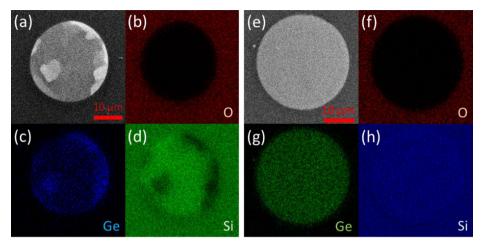


Fig. 4. Effect of the thermal annealing on SiGe-core fibers. (a), shows the cross-sectional SEM image of the core and (b), (c) and (d) shows EDX-based EDX elemental dot mapping of O, Ge and Si before thermal annealing respectively. (e), (f), (g) and (h) shows the fiber cross-section after the thermal annealing [52].

3.2. Ge alloy/compound fibers

Alloying Ge with other semiconductors can lead to additional advantages such as tuning the transmission window or forming GRIN fiber cores. GRIN structures are commonly used on multimode solid-core silica optical fibers to suppress the modal dispersion [51]. This structure can also decrease the transmission losses in the mid-IR spectrum by tightly confining the light in the fiber center, thus keeping it away from the lossy glass cladding. To-date, most of the efforts have focused on SiGe alloy-cores [23,41,52]. Three different research groups have successfully fabricated SiGe alloy-core glass-cladded fibers by using both the HP-CVD and the MC methods. SiGe alloy-core fibers drawn by the MC method showed large compositional fluctuations in the core. This was attributed to random nucleation of Si-rich regions during the rapid cooling associated with fiber drawing, leaving the last regions to solidify to be Ge-rich. In order to homogenize the core composition, fibers were annealed in a furnace in air. Fig. 4 shows the SEM-based EDX elemental dot mapping of the cross-sectional images of the fiber before and after the thermal annealing. The process was successful in increasing uniformity of the fiber. However, this was also accompanied by partial devitrification of the silica, leading to crack formation in the cladding (Fig. 3c) [52]. Re-melting and re-solidification of the SiGe alloy-core using a continuous-wave 10.6 µm CO2 laser at has also been successfully used to achieve improved compositional homogeneity [23]. The compositional uniformity of cores also improved the optical transmission properties of the fibers. SiGe alloy-cores have also been deposited inside silica capillaries at 460 °C by HP-CVD [41]. After deposition, the fibers had amorphous cores, which were converted to polycrystalline cores by annealing. Another study focused on forming Ge capped SiGe alloy-core fibers by heating the tip of the fibers with a commercial 10.6 µm CO₂ laser [49]. The laser-treated tips turned into convex structures (Fig. 3e) that acts as a lens to focus the multimode output of the fiber to a single point in space.

GeSe-core fibers with the commercial K9 glass cladding were recently fabricated by the MC method using a powder mixture of Ge and Se [25]. The GeSe-cores of the as-drawn fibers were crystalline with oxygen content less than 1%. Although the optical transmission measurement was not reported, the photoconductivity and thermoelectric properties of the fibers were investigated. Furthermore, Ge-core fibers with a Sn outer layer have been reported [26]. The Sn layer was aimed to confine the light in the core region by acting as a mirror. The presence of the Sn layer improved the optical transmission by 20%. However, in general, the losses in Ge-alloy/compound fibers are still much higher than in unary Ge-core fibers.

4. Optical properties

Investigations of optical properties such as optical transmission of semiconductor-core fibers have mainly focused on Si-core fibers, with an eye on applications such as nonlinear optics and optoelectronics [27,53,54]. In contrast, the study of optical properties of Ge-core fibers has not been as prevalent. Here, we discuss the optical performance of the Ge-based fibers and their comparison with other semiconductor-core fibers.

4.1. Optical transmission

The optical transmission measurements of Ge-based fibers were performed in a wide optical band in the mid-IR region spanning from $2.0~\mu m$ to $10.6~\mu m$. The first reported transmission loss measurement was on a Ge-core, silica glass-cladded fiber processed by the HP-CVD method [20]. The core structure of this fiber was amorphous, and the minimum losses were found to be 4.8 dB/cm at 10.6 µm. Subsequently, another silica glass-cladded crystalline Ge-core fiber, drawn by the MC method, was reported to have an optical transmission loss of 0.9 dB/cm at 3.39 µm [47]. A more recent study focused on borosilicate glass cladding that has a better coefficient of thermal expansion match with Ge-core. These fibers exhibited an average transmission loss of 5.1 dB/ cm in the range of $5.82-6.28 \mu m$ [46]. The region around $6 \mu m$ is important since the fundamental absorption region of many organic compounds such as proteins, nucleic acids, phospholipids and polymers are centered around this value [55,56]. To-date, the minimum reported transmission loss is 0.9 dB/cm at 3.39 μm for a Ge-core fiber with a polycrystalline core [47].

The mid-IR optical transmission losses of SiGe alloy-core fibers after post-fabrication processing to homogenize core composition vary from 9.7 to 28 dB/cm in the 2.0–6.1 μm range [23,52]. The transmission loss of the laser recrystallized SiGe core fibers with 6 at% Ge was reported to be 9.7 dB/cm at 2 μm . Another SiGe alloy-core fiber with silica cladding was found to have a transmission loss of 28 dB/cm at 6.1 μm after thermal annealing in a furnace [52]. A HP-CVD deposited SiGe alloy-core fiber with 2% Ge, exhibited a 7 dB/cm transmission loss at 1.55 μm (near-IR region) after thermal treatment [41]. However, this study did not report transmission losses in the mid-IR regime. The transmission losses in a Ge-core borosilicate glass-cladded fiber with tin interlayer was calculated to be 23.5 dB/cm at 3.39 μm . To date, the lowest reported mid-IR transmission loss in a Ge alloy-core fiber is 9.7 dB/cm at 2 μm [23].

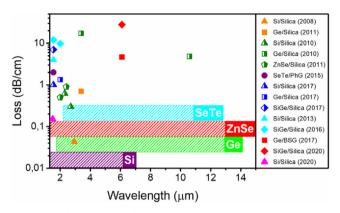


Fig. 5. Optical transmission losses of various reported semiconductor-core glass-cladded fibers in the near-IR (1.55 μm) and mid-IR regions. Each data is labeled with the core/cladding materials of fiber and the publication date of the work. The triangle, square, pentagon, circle and diamond symbols represents Sicore, Ge-core, ZnSe-core, SeTe-core and SiGe-core fibers respectively. Also data with fully-filled symbols are from fibers by rod-in-tube method and data with partially-filled symbols are from fibers by HP-CVD Research groups/collaborations that led to the fabrication and characterization of fibers are represented as different colors. Orange symbols are for Clemson University [27,47]; green symbols are for the collaboration between Pennsylvania State University (PSU) and Optoelectronics Research Center at University of Southampton (ORC) [20,31,58]; the purple symbol is for South China University of Technology (SCUT) [35]; blue symbols are for PSU [41,48,59]; cyan symbols are for Norwegian University of Science and Technology (NTNU) and collaborations between various universities and institutions led by NTNU [23,45], red symbols are for Boston University (BU) [46,52] and the magenta symbol is for Université de Lille [60]. The transmission windows of the bulk Si, Ge, ZnSe and SeTe are shown as dashed rectangles in the lower part of the figure. The corresponding positions of the rectangles within the figure do not represent the bulk optical losses of the materials. PhG is an abbreviation for phosphate glasses. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4.2. Comparison of optical losses in various semiconductor-core fibers

Fig. 5 summarizes the reported optical transmission losses of various semiconductor fibers as a function of wavelength in the mid-IR region. In the figure, several near-IR results (at 1.55 µm) were also plotted to give a wider overview of semiconductor-core fibers. As can be seen from the figure, most of the demonstrated transmission losses lie in the 1-10 dB/cm range for the mid-IR region. The Si-core silica glasscladded fiber outperforms all others with 4.3 dB/m transmission losses at 2.94 µm [27]. Even though unary Si-core fibers generally perform better than Ge-based fibers, the transmission losses of the semiconductor fibers fall in the same range. More research on Ge-based fibers can lead to the development of fibers with lower mid-IR transmission losses in the future. Furthermore, other promising semiconductor-core fibers such as tellurium, indium selenide, antimony selenide and gallium antimonide are excluded from the figure due to the lack of optical transmission measurements in the mid-IR wavelengths [33,36,37,57]. We expect to see more optical characterization studies of these fibers in the future.

5. Current and future applications

5.1. Applications

To-date, the applications of Ge-based fiber in the mid-IR spectrum have been focused mostly on the realization of optical transmission and nonlinear optics. The range of the demonstrated mid-IR transmission spans from 2.0 to 10.6 μ m [20,46]. Although, the demonstrated transmission losses are high comparing to other mid-IR fibers (10 s of dB/km to 100 s of dB/km for fluoride or chalcogenide-based fibers,

respectively, in the mid-IR), the wide coverage of the mid-IR region and chemical/mechanical stabilities of Ge-based fibers are important for robust future applications of these fibers. One important application is transmission at 10.6 μ m, which is the emission wavelength of commercially available CO₂ lasers [20].

Another important attribute of semiconductors is their high nonlinear properties. The nonlinear properties of Si-core fibers have been previously examined more thoroughly than any other semiconductorcore fibers [19]. There has been only a couple of studies of the nonlinear properties of Ge-core fibers [22,24]. The first study was focused on Raman scattering in a Ge-core borosilicate glass-cladded fiber. The Raman gain at ~6.8 µm was observed by pumping a 4 mm-long Ge-core borosilicate glass-cladded fiber with a 5.62 um quantum cascade laser (QCL) [22]. In a recent study, the detuning oscillations, a third-order (χ3) nonlinear off-resonance electronic response of transparent materials, were observed in the Ge-core fiber samples [24]. A femtosecond dispersed pump-probe spectroscopy setup that can also be utilized for the frequency dispersed optical heterodyne detections was used for demonstrating the nonlinearity of Ge [61]. In this work, three Ge-core borosilicate glass-cladded fiber samples with different core and cladding diameters were tested and the results were compared with the unprocessed Ge rod to evaluate the effect of the fiber drawing and the diameter on the nonlinearity of Ge. Fig. 6 shows the 2D plots of observed detuning oscillations as a function of frequency and the time delay between the pump and probe signals. In this work, the detuning oscillation can be observed on an unprocessed rod as well as Ge canes/ fibers with different diameters, stating that the nonlinearity of the Ge was maintained before and after fiber drawing. More studies are needed to investigate and exploit the nonlinear properties of the Ge-core optical fibers.

5.2. A perspective for future studies

The wide transmission window and highly nonlinear properties of Ge presents a significant potential for the future applications of Gebased fibers. Here, we discuss a few potential fiber designs that can significantly expand mid-IR applications for Ge-based fibers.

An important threshold of increasing the applicability of semiconductor-core fibers is to keep the transmission losses under 1 dB/m at any targeted wavelength region. One possible path to achieve this is to form GRIN structures. The numerical simulations of SiGe alloy-core fibers suggest the possibility of low optical losses through a wide spectral window with GRIN fiber cores [52]. Although, the demonstration of a low-loss GRIN fiber is yet to be achieved, a recent study showed preferential transmission of light through the Ge-rich region within the SiGe alloy-core after a laser-based post-drawing annealing process [62]. In principle, during the fiber drawing, if the solidification of the core occurs from the cladding to the fiber center with the nonhomogeneous distribution of materials, a GRIN structure can be made with different compositional rings (outer rings will be Si-rich, and inner rings and the center will be Ge-rich). However, forming the GRIN structure is still a challenging process due to the rapid cooling of the fiber after exiting the furnace of the draw tower and random nucleation in the core region. Another approach of decreasing transmission losses is developing cladding glasses with tailored working temperatures that are just above the melting temperature of the semiconductor core material [63]. This would allow fiber drawing to occur at temperatures as low as possible, thereby reducing impurity diffusion and thus decreasing transmission losses. However, finding suitable cladding glass compositions for semiconductors with high melting points is still a

The nonlinear properties of Ge-based fibers have not been fully explored unlike that for the case of Si-core fibers [19]. Higher nonlinearity of Ge could potentially lead to better results in nonlinear optical applications. One important nonlinear application of the semi-conductor-core fibers is the supercontinuum generation in the mid-IR

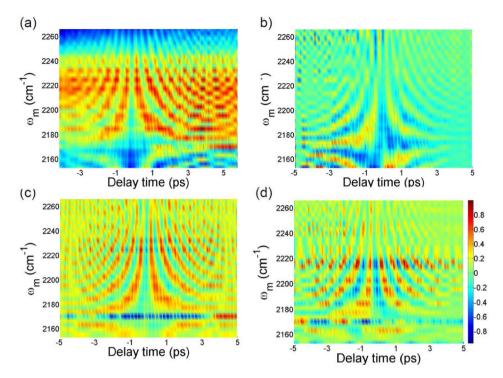


Fig. 6. Observation of detuning oscillation in four different Ge samples. Contour plots of (a) unprocessed Ge rod with 3 mm diameter, (b) Ge cane with 770 μm -core diameter, (c) Ge cane with 358 μm -core diameter and (d) Ge fiber with 132 μm -core diameter with respect to delay time (ps: picosecond) and wavenumber (cm $^{-1}$). Figures are unique for each sample but a common color code is applied. Maximum and minimum normalized intensities are represented with red and blue respectively [24]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

range [53]. The experimental supercontinuum generation in the mid-IR spectrum by pumping a tapered Si-core silica glass-cladded fiber with a femtosecond optical parametric oscillator was demonstrated recently [64]. A similar mid-IR supercontinuum generation with Ge waveguide was numerically proposed and supercontinuum generation can be achieved with low-loss Ge-core fibers in the future [65].

Silica hollow-core photonic crystal fibers (HC-PCFs) have demonstrated low-loss transmission in the mid-IR region where the silica has high bulk material losses [66,67]. Several different guidance mechanisms play a role in low-loss transmission in HC-PCFs, and one important mechanism is the photonic band gap (PBG) structures around the hollow-core [68,69]. Replacing the hollow-core with a semiconductor medium could be an alternative way to decrease the transmission losses of the semiconductor-core fibers [70]. Selective filling of semiconductors into the core and having hollow-cladding structures can lead to low transmission losses by limiting the interaction of the guided light with the glass cladding. Also, the nonlinearities of HC-PCFs due to the high figure of merit of these fibers can be enhanced in the mid-IR spectrum with the help of semiconductor cores.

In the recent years, the research trend of the Ge-based fibers has shifted towards the alloying/compounding of Ge with other elements due to the tuning of refractive index and transmission window. Also, aforementioned GRIN mid-IR fiber can be realized with Ge alloys. Lastly, various demonstrations of the nonlinear properties of the Gebased fibers are expected in the near future.

6. Conclusion

The quest for developing the 'ultimate low-loss mid-IR fiber' is still ongoing. Semiconductor-core fibers have introduced new aspects to IR optics with their unique materials properties. Ge-core fibers made by various fabrication and post-fabrication processes have demonstrated mid-IR transmission, nonlinear optical properties and photodetection. Even though the importance of Ge-core fibers has been currently overshadowed by Si-core fibers, there are strong reasons to pursue Ge-based fibers for potential future applications. The unique properties of Ge have been exploited in Ge waveguides; Ge-core fibers need to follow suit. Furthermore, the unexplored realm of the integration of semi-conductor-core fibers and on-chip waveguides can lead to many

attractive future applications. However, to achieve this, reaching the 1 dB/m transmission loss milestone is a key for these fibers, and advances in fiber design and processing will be required. Overall, Ge-core fibers have a bright future as they will play an important role in future mid-IR optical and optoelectronic applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] N. Kapany, R. Simms, Recent developments in infrared fiber optics*, Infrared Phys. 5 (2) (1965) 69–80, https://doi.org/10.1016/0020-0891(65)90009-6.
- [2] F. Kapron, D.B. Keck, R.D. Maurer, Radiation losses in glass optical waveguides, Appl. Phys. Lett. 17 (10) (1970) 423–425, https://doi.org/10.1063/1.1653255.
- [3] R. Soref, Mid-infrared photonics in silicon and germanium, Nat. Photonics 4 (8) (2010) 495, https://doi.org/10.1038/nphoton.2010.171.
- [4] J. Sanghera, I.D. Aggarwal, Active and passive chalcogenide glass optical fibers for IR applications: a review, J. Non-Cryst. Solids 256 (1999) 6–16, https://doi.org/10. 1016/S0022-3093(99)00484-6
- [5] J. Bei, T.M. Monro, A. Hemming, H. Ebendorff-Heidepriem, Fabrication of extruded fluoroindate optical fibers, Opt. Mater. Exp. 3 (3) (2013) 318–328, https://doi.org/ 10.1364/OME.3.000318.
- [6] A. Mori, Tellurite-based fibers and their applications to optical communication networks, J. Ceram. Soc. Jpn. 116 (1358) (2008) 1040–1051, https://doi.org/10. 2109/jcersj2.116.1040.
- [7] K. Kuriki, O. Shapira, S.D. Hart, G. Benoit, Y. Kuriki, J.F. Viens, M. Bayindir, J.D. Joannopoulos, Y. Fink, Hollow multilayer photonic bandgap fibers for NIR applications, Opt. Express 12 (8) (2004) 1510–1517, https://doi.org/10.1364/ OPEX.12.001510.
- [8] A. Peacock, U. Gibson, J. Ballato, Silicon optical fibres-past, present, and future, Adv. Phys.: X 1 (1) (2016) 114–127, https://doi.org/10.1080/23746149.2016. 1146085.
- [9] G.Z. Mashanovich, C.J. Mitchell, J.S. Penades, A.Z. Khokhar, C.G. Littlejohns,

- W. Cao, Z. Qu, S. Stanković, F.Y. Gardes, T.B. Masaud, Germanium mid-infrared photonic devices, J. Lightwave Technol. 35 (4) (2017) 624–630, https://doi.org/ 10.1109/JLT.2016.2632301.
- [10] N.K. Hon, R. Soref, B. Jalali, The third-order nonlinear optical coefficients of Si, Ge, and Si1 x Ge x in the midwave and longwave infrared, J. Appl. Phys. 110 (1) (2011) 9, https://doi.org/10.1063/1.3592270.
- [11] A. Malik, M. Muneeb, S. Pathak, Y. Shimura, J. Van Campenhout, R. Loo, G. Roelkens, Germanium-on-silicon mid-infrared arrayed waveguide grating multiplexers, IEEE Photonics Technol. Lett. 25 (18) (2013) 1805–1808, https://doi.org/ 10.1109/LPT.2013.2276479.
- [12] J. Liu, X. Sun, R. Camacho-Aguilera, L.C. Kimerling, J. Michel, Ge-on-Si laser operating at room temperature, Opt. Lett. 35 (5) (2010) 679–681, https://doi.org/10. 1364/OL 35 000679
- [13] M. Nedeljkovic, J.S. Penadés, C.J. Mitchell, A.Z. Khokhar, S. Stanković, T.D. Bucio, C.G. Littlejohns, F.Y. Gardes, G.Z. Mashanovich, Surface-grating-coupled low-loss Ge-on-Si rib waveguides and multimode interferometers, IEEE Photonics Technol. Lett. 27 (10) (2015) 1040–1043, https://doi.org/10.1109/LPT.2015.2405611.
- [14] A. Malik, S. Dwivedi, L. Van Landschoot, M. Muneeb, Y. Shimura, G. Lepage, J. Van Campenhout, W. Vanherle, T. Van Opstal, R. Loo, Ge-on-Si and Ge-on-SOI thermooptic phase shifters for the mid-infrared, Opt. Express 22 (23) (2014) 28479–28488, https://doi.org/10.1364/OE.22.028479.
- [15] Y.-C. Chang, V. Paeder, L. Hvozdara, J.-M. Hartmann, H.P. Herzig, Low-loss germanium strip waveguides on silicon for the mid-infrared, Opt. Lett. 37 (14) (2012) 2883–2885, https://doi.org/10.1364/OL.37.002883.
- [16] P.J. Sazio, A. Amezcua-Correa, C.E. Finlayson, J.R. Hayes, T.J. Scheidemantel, N.F. Baril, B.R. Jackson, D.-J. Won, F. Zhang, E.R. Margine, Microstructured optical fibers as high-pressure microfluidic reactors, Science 311 (5767) (2006) 1583–1586, https://doi.org/10.1126/science.1124281.
- [17] A.C. Peacock, J.R. Sparks, N. Healy, Semiconductor optical fibres: progress and opportunities, Laser Photonics Rev. 8 (1) (2014) 53–72, https://doi.org/10.1002/ lpor.201300016.
- [18] A.C. Peacock, N. Healy, Semiconductor optical fibres for infrared applications: A review, Semicond. Sci. Technol. 31 (10) (2016) 103004, https://doi.org/10.1088/ 0268-1242/31/10/103004.
- [19] L. Shen, H. Ren, M. Huang, D. Wu, A.C. Peacock, A review of nonlinear applications in silicon optical fibers from telecom wavelengths into the mid-infrared spectral region, Opt. Commun. (2020) 125437, https://doi.org/10.1016/j.optcom.2020. 125437
- [20] P. Mehta, M. Krishnamurthi, N. Healy, N.F. Baril, J.R. Sparks, P.J. Sazio, V. Gopalan, J.V. Badding, A.C. Peacock, Mid-infrared transmission properties of amorphous germanium optical fibers, Appl. Phys. Lett. 97 (7) (2010) 071117, https://doi.org/10.1063/1.3481413.
- [21] J. Ballato, T. Hawkins, P. Foy, B. Yazgan-Kokuoz, R. Stolen, C. McMillen, N. Hon, B. Jalali, R. Rice, Glass-clad single-crystal germanium optical fiber, Opt. Express 17 (10) (2009) 8029–8035, https://doi.org/10.1364/OE.17.008029.
- [22] P. Wang, et al., Mid-infrared Raman sources using spontaneous Raman scattering in germanium core optical fibers, Appl. Phys. Lett. 102 (1) (2013) 011111, https://doi.org/10.1063/1.4773884
- [23] D.A. Coucheron, M. Fokine, N. Patil, D.W. Breiby, O.T. Buset, N. Healy, A.C. Peacock, T. Hawkins, M. Jones, J. Ballato, Laser recrystallization and inscription of compositional microstructures in crystalline SiGe-core fibres, Nat. Commun. 7 (1) (2016) 1-9, https://doi.org/10.1038/ncomms13265.
- [24] M. Ordu, J. Guo, G. Ng Pack, P. Shah, S. Ramachandran, M. Hong, L. Ziegler, S. Basu, S. Erramilli, Nonlinear optics in germanium mid-infrared fiber material: Detuning oscillations in femtosecond mid-infrared spectroscopy, AIP Adv. 7 (9) (2017) 095125, https://doi.org/10.1063/1.5003027.
- [25] Y. Liu, M. Sun, G. Tang, G. Qian, W. Liu, Z. Shi, W. Zhu, Q. Qian, S. Xu, Z. Yang, Multifunctional GeSe core fibers, Mater. Lett. 247 (2019) 193–196, https://doi.org/ 10.1016/j.matlet.2019.03.124.
- [26] J. Shi, F. Han, C. Cui, Y. Yu, X. Feng, Mid-infrared dielectric-metal-semiconductor composite fiber, Opt. Commun. 459 (2020) 125093, https://doi.org/10.1016/j. optcom/2019.125093
- [27] J. Ballato, T. Hawkins, P. Foy, R. Stolen, B. Kokuoz, M. Ellison, C. McMillen, J. Reppert, A.M. Rao, M. Daw, Silicon optical fiber, Opt. Express 16 (23) (2008) 18675–18683, https://doi.org/10.1364/OE.16.018675.
- [28] B.L. Scott, K. Wang, G. Pickrell, Fabrication of n-type silicon optical fibers, IEEE Photonics Technol. Lett. 21 (24) (2009) 1798–1800, https://doi.org/10.1109/LPT.
- [29] P. Mehta, N. Healy, N. Baril, P. Sazio, J.V. Badding, A. Peacock, Nonlinear transmission properties of hydrogenated amorphous silicon core optical fibers, Opt. Express 18 (16) (2010) 16826–16831, https://doi.org/10.1364/OE.18.016826.
- [30] J. Ballato, T. Hawkins, P. Foy, C. McMillen, L. Burka, J. Reppert, R. Podila, A. Rao, R.R. Rice, Binary III-V semiconductor core optical fiber, Opt. Express 18 (5) (2010) 4972–4979, https://doi.org/10.1364/OE.18.004972.
- [31] J.R. Sparks, R. He, N. Healy, M. Krishnamurthi, A.C. Peacock, P.J. Sazio, V. Gopalan, J.V. Badding, Zinc selenide optical fibers, Adv. Mater. 23 (14) (2011) 1647–1651, https://doi.org/10.1002/adma.201003214.
- [32] B.L. Scott, G.R. Pickrell, Fabrication of GaSb optical fibers, in: Processing and Properties of Advanced Ceramics and Composites V: Ceramic Transactions, vol. 240, p. 65, 2013.
- [33] G. Tang, Q. Qian, X. Wen, G. Zhou, X. Chen, M. Sun, D. Chen, Z. Yang, Phosphate glass-clad tellurium semiconductor core optical fibers, J. Alloy. Compd. 633 (2015) 1–4, https://doi.org/10.1016/j.jallcom.2015.02.007.
- [34] G. Tang, Q. Qian, K. Peng, X. Wen, G. Zhou, M. Sun, X. Chen, Z. Yang, Selenium semiconductor core optical fibers, AIP Adv. 5 (2) (2015) 027113, https://doi.org/ 10.1063/1.4908020.

- [35] G. Tang, Q. Qian, X. Wen, X. Chen, W. Liu, M. Sun, Z. Yang, Reactive molten core fabrication of glass-clad Se 0.8 Te 0.2 semiconductor core optical fibers, Opt. Express 23 (18) (2015) 23624–23633, https://doi.org/10.1364/OE.23.023624.
- [36] G. Tang, W. Liu, Q. Qian, G. Qian, M. Sun, L. Yang, K. Huang, D. Chen, Z. Yang, Antimony selenide core fibers, J. Alloy. Compd. 694 (2017) 497–501, https://doi. org/10.1016/j.jallcom.2016.10.043.
- [37] M. Sun, G. Tang, G. Qian, W. Liu, Z. Shi, D. Chen, Q. Qian, Z. Yang, In4Se3 alloy core thermoelectric fibers, Mater. Lett. 217 (2018) 13–15, https://doi.org/10. 1016/i.matlet.2018.01.050.
- [38] M. Sun, Q. Qian, G. Tang, W. Liu, G. Qian, Z. Shi, K. Huang, D. Chen, S. Xu, Z. Yang, Enhanced thermoelectric properties of polycrystalline Bi2Te3 core fibers with preferentially oriented nanosheets, APL Mater. 6 (3) (2018) 036103, https://doi. org/10.1063/1.5018621.
- [39] B. Scott, K. Wang, V. Caluori, G. Pickrell, Fabrication of silicon optical fiber, 100501–100501-3, Opt. Eng. 48 (10) (2009), https://doi.org/10.1117/1.3250189.
- [40] D.-J. Won, M.O. Ramirez, H. Kang, V. Gopalan, N.F. Baril, J. Calkins, J.V. Badding, P.J. Sazio, All-optical modulation of laser light in amorphous silicon-filled microstructured optical fibers, Appl. Phys. Lett. 91 (16) (2007) 161112, https://doi.org/ 10.1063/1.2790079.
- [41] S. Chaudhuri, X. Ji, H.-T. Huang, T. Day, V. Gopalan, J. Badding, in: Small core SiGe alloy optical fibers by templated deposition, CLEO: Applications and Technology, Optical Society of America, 2017, p JW2A. 69, https://doi.org/10.1364/CLEO_AT. 2017.JW2A.69.
- [42] R. He, P.J. Sazio, A.C. Peacock, N. Healy, J.R. Sparks, M. Krishnamurthi, V. Gopalan, J.V. Badding, Integration of gigahertz-bandwidth semiconductor devices inside microstructured optical fibres, Nat. Photonics 6 (3) (2012) 174–179, https://doi.org/10.1038/nphoton.2011.352.
- [43] L. Lagonigro, N. Healy, J.R. Sparks, N.F. Baril, P.J. Sazio, J.V. Badding, A.C. Peacock, Low loss silicon fibers for photonics applications, Appl. Phys. Lett. 96 (4) (2010) 041105, https://doi.org/10.1063/1.3294630.
- [44] J. Ballato, E. Snitzer, Fabrication of fibers with high rare-earth concentrations for Faraday isolator applications, Appl. Opt. 34 (30) (1995) 6848–6854, https://doi. org/10.1364/AO.34.006848.
- [45] E.F. Nordstrand, A.N. Dibbs, A.J. Eraker, U.J. Gibson, Alkaline oxide interface modifiers for silicon fiber production, Opt. Mater. Exp. 3 (5) (2013) 651–657, https://doi.org/10.1364/OME.3.000651.
- [46] M. Ordu, J. Guo, B. Tai, M.K. Hong, S. Erramilli, S. Ramachandran, S.N. Basu, Midinfrared transmission through germanium-core borosilicate glass-clad semiconductor fibers, Opt. Mater. Exp. 7 (9) (2017) 3107–3115, https://doi.org/10. 1364/OME.7.003107.
- [47] J. Ballato, T. Hawkins, P. Foy, S. Morris, N. Hon, B. Jalali, R. Rice, Silica-clad crystalline germanium core optical fibers, Opt. Lett. 36 (5) (2011) 687–688, https://doi.org/10.1364/OL.36.000687.
- [48] X. Ji, R.L. Page, S. Chaudhuri, W. Liu, S.Y. Yu, S.E. Mohney, J.V. Badding, V. Gopalan, Single-crystal germanium core optoelectronic fibers, Adv. Opt. Mater. 5 (1) (2017). https://doi.org/10.1002/adom.201600592.
- [49] W. Wu, M.H. Balci, K. Mühlberger, M. Fokine, F. Laurell, T. Hawkins, J. Ballato, U.J. Gibson, Ge-capped SiGe core optical fibers, Opt. Mater. Exp. 9 (11) (2019) 4301–4306, https://doi.org/10.1364/OME.9.004301.
- [50] H. Tyagi, M. Schmidt, L.P. Sempere, P.S.J. Russell, Optical properties of photonic crystal fiber with integral micron-sized Ge wire, Opt. Express 16 (22) (2008) 17227–17236, https://doi.org/10.1364/OE.16.017227.
- [51] J.M. Senior, M.Y. Jamro, Optical Fiber Communications: Principles and Practice, Pearson Education, 2009.
- [52] M. Ordu, J. Guo, A.E. Akosman, S. Erramilli, S. Ramachandran, S.N. Basu, Effect of thermal annealing on mid-infrared transmission in semiconductor alloy-core glasscladded fibers, Adv. Fiber Mater. (2020) 1–7, https://doi.org/10.1007/s42765-020-00030-2.
- [53] L. Shen, N. Healy, L. Xu, H. Cheng, T. Day, J. Price, J.V. Badding, A. Peacock, Four-wave mixing and octave-spanning supercontinuum generation in a small core hydrogenated amorphous silicon fiber pumped in the mid-infrared, Opt. Lett. 39 (19) (2014) 5721–5724, https://doi.org/10.1364/OL.39.005721.
- [54] C. Hou, X. Jia, L. Wei, S.-C. Tan, X. Zhao, J.D. Joannopoulos, Y. Fink, Crystalline silicon core fibres from aluminium core preforms, Nat. Commun. 6 (1) (2015) 1–6, https://doi.org/10.1038/ncomms7248.
- [55] R. Bhargava, Infrared spectroscopic imaging: the next generation, Appl. Spectrosc. 66 (10) (2012) 1091–1120, https://doi.org/10.1366/12-06801.
- [56] P.R. Griffiths, J.A. De Haseth, Fourier Transform Infrared Spectrometry vol. 171, (2007), https://doi.org/10.1002/047010631X.
- [57] S. Song, N. Healy, S. Svendsen, U. Österberg, A.C. Covian, J. Liu, A. Peacock, J. Ballato, F. Laurell, M. Fokine, Crystalline GaSb-core optical fibers with roomtemperature photoluminescence, Opt. Mater. Exp. 8 (6) (2018) 1435–1440, https:// doi.org/10.1364/OME.8.001435.
- [58] L. Shen, N. Healy, P. Mehta, T. Day, J. Sparks, J.V. Badding, A. Peacock, Nonlinear transmission properties of hydrogenated amorphous silicon core fibers towards the mid-infrared regime, Opt. Express 21 (11) (2013) 13075–13083, https://doi.org/ 10.1364/OE.21.013075.
- [59] X. Ji, S. Lei, S.-Y. Yu, H.Y. Cheng, W. Liu, N. Poilvert, Y. Xiong, I. Dabo, S.E. Mohney, J.V. Badding, Single-crystal silicon optical fiber by direct laser crystallization, ACS Photon. 4 (1) (2017) 85–92, https://doi.org/10.1021/acsphotonics. 6b00584.
- [60] M. Kudinova et al., Hundreds of meter-long low-loss silicon-core optical fiber, in: Optical Components and Materials XVII, vol. 11276, International Society for Optics and Photonics, 2020, pp. 112760W, https://doi.org/10.1117/12.2544173.
- [61] Y. Zhou, S. Constantine, J. Gardecki, L. Ziegler, Dispersed ultrafast nonresonant electronic responses: detuning oscillations and near resonance effects, Chem. Phys.

- Lett. 314 (1-2) (1999) 73-82, https://doi.org/10.1016/S0009-2614(99)01079-9.
- [62] W. Wu, M. Balci, S. Song, C. Liu, M. Fokine, F. Laurell, T. Hawkins, J. Ballato, U.J. Gibson, CO₂ laser annealed SiGe core optical fibers with radial Ge concentration gradients, Opt. Mater. Exp. 10 (4) (2020) 926–936, https://doi.org/10.1364/ OME.390482.
- [63] S. Morris, T. Hawkins, P. Foy, J. Ballato, S.W. Martin, R. Rice, Cladding glass development for semiconductor core optical fibers, Int. J. Appl. Glass Sci. 3 (2) (2012) 144–153, https://doi.org/10.1111/j.2041-1294.2012.00085.x.
- [64] H. Ren, L. Shen, D. Wu, O. Aktas, T. Hawkins, J. Ballato, U.J. Gibson, A. Peacock, Nonlinear optical properties of polycrystalline silicon core fibers from telecom wavelengths into the mid-infrared spectral region, Opt. Mater. Exp. 9 (3) (2019) 1271–1279, https://doi.org/10.1364/OME.9.001271.
- [65] F. De Leonardis, B. Troia, R.A. Soref, V.M. Passaro, Modelling of supercontinuum generation in the germanium-on-silicon waveguided platform, J. Lightwave Technol. 33 (21) (2015) 4437–4444, https://doi.org/10.1109/JLT.2015.2474133.
- [66] A.N. Kolyadin, A.F. Kosolapov, A.D. Pryamikov, A.S. Biriukov, V.G. Plotnichenko, E.M. Dianov, Light transmission in negative curvature hollow core fiber in extremely high material loss region, Opt. Express 21 (8) (2013) 9514–9519, https:// doi.org/10.1364/OE.21.009514.
- [67] F. Yu, W.J. Wadsworth, J.C. Knight, Low loss silica hollow core fibers for 3–4 μm spectral region, Opt. Exp. 20 (10) (2012) 11153–11158, https://doi.org/10.1364/OE.20.011153.
- [68] F. Couny, F. Benabid, P. Roberts, P. Light, M. Raymer, Generation and photonic guidance of multi-octave optical-frequency combs, Science 318 (5853) (2007) 1118–1121, https://doi.org/10.1126/science.1149091.
- [69] F. Poletti, Nested antiresonant nodeless hollow core fiber, Opt. Express 22 (20) (2014) 23807–23828, https://doi.org/10.1364/OE.22.023807.
- [70] N. Healy, J. Sparks, M. Petrovich, P. Sazio, J.V. Badding, A. Peacock, Large mode area silicon microstructured fiber with robust dual mode guidance, Opt. Express 17 (20) (2009) 18076–18082, https://doi.org/10.1364/OE.17.018076.