GLASS-CLAD SEMICONDUCTOR CORE OPTICAL FIBERS

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ABSTRACT

Glass-clad optical fibers comprising a crystalline semiconductor core have garnered considerable recent attention for their potential utility as novel waveguides for applications in nonlinear optics, sensing, power delivery, and biomedicine.

As research into these fibers has progressed, it has become evident that excessive losses are limiting performance and so greater understanding of the underlying materials science, coupled with advances in fiber processing, is needed. More specifically, the semiconductor core fibers possess three performance-limiting characteristics that need to be addressed: (a) thermal expansion mismatches between crystalline core and glass cladding that lead to cracks, (b) the precipitation of oxide species in the core upon fiber cooling, which results from partial dissolution of the cladding glass by the core melt, and (c) polycrystallinity; all of which lead to scattering and increased transmission losses. This dissertation systematically studies each of these effects and develops both a fundamental scientific understanding of and practical engineering methods for reducing their impact.

With respect to the thermal expansion mismatch and, in part, the dissolution of oxides, for the first time to our knowledge, oxide and non-oxide glass compositions are developed for a series of semiconductor cores based on two main design criteria: (1) matching the thermal expansion coefficient between semiconductor core and glass cladding to minimize cracking and (2) matching the viscosity-temperature dependences, such that the cladding glass draws into fiber at a temperature slightly above the melting point of the semiconductor in order to minimize dissolution and improve the fiber draw
process. The \( x[Na_2O:Al_2O_3] + (100 - 2x)SiO_2 \) glass compositional family was selected due to the ability to tailor the glass properties to match the aforementioned targets through slight variations in composition and adjusting the ratios of bridging and non-bridging oxygen; experimental results show a decrease in fiber core oxygen content in the fibers drawn with the tailored glass composition.

In a further attempt to reduce the presence of oxide species in the core, a reactive molten core approach to semiconductor optical fibers are developed. Specifically, the addition of silicon carbide (SiC) into a silicon (Si) core provides an \textit{in-situ} reactive getter of oxygen during the draw process to achieve oxygen-free silicon optical fibers. Elemental analysis and x-ray diffraction of fibers drawn using this reactive chemistry approach show negligible oxygen concentration in the highly crystalline silicon core, a significant departure from the nearly 18 atom percent oxygen in previous fibers. Scattering of light out of the core is shown qualitatively to have been reduced in the process.

The role of the cross-sectional geometry on the resultant core crystallography with respect to the fiber axis is explored in a continued effort to better understand the nature of the crystal formation and structural properties in these semiconductor core optical fibers. A square cross-sectional geometry was explored to determine if core non-circularity can enhance or promote single crystallinity, as the semiconductors studied have a preference to form cubic crystals. Resultant crystallography of the non-circular core showed a significant improvement in maintaining a preferred crystallographic orientation, with the square core fibers exhibiting a 90% preference for the \( < 1 1 0 > \)
family of directions occurring closest to the longitudinal direction of the fiber. The ability
to orient the crystallography with respect to the fiber axis could be of great value to future
nonlinear optical fiber-based devices.

In summary, this dissertation begins to elucidate some of the microstructural
features, not present in conventional glass optical fibers, which could be important for
future low-loss single crystalline semiconductor optical fibers. Additionally, this
dissertation offers novel insight into the various aspects of materials science of non-
conventional glass optical fibers, such as crystallization and solidification under highly
non-equilibrium and confined conditions, phase equilibria and in-situ reactions, and the
interplay between thermodynamics and kinetics.
DEDICATION

This dissertation is dedicated to the following people, to whom I am greatly and forever indebted:

To my parents, my sister, and my grandparents: Your never-ending support, encouragement, faith, confidence and unconditional love provide the backbone to my life. Thank you for always believing in me.

To my friends: Your support, commiseration, encouragement, and shared laughter and tears along the way have made this dissertation possible.

To the many baristas who have fueled the past four years of my life.

To Ella, Jackson and Hunter.
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CHAPTER ONE

INTRODUCTION

Whether seeking to explain the physical, as did Huygens in 1690 [1], Newton in 1704 [2], and Maxwell in 1873 [3], or routes to truth and enlightenment, as did Shakespeare in 1598 (“Light, seeking light, doth light of light beguile”) [4], light has always fascinated us.

Beyond the physical, metaphysical, and poetic, light is immensely useful and central to modern life, as detailed in the recent report “Optics and Photonics, Essential Technologies for Our Nation,” published by the National Research Council of the National Academies [5]. For example, photonics enables about $7 trillion in global products, equivalent to about ⅓ of the Gross Domestic Product (GDP) of the United States. The European Physical Society, representing the 41 National Physical Societies in Europe, is coordinating a proposal, enthusiastically supported by UNESCO, for the proclamation by the United Nations for an International Year of Light in 2015.

The technological utility of light is remarkably broad, so, for the purposes of this Dissertation, the focus is on one subset, that relating to optical fiber. Beyond the awarding of the 2009 Nobel Prize in Physics to Dr. Charles Kao "for groundbreaking achievements concerning the transmission of light in fibers for optical communication," present and future demands for information have caused a dramatic shift from long haul and regional deployments to broadband. As a result, optical fiber production is projected to increase from about 150 million kilometers of fiber at present to well over 200 million kilometers per year by 2017 [6].
While the vast majority of this fiber will be for “conventional” telecommunication applications, there is a growing need for specialized optical fibers; i.e., those providing greater or enhanced functionality. The driver for higher performance rests in the nature of specific applications. For example: (1) fibers are being deployed deep into the earth to sense for gas and oil where the temperatures, pressures, and chemical environment are quite extreme [7], (2) fibers are gaining a strong foot-hold in high energy laser systems where optical nonlinearities such as stimulated Brillouin scattering (SBS) are a present limitation to continued power-scaling [8], and (3) all-optical signal processing, no longer just amplification, in optical communication systems is motivating work into more highly nonlinear glasses [9].

In order to realize enhanced performance from fibers, two general trends have emerged. The first, historically, were new materials that possessed properties not available in conventionally optical glasses like silica. Examples include fluoride glasses for reduced losses and more efficient emissions from active dopants or tellurite and chalcogenide glasses for extended infrared transparency and stronger optical nonlinearities (e.g., strong nonlinear refractive index, $n_2$). The second, somewhat more recent, trend has been to accept the material limitations of silica and focus instead on inducing optical behaviors through the microstructure. Examples of such microstructural engineering are microstructured optical fibers (MOFs) or photonic crystal fibers (PCFs) where periodic combinations of silica rods and tubes are constructed and drawn into fiber such that the periodicity in refractive index controls various aspects of the electromagnetic mode propagating down the fiber. Such MOFs and PCFs can exhibit
marked changes to the fiber’s dispersion, nonlinearity, and spectral loss even though it is still, materially, silica.

The focus of this dissertation is to suggest and support a third option: novel fibers from not-so-novel materials and a return to simplicity. Specifically, the sections that follow will summarize recent developments in the use of materials that are new with respect to optical fibers but not new to the broader materials community; materials such as silicon and germanium. They are commodity materials in their own right but novel and non-obvious materials with respect to optical fibers.

1.1 Fabrication Approaches

Over the years, several methods have been implemented for fabrication of optical fiber from nontraditional and dissimilar core and clad materials, each with their own distinct advantages and disadvantages. Early techniques include the Taylor wire method [10, 11], which implements fast quenching rates to create glass-coated metal wires in a relatively inexpensive manner. The Wollaston wire approach also has been used to generate fibers from differing core and cladding materials, particularly those exhibiting steep viscosity-temperature behaviors [12]. This method allows for the use of materials that otherwise would have a tendency to devitrify, such as fluorozirconate glasses. However, care must be taken to ensure that materials are matched so that the chemically aggressive fluorozirconate melt does not attack the cladding glass, and that their reasonably high vapor pressures are accounted for. A “core-suction” technique has been used to fabricate preforms with multicomponent glass cores by melting and drawing-up
the core glass melt into a cladding tube under vacuum [13, 14]. The core material must necessarily melt at a lower temperature than the cladding tube material. With respect to crystalline fibers, laser heated pedestal growth (LHPG) and micro-pull-down techniques have been well-studied and used with increasing success [15]. However these methods are generally slow in the grand scheme of fiber fabrication methods (e.g., draw) and it can be difficult to achieve a high quality core/clad interface.

An alternative approach to be detailed now is the molten core method, which allows for the direct fiberization of a range of unconventional core materials, either amorphous or crystalline. Additionally, it is a versatile and practical approach to obtaining long lengths of optical fiber. In general, a precursor core phase is sleeved inside a tube; this tube serves as the cladding glass (Fig. 1.1). At the temperature where the cladding glass tube draws into fiber, the core precursor phase is molten. As the cladding glass draws into fiber, the fluent core melt inevitably conforms to the geometry of the inner surface of the cladding tube and ultimately solidifies as the fiber subsequently cools. Originally developed as a means to make all-glass fiber with core compositions not stable enough against crystallization to permit their fabrication into conventional preform geometry and to subsequently draw[16], the molten core method is a direct method to make long lengths of fiber from a simple preform and from a range of common materials such as Si, Ge, YAG (Y$_2$Si$_3$O$_{12}$), and Al$_2$O$_3$ [17].
While the process is straightforward, the materials science of what happens during this process is not. In general, one has a melt (core) in contact with a soft glass (clad); the two necessarily interacting via dissolution and subsequent diffusion. Being a thermally activated process, the higher the draw temperature, the greater the amount of dissolution and shift in composition from precursor phase to final core phase. This is both a blessing and a curse, depending on what is desired in and of the fiber. Let us take a few examples:

1.1a Novel All-Glass Crystal-Derived Optical Fibers

Technically, as long as the initial core phase is molten at the draw temperature, there is no reason any particular phase cannot be used. However, practical considerations do tend to limit selection, such as restricting materials that possess high vapor pressures,
which can (and do…) blow out the softened glass cladding tube during the draw. That said, whether the initial core phase is a glass, single crystalline, polycrystalline or powder is immaterial as long as it melts at the draw temperature. In the latter case of powders, one does have to concern themselves with removal of the bubbles in the melt resulting from the porosity of the powder.

Starting with crystalline core phases does have an advantage over amorphous materials in that one can begin with phases that could not otherwise be made into glass. Two exemplars of this are YAG-derived [18-22] and sapphire-derived [23] optical fibers fabricated using the molten core approach. Yttria and alumina additions to silica have been shown to greatly reduce Brillouin gain which thereby lessens the potential for stimulated Brillouin scattering (SBS) in optical fibers. SBS is a principal limitation in high power fiber lasers and high capacity telecommunication systems. However, both the Y$_2$O$_3$-SiO$_2$ and Al$_2$O$_3$-SiO$_2$ systems show liquid-liquid immiscibility in the melt that generally restricts the range of compositions obtained to very high silica contents. However, in both cases, silica dissolves in from the (pure silica) cladding glass at the ~2000 °C draw temperature, promoting the formation of yttrium aluminosilicate (for YAG-derived) or aluminosilicate (for sapphire-derived) glass cores, given the high quench rates of the drawn optical fibers. In these cases, the resultant core glasses contain much higher Y$_2$O$_3$ and Al$_2$O$_3$ concentrations than would otherwise be possible, opening the door to novel fibers from common materials (just not common when it comes to optical fibers). For example, the YAG-derived fibers with high yttria and alumina contents have shown cooperative up-conversion and photodarkening. As another
example, the sapphire-derived fibers possess alumina concentrations up to about 54 mol%, which is the highest alumina concentration reported for a silicate glass not made using more extreme methods like melt levitation. By comparison, given the immiscibility and time/temperature requirement on conventional modified chemical vapor deposited optical fiber preforms, alumina contents typically are limited to about 8 mol%. It is further worth noting that the melt viscosity increases and liquidus temperature decreases as the alumina melt dissolves the silica cladding glass, further hindering the phase-separation of the high alumina-content core glass. The sapphire-derived high alumina-content aluminosilicate glass optical fibers have shown the lowest reported Brillouin gain coefficient; nearly 100 times lower than conventional silica fibers. These selected aluminosilicate compositions were also found to be Brillouin athermal (i.e., the Brillouin frequency does not change with temperature), permitting novel sensor and laser systems whose Brillouin performance is immune to changes in temperature. There also are compositions that conceivably could exhibit zero Brillouin scattering, so called zero Brillouin activity (ZeBrA) fibers. The molecular origins of zero Brillouin, hence zero photoelasticity, glasses is under study and could be exceedingly useful to future fiber-based laser and communication systems.

1.1b Novel Glass-Clad Crystalline-Core Optical Fibers

The aforementioned approaches have been used with varying levels of success to make fibers from various glasses (fluorides, tellurites, chalcogenides) and crystals (metallic and oxide). Semiconductors represent another class of materials that have had a
profound impact in electronic and optoelectronic applications. Indeed, silicon photonics is a rapidly growing area of global interest [24] and the extension of semiconductors to optical fiber formats would open up entirely new opportunities. As noted above, it is reasonable to expect that molten core derived fibers possess amorphous cores given the quench rates of the drawn fibers. It was therefore especially nonobvious when the process was applied to realize long-lengths of glass-clad fibers with (poly)crystalline cores. This has been applied to technologically important unary and binary semiconductors including silicon (Si), germanium (Ge), and indium antimonide (InSb). The field of semiconductor optical fiber, though nascent, has generated considerable attention recently and relies on several principle fabrication methods.

The first, specific to Group IV semiconductors, is a high pressure microfluidic chemical deposition of the semiconductor inside a silica microstructured optical fiber [25-29]. In general, CVD techniques utilize gaseous precursors that undergo vapor-phase chemical reactions that yield a different (solid) material. In conventional silica optical fibers, this is exemplified by the reaction: $\text{SiCl}_4^{(\text{gas})} + \text{O}_2^{(\text{gas})} \rightarrow \text{SiO}_2^{(\text{solid})} + 2\text{Cl}_2^{(\text{gas})}$. CVD processes rely on precursors that possess a suitable vapor pressure or chemical reactivity at a given temperature necessary to yield the desired material or phase. The semiconductor deposition is achieved by flowing a silane/helium mixture through the capillary hole at a temperature range where the material would remain amorphous, with subsequent annealing used to control the polycrystallinity of the silicon. Raman spectra of the silicon tubes was observed to be red-shifted with respect to that of single crystalline silicon due in part to effects of tensile strain induced at the silicon-silica
interface during cooling [30]. Optical transmission losses were determined for both amorphous and polycrystalline samples. High losses of around 50 dB/cm at 1550 nm were originally reported for the amorphous sample, and loss decreased with both increased annealing temperature and increasing wavelength for the polycrystalline samples. The lowest reported loss from these fibers was approximately 5 dB/cm at 1550 nm [31]. Subsequent efforts by this group as well as by the Erlangen–Nuremberg group have focused on the interesting optical and modal properties of high index semiconductor-filled photonic crystal and microstructured optical fibers; including large mode areas and optical multistabilities [32-34]. The advantages of this method are that it is sufficiently low temperature that either amorphous or crystalline semiconductors can be deposited as can layers of different semiconductors therein enabling in-fiber optoelectronic junctions. Additionally, the deposition can be done in silica MOFs with small core sizes. To date, silica-clad fibers with cores of amorphous or crystalline Si and Ge have been realized, as have ZnSe-based fibers.

For completeness, it is worth noting that semiconductor optical fibers also have been made using a powder-in-tube method [35, 36] as well as a melt-infiltration approach [37]. The powder-in-tube method, employed by Virginia Tech to fabricate silicon core optical fibers, involves packing silicon powder into a silica tube on which a vacuum is subsequently pulled in order to evacuate the preform therefore limiting silicon oxidation [35, 36]. Fibers produced by this powder-in-tube technique were drawn at around 1600 ºC and averaged an overall length of approximately 7 cm. Based on electron dispersive spectroscopy (EDS) results, both silicon and oxygen were present in the cladding
material but only silicon was present throughout the core. High optical losses were reported, which were attributed to irregularities, such as thermal expansion induced micro-cracks, at the boundary between the core and the cladding materials. Electron backscatter diffraction (EBSD) confirmed several crystalline orientations along the fibers, as well as the presence of large grained polycrystallinity along the fiber axis. Efforts at the Massachusetts Institute of Technology have focused principally on optical fibers comprising an amorphous chalcogen-based semiconductor that can be co-processed with high glass transition-temperature polymers. This approach also permits the inclusion of other optical and electronic materials and enables a wide range of optoelectronic properties and responses [38]. More recently, crystallinity has been induced in semiconducting Se regions by thermal and optical stimuli [39].

It is desirable to employ a route that fabricates the semiconductor core fiber in a single step and utilizes conventional fiber draw methods to enable the necessarily long lengths of fiber that would be required for practical commercial use based on an economy of scale. To this aim, our group at Clemson University utilized the aforementioned molten core method, which serves as the principle fabrication method of this Dissertation, where a rod of single crystalline or polycrystalline semiconductor is placed inside a cladding glass tube. The cladding glass is chosen such that the semiconductor core is molten at the temperature where the glass cladding is drawn into fiber. Essentially, the cladding glass serves as a crucible to confine the molten semiconductor as the glass crucible is drawn directly into optical fiber. While fibers fabricated to-date have been of more conventional designs, as shown in Fig. 1.2, there is nothing fundamentally limiting
about the approach that could not be applied to microstructured optical fibers akin to those of Refs. [26-28, 31-34, 40], though longer in length. Photonic crystal fibers with significantly smaller dimensions for the high refractive index semiconductor phase, such as those reported in Ref. [41], are likely not possible given diffusion-related issues that will be discussed in greater detail below.

Fig. 1.2 Electron microscope images of crystalline core optical fibers: a) silicon [42], b) germanium [43], and c) indium antimonide [44].

1.2 Applications

The development of optical fibers comprising a crystalline semiconductor core in a glass cladding potentially enables a number of interesting device applications. Semiconductor crystals are typically grown by one of several processes including, for example, the Czochralski, Bridgeman, and epitaxial methods, but in all cases, the growth process is slow and the size of the grown crystals tends to be somewhat limited. Nonlinear effects in crystalline materials tend to be proportional to the product of pump intensity and propagation distance, so many interesting device applications require long crystal lengths and small beam diameters. Hence, exploitation of the nonlinear optical properties of these crystals can require the growth of large crystals and complex fabrication techniques, and may additionally need sophisticated beam focusing optics.
The result is frequently high cost and limited availability. The recently demonstrated capability by our group at Clemson to draw long fibers having crystalline semiconductor cores by conventional and commercially accepted methods [42, 45] opens the possibility of achieving very long propagation distances in these materials while at the same time utilizing waveguide optical confinement to maintain high pump intensity. In addition, an optical fiber provides far better removal of dissipated heat from the beam than does a nonlinear optical device fabricated from a traditional bulk crystal, which promises higher operating power levels, better thermal stability and improved control of phase matching if required.

The unary semiconductors such as silicon, germanium, and perhaps selenium [39] and related elements, are characterized by high refractive index and large third order \( \chi_3 \) nonlinearity. The Raman gain coefficients in silicon and germanium are much higher than in silica or germanosilicate fiber cores. For example, the Raman gain coefficient for silicon is approximately \( 10^4 \) times greater than that of silica, which suggests that silicon core fibers might make excellent Raman amplifiers for the mid-wave infrared (MWIR) spectral region. Recent work in silicon single crystals and waveguides has demonstrated Raman lasing, amplification and beam clean-up in the 3–5 \( \mu \)m wavelength band of the MWIR [46, 47], which is an especially important spectral region. This band includes chemical absorption lines associated with the chemical precursors of weapons of mass destruction (WMD), and has very low solar and thermal background radiation. In addition, there are good atmospheric transmission windows in the 3–5 \( \mu \)m band that enable countermeasures against infrared countermeasure/ missile guidance seekers
(IRCM), laser radar and free space optical (FSO) communications. The impact of atmospheric turbulence on the propagation of free space laser beams is much less in this band than in the visible and near-infrared (NIR). Hence, crystalline optical fibers that can be used as oscillators and amplifiers in the MWIR have great potential utility. If transmission losses can be reduced sufficiently, they may also be useful as transmission fibers for high power applications such as IRCM.

Raman fiber amplifiers have also demonstrated the potential to combine multiple pump beams and amplify a single mode beam at the Stokes wavelength [48]. The Stokes shift in a crystal or glass is a material property related to the Raman-active phonons supported by the lattice. In silicon, this shift is about 520 cm$^{-1}$, and about 300 cm$^{-1}$ in germanium. The peak Raman gain occurs at a photon energy equal to the pump photon energy minus the Stokes shift, which enables tunable operation by tuning the pump wavelength. The Raman amplifier fiber may be cladding pumped by multiple multi-mode pump lasers in a dual clad fiber (DCF) configuration [49], just as in a conventional rare earth (RE) doped DCF amplifier fiber. The promise of a silicon or germanium fiber Raman amplifier is a dramatic reduction in fiber length, and a large increase in average output power. In germanium, the transmission window extends well past 10 µm, enabling beam combining with CO, CO$_2$ and LWIR quantum cascade lasers (QCL). It may even be feasible to use germanium fibers as THz waveguides given the low loss of this crystal in the THz region. The losses in semiconductor core fibers depend on the levels of unintentional dopants and impurities that become incorporated in the crystal core as the
fiber is drawn; if those levels can be controlled, low attenuation should be feasible (e.g., 0.1–0.001 m\(^{-1}\)).

The transmission and phase of light propagating in a crystalline semiconductor core fiber can be modulated by absorption of pump light propagating in the cladding and having a photon energy greater than the semiconductor bandgap energy. Photo-carriers induced by pump light absorption in the fiber core change its refractive index, thereby producing optical phase modulation of the transmitted signal, and at a sufficient density, can absorb the signal, thereby producing amplitude modulation of the transmitted signal. In a related application, the induced photo-carriers can transform the fiber core from a non-conducting to a conducting state. The potential application for such a photoconducting fiber is as an antenna similar to a plasma antenna that has no radar cross section (RCS) in the absence of optical pumping, but can be instantly reconfigured [50].

With the recent demonstration of a crystalline binary semiconductor (InSb) core optical fiber, new possibilities for nonlinear devices are enabled [44]. With a compound semiconductor such as InSb, InP or GaAs, the unit cell lacks a center of symmetry, so that a second order \(\chi^2\) optical nonlinearity is possible. In fact, GaAs is used as a parametric amplifier gain medium for the MWIR in the quasi-phase matched (QPM) configuration. Most applications of \(\chi^2\) materials require phase matching among the interacting waves, so some technique must be devised to enable this process in the semiconductor core optical fiber. This has not yet been demonstrated to our knowledge in such fibers, but there are methods based on poling techniques that have induced quasi-phase matching condition in silica-based glass fibers [51].
Another application of potential importance is as an IR laser ion host such as Cr$^{2+}$ and Fe$^{2+}$ in ZnSe. The cubic phase of ZnSe possesses the same zincblende structure type as cubic InSb (space group F -43 m). Interestingly, these binary systems might open the door to ternary and quaternary semiconductor core fibers since they can be amenable to solid solutions. For example, the Si–Ge system is well known [52, 53] and enables a tailorability of electronic and optical properties between the Si and Ge end-members. So too do the In–Ga–Sb ternary [54] (InSb–GaSb) or Ga–In–As–Sb quaternary [55] (InSb–GaSb–GaAs) systems.

Some crystals such as GaAs, ZnS, and ZnSe will have other fiber fabrication issues such as high vapor pressure at the drawing temperature, core-cladding expansion mismatch, or sensitivity to contamination by glass cladding material that will be quite difficult to overcome. In these cases, the aforementioned chemical vapor deposition approaches might be useful for short lengths of fiber [26]. The benefit of fibers comprising doped crystalline cores with glass cladding will be high gain, narrow gain spectra, and excellent thermal conductivity. This will enable short fibers for reduced nonlinear effects when desired (SBS, SRS, FWM, etc.), and could potentially reduce the cost of diode pumped crystal host lasers drastically.

1.3 Crystallinity and Crystallography

A significant number of X-ray diffraction studies have been carried out in order to characterize the core crystallinity of the molten core-derived optical fibers drawn in initial attempts. In the simplest experiments, powder X-ray diffraction was used to
identify whether the core was crystalline or amorphous, and determine the phase purity of the core material. Initial expectations were for the cores to be amorphous given the highly non-equilibrium conditions under which fibers are drawn. The X-ray diffraction patterns of these fibers are shown in Fig. 1.3. In all cases and under all draw conditions, the unary (Si [42], Ge [45]) and binary (InSb [44]) semiconductor fiber were found to be highly crystalline and phase pure. Given that there are no extraneous peaks in the diffraction patterns, any oxygen present indicated by elemental analysis (Fig. 1.4) is likely present as an amorphous oxide precipitate or another amorphous non-equilibrium phase.

Fig. 1.3. Powder X-ray diffraction patterns of semiconductor fibers. Intensities are offset for clarity.

Elemental profiles for the silicon and germanium core optical fibers are shown in Fig. 1.4a. As an initial expedient, silica glass was used as the cladding for the silicon core
fiber and DURAN®, an alkali borosilicate glass, was used for the germanium core fiber. Silicon melts at about 1414°C whereas silica draws at about 1950°C. While it would be preferred that the draw temperature better match the core melting point, silica is high strength, commercially available, and proves the concept. Germanium melts at about 938°C whereas DURAN draws at about 1000 °C. In this case, a much better thermal match is realized. In each case, oxygen is present in the core and is found to increase with decreasing core size (Fig. 1.4b). The most likely source of this oxygen is dissolution of the cladding glass by the core melt.

Fig 1.4. (a) Comparison of the elemental profiles, most notably oxygen content, between the silicon and germanium core optical fibers (a relative distance of zero denotes the core/clad interface) and (b) the change in silicon and oxygen content in the core of the molten core-derived silica-clad silicon core optical fiber as a function of core diameter.

The nature of the crystallinity in the Ge, Si and InSb core fibers was examined using single crystal X-ray diffraction. Given the rapid rate of crystallization associated with the fiber draw process, an especially interesting question is whether these crystal-core optical fibers contain significantly large regions of single crystalline material and, if
so, what crystallographic orientations can be resolved. A convenient technique for tracking crystallite orientations as a function of position along the longitudinal direction of the fiber was developed and permits the direct measurement of crystal domain size and polycrystallinity in regions where more than one crystallographic orientation is present in close proximity (i.e., within the 0.5 mm beam diameter of the collimated X-rays) [56].

While each of the crystalline core semiconductor fibers studied thus far has proven to be polycrystalline with respect to the entire length of fiber (ranging from several meters to over 200m of single length continuous fiber), they do exhibit localized single crystalline regions with the total amount and maximum lengths of these regions varying for each semiconductor core material. For example approximately 85% of the Ge fiber studied exhibited this localized single crystallinity (i.e., only one crystallographic orientation was observed in a given 0.5 mm increment), and a given orientation was observed to persist for lengths up to 15 mm before an entirely new crystallographic orientation was encountered. The Si fiber had localized single crystallinity at approximately 67% of the positions studied, but here the longest persisting domain was limited to about 5 mm. It is possible that these differences are related to the slightly higher oxygen content in the Si-core fiber (17 atom% or, equivalently, 10.4 weight%) versus the Ge-core fiber (6 atom% or, equivalently, 1.4 weight%) since amorphous oxide precipitates present in such concentrations could conceivably interrupt continuous growth of the semiconductor core by providing secondary nucleation sites. However, it remains remarkable that such large single crystalline domains are observed given the geometrical strain imposed by the cladding glass and extremely rapid crystallization rates inherent to
the drawing process. The InSb fiber did not exhibit such crystallographic organization, as only 10% of the positions studied on that fiber could be resolved as single crystal grains. These grains were limited to sizes below 2 mm. Interestingly, the InSb fiber also possessed a significantly higher oxygen content, nearly 40 atom% (≈9 weight%), further suggesting there may be some correlation between oxygen content (or perhaps structural complexity of the semiconductor) and polycrystallinity in the core in this sampling of fibers.

Given the long-range polycrystallinity observed in these semiconductor fibers, it was also sought to understand the nature of the changing crystallographic orientations in each by aligning the longitudinal direction of the fiber in a reference position and determining the rotation and tilting angles required to bring a crystallographic direction of interest into that same reference position. At no point in any of these X-ray studies of the semiconductor fibers did the unit cell axes, face diagonals or body diagonals directly correspond to the longitudinal direction of the fiber. However, the empirical observation is that the longest single crystal grains were generally those where crystallographic directions in the {1 0 0} and {1 1 0} families of orientations were aligned within 5–25° of the longitudinal fiber [56]. Even in these longest single crystalline regions there was a small but observable misorientation that caused the crystallographic alignment of the core to shift by a few degrees over the entirety of the region. The transition between neighboring regions having different orientations usually occurred over distinct grain boundaries where an immediate change in the diffraction pattern was observed.
Fig. 1.5 is a representative example of the changing orientation as a function of position in two adjacent regions in a continuous length of the Ge semiconductor fiber showing both the gradual misorientation (from 0 to 15 mm and 16 to 21 mm) and the abrupt orientation change across a grain boundary (between 15 and 16 mm). The diffraction patterns at the grain boundaries were especially complex (such that reliable unit cell parameters could not be determined) consisting of contributions from both neighboring regions. The presence of distinct grain boundaries was also verified visually in the crystalline cores of side-polished samples using electron microscopy [56].

![Graph showing tilting component of crystallographic orientation](image)

**Fig. 1.5.** Tilting component of the crystallographic orientation relative to the longitudinal direction of the fiber in a continuous 21 mm length of Ge semiconductor core optical fiber.
Occasionally the transition between regions of differing orientations was more subtle, in the form of related twinned crystals. Here, twinning would occur along certain crystallographic directions that would remain essentially unchanged as a function of position along the fiber while the remaining directions would invert their orientation from one twin region to the other (for example, in two twins sharing a common angular orientation for the [1 0 0] axis, the angular orientation of [0 1 0] in one twin would be identical to the angular orientation of [0 0 1] in the adjacent twin region). This particular polycrystallinity was observed in both the Si and Ge fibers. Such twinning could not be resolved in the InSb fiber, probably due to the greater propensity toward polycrystalline regions comprised of a large number of small crystallites within the diameter of the X-ray beam.

1.4 Thermodynamic and Kinetic Interplay

Crystalline core fibers, particularly those fabricated by the molten core approach, raise a series of intriguing fundamental scientific questions. Further, as is shown in Table 1.1, conventional methods for growing crystals employ growth rates that range from mm/day (e.g., hydrothermal) to mm/min (e.g., laser-heated pedestal growth). The molten core-derived crystalline core optical fibers are fabricated at rates of meters per second, which are about $10^3$ times faster than LHPG and over $10^6$ times faster than hydrothermal methods also employed by nature. This begs the inevitable question: where does thermodynamics end and kinetics take over?
Table 1.1. Relative growth rates for various crystal growth processes

<table>
<thead>
<tr>
<th>Crystal Growth Technique</th>
<th>Growth Rate</th>
<th>Relative Rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrothermal</td>
<td>&lt;mm/day</td>
<td>1</td>
<td>26</td>
</tr>
<tr>
<td>Czochralski</td>
<td>mm/h</td>
<td>~25</td>
<td>27</td>
</tr>
<tr>
<td>Micro-pull down</td>
<td>≤mm/min</td>
<td>~1000</td>
<td>28</td>
</tr>
<tr>
<td>Laser heated pedestal growth (LHPG)</td>
<td>~mm/min</td>
<td>~1500</td>
<td>30</td>
</tr>
<tr>
<td>Molten core (cane; i.e., thick fiber)</td>
<td>m/min</td>
<td>&gt;1,500,000</td>
<td>42</td>
</tr>
<tr>
<td>Molten core (fiber; i.e., thin fiber)</td>
<td>≤m/s</td>
<td>&gt;20,000,000</td>
<td>43</td>
</tr>
</tbody>
</table>

The high degree of crystallinity and phase purity from the molten core fibers shown in Fig. 1.3 implies that thermodynamics still dominates even at these rapid quench rates. It is additionally worth-noting that, unlike all other conventional crystal growth methods, the crystallization of the core proceeds without a nucleating seed crystal. In other words, upon cooling the fiber as it transitions down the draw tower, there must be a spontaneous nucleation event from which the core crystal coherently solidifies. This would indicate a range of fiber draw speeds and temperatures where crystallization cannot just occur, but can occur over long distances. The results of Fig. 1.5 show that this can be an impressively long range given the draw speeds, though an exhaustive evaluation of this has not been performed to-date. If one, perhaps naively, assumes that the rate of crystallization of an amorphous material is roughly equivalent to the critical velocity for amorphization, then draw speeds on the order of 18 m/s might be possible for silicon [57]. In other words, draw speeds to date, albeit very fast for conventional crystal
growth, might not be near the fundamental upper limits. This suggests an additional advantage of molten core-derived fibers over the other semiconductor core fiber fabrication approaches, which is that long continuous lengths can be made at industry-relevant manufacturing rates.

Given the oxygen content measured in the fiber, likely arising from dissolution of the cladding glass into the core melt during the draw, the Si–O [58] and Ge–O [59] phase diagrams are instructive. While silicon and germanium are similar in many ways, their phase diagrams with respect to oxygen are different in several important ways. Above the liquidus, at the oxygen concentrations measured in the fibers, the stable phases in the Si–O system are liquid and vapor [58] whereas, for the Ge–O system, there is only liquid (though there is indication of liquid–liquid immiscibility) [59]. This suggests that the core melt in the case of silicon optical fiber has vapor, i.e., bubbles, that form during reactions with the oxide cladding glass, which have to be fined through the melt if continuous bubble-free lengths of fiber are to be realized. Bubbles in the drawn fiber have not been encountered, though they might evolve during the processing. The presence of only liquids above the liquidus in the case of the germanium optical fibers is a natural benefit of this system, from a thermodynamic perspective, relative to the case of silicon. However, if indeed there is a liquid–liquid immiscibility, depending on the dimensions of the heterogeneities, this could lead to increased optical scattering in the solidified fibers. A second important difference between the Si–O and Ge–O phase equilibria is that, in the case of Si–O, the first solid to form upon cooling is the oxide (cristobalite) whereas, for the Ge–O system, the first solid to form is germanium. Germanium oxide is
also volatile at such high temperatures, and likely would fine out of the molten core, given the low melt viscosity of germanium. This suggests that the thermodynamics of the Ge-O system favor a self-purification in the melt phase [60, 61]. For silicon, the oxide precipitates form first and may have a longer time to grow in size as opposed to the germanium fiber, where the oxides remain as a liquid. The SiO₂ precipitates not only likely cause increased optical scattering but also (along with being in greater concentration) might act as nucleating sites which limit the coherent crystallization of the silicon; possibly also contributing to the aforementioned trend that the polycrystalline grain size in the silicon core fibers is generally less than that in the germanium core fibers. It is worth-noting that both silicon and germanium are anomalous liquids; that is, like water, the density of the melt is higher than the density of the solid and so the solid floats atop the melt [62, 63]. This possibly facilitates consistent fiber draw since any unmelted core material rises to the top of the preform, and only the fluent liquid transitions through the next-down region.

Another interesting feature found in Fig. 1.4a is the flat elemental profile of the core. Typically drawn optical fibers show compositional profiles that follow a diffusion-related trend [64]. The flat profile found in the molten core-derived fibers is believed to be due to convective flows in the low viscosity molten core at the draw temperatures. The convective flows, very possibly turbulent based on the Rayleigh and Prandtl numbers for semiconductor melts [61], are driven by multiple gradients: (a) a chemical gradient arising from the dissolution of the cladding at the core/clad interface, (b) a thermal gradient arising from the finite size of the heat zone inside the draw furnace, and (c) a
flow-induced gradient arising from the transition of the preform into fiber at the neck-down region. It is reasonable to expect that these gradients, particularly the flow of the molten core through the neck-down region, facilitate homogenization and yield the observed cross-sectional constancy of the core composition. Another benefit of the low melt viscosity of the silicon and germanium is that they should flow during the draw process and take the shape of the container (i.e., the glass cladding) leading to good continuity along the length.

For completeness, it is also worth noting that the oxide precipitates believed to be the main source of oxygen measured in the fibers are not identifiably crystalline. So while the semiconductors crystallize and are “thermodynamic”, the oxides are amorphous, hence kinetically hindered. Several other intriguing features of silicon and germanium melts that may contribute to their crystallization during molten core fiber fabrication are high thermal conductivity and diffusivity [61], which might hasten the removal of heat and contribute to the coherent solidification that results in high degrees of crystallinity and relatively large grain sizes.

This dissertation aims to identify some of the microstructural features that could be important for future low-loss single crystalline semiconductor optical fibers and to advance the current state of knowledge by fabricating such novel optical fibers via the conventional molten core technique. In addition, this dissertation offers novel insight into the various aspects of materials science of non-conventional semiconductor core glass-clad optical fibers, such as crystallization and solidification under highly non-equilibrium
and confined conditions, phase equilibria and in-situ reactions, and the interplay between thermodynamics and kinetics.


CHAPTER TWO

INFLUENCE OF CORE GEOMETRIES

Glass (i.e., silica) optical fibers generally possess cores of circular cross-section that are natural byproducts of the various chemical vapor deposition processes used in their fabrication. Additionally, cores of circular cross-section facilitate low-loss splicing and connectorization, and the modal properties of cylindrical waveguides have been well established for many years [1]. However, since these semiconductors of interest, such as silicon and germanium, form cubic crystals, the core material to this point has essentially been forced to conform a proverbial square peg to a round hole. It has therefore been hypothesized that allowing the cubic crystal structures to preferentially conform to their preferred crystallographic geometry may prove beneficial to improving these semiconductor core fibers. While extensive modeling of heat flow, stress and strain, and applied external electromagnetic fields has been reported in the past for fiber cores of circular cross-section, relatively little work has been devoted to fiber cores of square symmetry. Such square silicon core fibers would be of interest for intriguing device applications in nonlinear optics, image relay, or enabling integration with planar optoelectronic circuits. The work in this section therefore focuses on the role that the geometry of the core can play on the crystallinity and crystallography of crystalline semiconductor core optical fibers.

More specifically, this Chapter focuses on the fabrication of silicon core optical fibers drawn using silica cladding tubes that possess either a conventional circular cross-
section or square cross-section. The underlying question posited here is whether or not the cross-sectional geometry of the core influences the crystallographic orientation of the crystalline Si core (with respect to the fiber axis). The elemental profiles, crystallinity, and crystallography of said round and square-core fibers are evaluated and discussed. Hypercircles, detailed in Appendix A, are employed as a convenient and simple approach to quantifying the degree to which the square-core preform maintains its geometry during subsequent fiber fabrication. While it is found that the square-core fiber is more similar mathematically to a round fiber than a pure square cross-section, the impact on crystallinity and crystallography is discernable.

High purity silica cladding tubes, purchased from VitroCom, Inc., with an outer diameter of 30 mm and inner diameter of either 3.2 ± 0.2 mm (round-core) or 3.2 ± 0.2 mm flat-to-flat (square-core) were employed in this work. Silicon rods of approximately 3 mm in diameter and 40 mm in length were placed into the silica cladding tubes and drawn into fiber at 1925°C using a carbon resistance furnace purged with argon. The target fiber diameter was 1 mm, yielding a core size of about 100 µm, and the draw speed was 1 meter/minute. Since this molten core approach yields a fluent melt that fills and accommodates the volume and geometry of the core tube [2], the use of a round silicon rod inside the square-core preform is of little consequence.

2.1 Electron Microscopy

Electron microscopy was performed using a Hitachi SU-6600 scanning electron microscope (SEM). Images were obtained under variable pressure at 20kV and a working
distance of approximately 10 mm. Elemental analysis was conducted under high vacuum, in secondary electron (SE) mode, using energy dispersive x-ray (EDX) spectroscopy in order to determine the elemental composition across the core and core/clad interface. Prior to any microscopy, the samples were polished to a 0.5 micrometer finish. Figure 2.1 provides electron micrographs of the as-drawn round- (Figure 2.1a) and square- (Figure 2.1c) core silicon optical fibers. As is evidenced by the images, clearly some rounding of the edges has occurred during the drawing of the square-core optical fiber.

Since the focus of this work is to determine if non-circularity of the core can enhance the single crystallinity of (cubic) crystalline core optical fibers, then a means to quantify the degree to which the core is round or square becomes necessary. For this purpose, Lamé curves (also known as hypercircles) are employed; see Appendix A for more detail. Based on measured dimensions using the electron microscope, the hypercurve exponent, $n$, was found to be 3 for the square-core optical fiber. While this value is mathematically closer to a circle ($n = 2$) than to a true square ($n = \infty$), the core shown in Figure 2.2d is more reminiscent of a square than the round-core optical fiber of Figure 2.2b; see Appendix A for a more detailed comparison of this feature.
Figure 2.1 Electron micrographs of round-core silicon optical fiber (a) with core region further magnified (b) and square-core silicon optical fiber (c) with core region further magnified (d).
Figure 2.2. (a) Schematic representations of selected hypercurves: $n = 2$ (ideal circle), $n = 3$ (square-core fiber treated in this work), $n = 10$ (square-core preform from which the square-core fiber was drawn), and $n = 100$ (an approximation to an idealized square, $n = \infty$). (b) Optical micrograph of initial square-core silica preform from which the square-core fiber was drawn with overlay of $n = 10$ hypercircle. (c) Electron micrograph of round-core silicon optical fiber with overlay of $n = 2$ (ideal circle) hypercircle. (d) Electron micrograph of square-core silicon optical fiber with overlay of $n = 3$ hypercircle.

It is worth noting that fibers which would increase the hypercurve exponent (i.e., possess a more square-core) could be fabricated, which could be beneficial both from the perspective of single-crystallinity as well as from the perspective of modal behavior. In the latter case, square-cores are somewhat analogous to round-cores in that they possess two degenerate orthogonal modes with no cutoff for the lowest order mode [3]. However,
as the dimensions deviate into either rectilinear or elliptical geometries, the modal properties can be quite different, [4] and potentially advantageous, in these fibers where strong nonlinearities are expected. To the best of our knowledge, no one has studied in detail the modal behavior of a fiber as a function of such a geometric continuum; i.e., mode curves as a function of hypercircle parameter, nor in such strongly guided fibers.

2.2 Crystallography

The crystallography of the silicon core in the as-drawn fibers was measured and analyzed in an equivalent manner to that reported previously, in Chapter 1, on germanium core optical fibers. Briefly, samples of approximately 2 cm in length were affixed to a goniometer and first aligned vertically (within 2° of the longitudinal axis) in the x-ray beam. A Rigaku AFC8S diffractometer equipped with MoKα radiation and a Mercury CCD area detector was used. The x-ray beam was collimated to a diameter of 0.5 mm. Upon centering, images were collected and a preliminary cubic unit cell was determined [5]. The crystallinity of the silicon core was determined using axial photographs with the fiber in its vertical orientation and, subsequently, in specific crystallographic orientations: [1 0 0], [0 1 0], [0 0 1], [1 1 0], [1 0 1], [0 1 1], [1 1 1], and [2 1 0]. The process of centering, screening, cell determination and axial orientation was repeated in 1 mm steps along the length of both the round- and square-core optical fiber.

Tilt (χ) and rotation (ϕ) angles relative to the original vertical fiber orientation, required to match the above crystallographic orientations, were recorded for each position along the length [6]. In order to ensure consistency in the determination of
crystallographic orientations, only the angular combination with the lowest positive $\chi$ angle for each direction was determined at each consecutive position along the fiber.

The round-core silicon fiber exhibited local single-crystallinity (at individual 1 mm positions) over about 70% of the length examined whereas this was closer to 90% in the case of the square-core fiber (see Figure 2.3). In both cases, the longest single crystalline length was found to be between 4 – 5 mm. The longest single crystal length in the square-core fiber (relative positions 3 – 7 mm) extended to the end of the fiber accessible for analysis so it is unclear exactly how long this grain was in its entirety. The results from the round-core fiber are consistent with those measured (not reported) on previous silica-clad crystalline silicon core optical fibers indicating that a more square cross-section promotes higher single-crystallinity.

The change in orientation between the two primary crystal grains observed in the square-core fiber appears to occur over a distinct grain boundary between the grains (at a relative position between 2 – 3 mm). Alternatively, in the round-core fiber there exists a longer region of polycrystallinity between 0 – 3 mm relative positions where many polycrystals coexist. A distinct grain boundary between two crystal grains also is observed between relative positions 7 – 8 mm in the round-core fiber.
Figure 2.3. (a) Representative drawing defining the tilt angle, \( \chi \), and the rotation angle, \( \phi \), necessary to orient a given (hkl) crystallographic plane for obtaining the axial photographs. Tilt angle required to align the given crystallographic orientation with the fiber axis: round (b) and square (c) core. Rotational angle required to align the given crystallographic orientation with the fiber axis: round (d) and square (e) core. Yellow boxes denote regions of polycrystallinity where a single orientation could not be uniquely determined. Black lines connecting equivalent crystallographic orientations across regions of polycrystallinity are intended only as a guide to the eye [6].
There is also an observed misorientation in the longest single crystal grains of both fibers studied, where the orientation gradually changes in small increments along the fibers’ lengths. For the square-core fiber, the maximum tilting misorientation was 1.2°, observed for the [0 0 1] and [1 1 1] directions, and the maximum rotational misorientation was 5.3°, observed for the [2 1 0] orientation. Average misorientation values for all directions were 0.9° in tilt angle and 2.8° in rotational angle. In the longest single crystal grain of the round-core fiber, more extensive misorientation was observed. A maximum tilting misorientation of 5.6° (for [0 0 1]) and a maximum rotational misorientation of 7.3° (for [0 1 0]) were observed. Average tilting and rotational misorientation values for all directions were 2.9° and 3.8°, respectively. Thus, not only does the square-core fiber exhibit more single crystalline behavior on the local scale than the round-core fiber, its longest single-crystal grain also shows less variation in its orientation over the fiber’s length than does a grain of comparable length in the round-core fiber.

As was also observed for a crystalline germanium round-core optical fiber [6], at no point in either the square-core or the round-core silicon fiber did a specific crystallographic direction correspond to the longitudinal direction of the fiber. Some combination of tilting and rotation was always required to move the crystallographic direction of interest into the reference (longitudinal) position. For the round-core germanium and silicon fibers, as well as the square-core silicon fiber, the closest orientations of interest were most often offset from the longitudinal direction by a tilting
angle of 5-15° (though sometimes up to 35°, as in the round-core fiber length shown in Figure 2.3b). Figure 2.4 summarizes, as a percentage of the fiber, which families of crystallographic directions were closest in tilting orientation to the longitudinal dimension of the fiber. While the sampling size is admittedly small for this preliminary study of the square-core fiber, the initial results could suggest an interesting feature of this core geometry.

![Graph showing crystallographic orientation](attachment:image.png)

**Fig. 2.4.** A comparison of the percentage occurrence of crystallographic axes closest in orientation to the fiber longitudinal axis for a crystalline germanium core optical fiber [7] and the round and square crystalline silicon core optical fibers treated in this work.

For the round-core silicon fiber, analyzed in 1 mm increments over approximately 60 mm, 30% was found to be polycrystalline, whereas 35% corresponded to the $<110>$
family of directions closest to the longitudinal direction of the fiber, 20% had the $<100>$ family closest to the fiber axis, and 15% favored the $<210>$ family of planes. This distribution differs only somewhat from what was observed in the round-core germanium fiber. Alternatively, the square-core Si fiber exhibited only about 10% polycrystallinity, with the remaining 90% having the $<110>$ family of directions closest to the longitudinal direction of the fiber. This striking preference for the $<110>$ orientations occurring closest to the longitudinal direction is a significant departure from what is observed in round silicon and germanium fibers, though further studies should be performed to examine these initial results in a broader context. For completeness it is worth noting that the core sizes, i.e., solidification cross-sections, were quite different in the case of the round-core silicon treated here and the round-core germanium fiber treated previously [6]. However, as noted above, the distribution of crystallographic orientations most closely aligned with the fiber axis was reasonably similar.

2.3 Optical Transmission

Transmission measurements were made at 1.3 $\mu$m in a manner equivalent to that described in Ref. [8]. The output beam was imaged under 20x magnification using an optical microscope and viewed with an IR viewer (Find-R-Scope 84499(A)-5) to ensure that the measured light was propagating in the core. The total attenuation, measured at 1.3 $\mu$m, was 7.4 dB/cm for the square core fiber and 7.8 dB/cm for the round core fiber, after subtracting Fresnel reflections. While difficult to ascribe these nominal attenuation
differences to the core geometry or resultant reduction in polycrystallinity, they are consistent with published losses in silicon optical fibers [9, 10], at a similar wavelength.

It is worth noting that the fibers treated here do still possess polycrystallinity, albeit reduced in the square core case with respect to the conventional round core optical fibers. It is known that grain boundaries, inevitably present in polycrystalline materials, induce gap-states that contribute significantly to attenuation [11]. Interestingly, Ref. 11 also details that amorphous semiconductors possess even higher losses than polycrystalline analogs, suggesting that such fibers are not the best route to low loss semiconductor core optical fibers.

Sub-bandgap radiation also is attenuated by free carrier absorption, which depends quadratically on wavelength and directly on carrier concentration and other semiconductor parameters [12, 13]. In addition to intrinsic band-to-band absorption, which requires photons more energetic than the bandgap, nonlinear two-photon absorption, which requires photons with more than half the bandgap energy, directly promotes carriers to the conduction band where they produce even further attenuation through free carrier absorption. There are various strategies for mitigating free carrier absorption, including operating the fibers at reduced or cryogenic temperatures and doping for semi-insulating conditions. Free carrier absorption has even been suppressed by an applied bias to sweep free carriers from the center of the beam in a silicon rib waveguide [14], though complex electrode structures might be difficult to implement in fibers.
It is not the intent of this Chapter to assert that core geometry is the singular solution to enhanced crystallinity and, therefore, reduced loss in these crystalline core optical fibers. Recent work [15], to be detailed later in this Dissertation, has shown that the annealing of silicon fibers can also greatly enhance single crystallinity. Accordingly, the continued optimization of these fibers will almost certainly rely on multiple factors that include, but are likely not limited to the influences of core geometry, annealing, and controlled doping. However, polycrystallinity and defects will almost certainly be reduced. Ultimately, though, the application will determine the requisite level of acceptable attenuation, which could require single crystallinity over centimeter length-scales (e.g., Raman amplifiers) or some polycrystallinity over meter length-scales (e.g., IR power transmission). The results presented here suggest strongly that fiber cross-section can facilitate greater single crystallinity in these crystalline core semiconductors.


CHAPTER THREE
EFFECTS OF TAPERING AND ANNEALING

For continued practical implementation of crystalline semiconductor core optical fibers, geometric and crystallographic control of the fiber and core phase, respectively, are important. In addition to core geometry design, post-annealing [1] or tailored time, temperature profiles/gradients, akin to zone-refining [2] but potentially performed in-situ during the fiber draw, may prove to be valuable tools to the continued evolution of crystalline semiconductor fibers into practical photonic and optoelectronic devices and applications. Rapid photothermal processing (RPP), using thermal energy, ultraviolet (UV) and vacuum ultraviolet (VUV) photons, was performed ex-situ to anneal silica-clad silicon core optical fibers in an ultrahigh purity (UHP) nitrogen atmosphere at 950°C for 10 minutes, as shown in Figure 3.1 [1].

Fig. 3.1. Rapid photothermal processing (RPP) system for the ex-situ annealing of silicon core optical fibers.
Prior to annealing, samples between 9 and 15 mm in length were polished to a surface finish of about 0.5 microns. Determination of crystallographic orientation using single crystal x-ray diffraction (XRD) was performed as described previously in this Dissertation. [3] Briefly, a Rigaku AFC8-S diffractometer equipped with MoKα radiation and a Mercury CCD area detector was used and the x-ray beam was collimated to a diameter of 0.5 mm. The unit cell parameter, and tilt and rotational angle orientations were determined relative to the longitudinal direction of the fiber in order to determine distinct changes in angular orientations. The orientations are thus given in relation to the longitudinal direction of the fiber, and changes in these relative orientations were noted as a function of position on the fiber. X-ray diffraction profiles were taken at identical positions along the fiber lengths both before and after RPP treatment. Fewer reflections, with much smaller scatter in their intensity, were observed in the diffraction profiles post-treatment. In addition, the RPP-treated fibers maintained the same local single crystalline orientations over the entire lengths of the analyzed fibers, as shown in Figure 3.2 (from Ref. [1]). While the longest persistent crystalline orientation was maintained for 2-3 mm in the as-drawn fiber, each crystallographic orientation analyzed in the post-treated fiber exhibited the same orientation, corresponding to a single crystal length of at least 9 mm. This suggests that the RPP treatment was beneficial in improving the crystallinity of these semiconductor core optical fibers.
Fig. 3.2. Longitudinal x-ray measurements in the as-drawn fiber (a) and rapid photothermal processing (RPP) post-treated fiber (b) [1].
Additionally, an important challenge is the fabrication of single-mode single-crystalline semiconductor waveguides, which would dramatically increase the range of applications, such as passive and active mid-wave and long-wave infrared fiber-based devices, for such fibers. Conventional methods of fabricating glass-clad semiconductor fibers lead to multimode cores and so a post-processing step, such as tapering [4], is needed to reduce the core size.

In this tapering work, the influence of the tapering process on the crystallographic properties of germanium core optical fiber is studied and reported in first-ever attempts. To achieve these fibers, a 3 mm rod was core-drilled out of a slab of 99.999% pure, n-type germanium of unknown dopant concentration (purchased from Lattice Materials), and was sleeved into a DURAN® glass tube, with an inner diameter slightly larger than 3 mm and outer diameter of 30 mm, which had been pre-drawn in order to collapse and seal one end. Approximately 250 m of 150 µm outer diameter fiber were subsequently drawn at approximately 1000°C, and coated using a conventional UV-curable acrylate to an outer diameter of about 240 µm, using the Heathway draw tower. Germanium was used, as relative to silicon, germanium possesses an extended infrared transparency, higher Raman gain coefficients, and lower melting point, and the crystallography of germanium core fibers has been previously studied [5].

Prior to tapering, the fiber coating was removed using a 50:50 solution of dichloromethane and acetone in an ultrasonic bath for 15 min. Uncoated fibers were then cleaned with conventional solvents (acetone, isopropanol, and methanol) and then placed onto the tapering rig. A “micro-heater brushing technique” was used to fabricate the
tapers, whereby the fiber ends, under strain, are clamped onto stages connected to a computer [6]. A micro-heater periodically moves across the optical fiber, and the taper shape can be set to an extremely high degree of accuracy by controlling the fiber stretch [7]. The micro-heater maximum temperature during taper fabrication was approximately 1270°C, and drawing speeds were set to 2 mm/s. Electron micrographs of the as-drawn and tapered fiber cross-sections are shown in Fig. 3.3 (from Ref. 8).

Fig. 3.3. Scanning electron micrographs of the (a) as-drawn and (b) tapered crystalline germanium core optical fiber [8].
Crystallographic analysis of the tapered fibers was performed as described above, using a Rigaku AFC8-S diffractometer, on fibers that were 16 mm in length. The crystallographic orientation could be reliably determined, indicating single crystal grain sizes exceeding 0.5 mm in length, for 15 mm of the fiber. In comparison to previous results, detailed in Chapter 1.3, the tapers appear to be comparable or slightly more single-crystalline (~94% as compared to ~85% local single crystallinity). As shown in Fig. 3.4, the $<110>$ family of directions most often occurred closest to (though not necessarily aligned with) the longitudinal direction of the fiber in the tapered fibers. This is a departure from the as-drawn fibers, where the $<100>$ directions were most common closest to the fiber axis [3]. Also unique to these tapered fibers is the frequency that the $<210>$ family of directions occurs closest to the longitudinal direction of the fiber, implying that the tapering process does not just reduce the fiber dimension but also reorients the crystallographic axes of the crystalline core. On a larger scale, the tapers, like the as-drawn fibers, are polycrystalline along their entire length; however, routinely observed in these tapered fibers are single crystalline regions of approximately 3–4 mm in length where a common orientation is maintained, namely the $<110>$ family of directions oriented to align with the fiber axis. While the aforementioned RPP treatment has been shown to enhance single crystallinity in as-drawn semiconductor core optical fibers, it does not yield an alignment of a crystallographic axis with the fiber’s longitudinal axis as tapering has shown to do [1, 9].
Fig 3.4. Histogram comparing the frequency of occurrences for each crystallographic orientation closest to the longitudinal direction of the fiber for the as-drawn and tapered glass-clad germanium core optical fiber.

Tapering and annealing crystalline semiconductor core optical fibers have both shown to be effective in controlling core crystallography and enhancing the degree of single crystallinity. Deeper understanding of the mechanisms that influence crystallographic orientation is needed, yet both techniques show promise for the continued evolution of these semiconductor core fibers towards eventual single-mode fibers.


CHAPTER FOUR

REACTIVE MOLTEN CORE

This Chapter addresses the concept of in-situ draw reactions and specifically treats solid-liquid (melt) phase chemical reactions during the molten core fabrication of silicon optical fiber in order to achieve low oxygen content cores with reduced scattering. In the system of silica glass-clad silicon core optical fibers, where only the elements Si and O are present, the issue becomes the removal of oxygen present in the silicon core [1]. The presence of oxygen, as oxide precipitates, is postulated to dominate scattering losses and also limit the minimum core size that can be achieved [2]. Removing, or at least greatly decreasing, the oxygen content would be an important step towards the ultimate realization of single mode silicon optical fibers.

Specifically, in this Chapter, silicon carbide (SiC) is blended with silicon (Si) and used to reduce silica (SiO$_2$) that enters the silicon core melt from the cladding via the following reaction: SiO$_2$ + SiC $\rightarrow$ Si + SiO + CO. The latter two reaction products (SiO and CO) are vapors and evolve out of the fluent melt such that the resultant optical fiber core is oxygen-free. This work further advances molten core fiber fabrication to include chemical reactivity whereby the high temperature processing, often considered a disadvantage, is employed to drive thermodynamics rather than be limited by it.

Silicon rods, equivalent to those used in Ref. 1, were pulverized, mixed with SiC powder, obtained from ABO Switzerland Co., Ltd., and the resultant powder blend placed into a high purity silica cladding tube, obtained from VitroCom, Inc., of 30 mm
outer diameter and about 3.2 mm inner diameter. The amount of SiC that was added to
the Si powder was determined based on the SiO$_2$ – SiC phase diagram, discussed later in
this Chapter, given the oxygen content found in the original molten core silicon optical
fibers of Ref. 1. The fibers were drawn at a speed of about 2 meters/minute at a
temperature of 1925°C using a carbon resistance furnace purged with argon. Generally
speaking, this molten core approach yields a fluent melt that flows along with the
cladding tube as it draws into fiber [3]. Hereafter, said fibers will be referred to as “Si +
SiC”-derived silicon optical fibers.

4.1 Electron Microscopy

Characterization using electron microscopy was employed to image the cross-
section of the as-drawn and polished fiber using a Hitachi S-3400 variable pressure
scanning electron microscope (SEM) operating under variable pressure at 20kV and a
working distance of about 10 mm. Elemental analysis was conducted under high vacuum,
using energy dispersive x-ray (EDX) spectroscopy in secondary electron (SE) mode, in
order to evaluate the elemental profile across the core/clad interface and to determine the
effect of SiC on the oxygen content in the core. Prior to microscopic evaluation, samples
were polished to a surface finish of about 0.5 micron. As can be seen in Figure 4.1a, there
is good core circularity, core/clad concentricity and interfacial integrity. Figures 4.1b and
4.1c provide spatial maps of the elemental distribution of silicon and oxygen,
respectively, obtained using energy dispersive x-ray spectroscopy (EDX). Most striking
is the lack of oxygen in the core (Figure 4.1c).
Figure 4.1. (a) Scanning electron microscope (SEM) image of a silica glass-clad silicon core optical fiber drawn using a reactive molten core of Si + SiC. Energy dispersive spectroscopic (EDX) spatial maps qualitatively show the concentration of silicon (b) and oxygen (c) where a brighter region indicates higher elemental content.

Albeit qualitative, these results provide an initial indication as to the efficacy by which SiC can getter oxygen in this reactive molten core approach. Quantitative determination of composition also was performed using energy dispersive x-ray spectroscopy (EDX) by conducting elemental analysis at numerous points in a straight line across the fiber. As is shown in Figure 4.2, the cladding is stoichiometric SiO₂ and the core has negligible oxygen, especially as compared to the approximately 18 atom percent of previous molten core fibers [1]. There are indications of oxygen present near the core/clad interface and it is uncertain if this influences optical scattering. Interestingly, oxide precipitates in silicon do have the beneficial effect of helping to pin dislocations thereby enhancing strength [4].
4.2 Crystallography

Powder x-ray diffraction (PXRD) was performed on pulverized samples of both the precursor powder blend and the as-drawn fibers using a Rigaku Ultima IV powder diffractometer with Cu Kα radiation (λ = 1.5418 Å). Diffraction patterns were collected from 5-65° in 2-theta at a rate of 0.75 deg./min for the precursor blend and 0.1 deg./min. for the powdered fiber. The powdered sample of the fiber contained material from both the crystalline core and glass cladding, and a background correction was applied to remove the amorphous hump contributed by the cladding glass. A slower scan (0.025
deg./min) also was performed on the powdered fiber sample from 33-39° in 2-theta, targeting the region that would contain the strongest diagnostic peaks of SiC in order to examine the sample explicitly for consumption of SiC. Figure 4.3 provides powder x-ray diffraction (PXRD) results on the initial blend of Si and SiC powders that subsequently were loaded into the pure silica cladding tube and drawn into fiber. As is expected, there is a match between the Si and SiC (cubic, moissanite-3C phase) contributions with their respective standard reflection indices.

![Figure 4.3. Powder x-ray diffraction scans of the core precursor powder blend of Si and SiC with crystallographic indices given. Figure 4.3a is the full intensity range whereas Figure 4.3b is a magnified intensity range to accentuate the reflections and fit to the Si and SiC standards.](image)

Figure 4.4 provides the PXRD spectra from the drawn optical fiber. Clearly identified in Figure 4.4 are the peaks of silicon, with the narrowness in linewidth further indicating a high degree of crystallinity. Figure 4.4b shows, to the precision of XRD, that the SiC has been consumed during the fiber draw process since no reflections from SiC...
are observed, whereas there most certainly was SiC present in the initial preform (Fig. 4.3).

![Graphs showing X-ray diffraction patterns for Si and SiC]  

Figure 4.4. (a) Powder x-ray diffraction (P-XRD) scan of the “Si + SiC”-derived silicon optical fiber with Si standard overlay and crystallographic indices for comparison; spectrum corrected to remove amorphous signature from cladding. (b) P-XRD scan of “Si + SiC”-derived silicon optical fiber over the selected two-theta region where SiC reflections should exist including an overlay of the SiC reflections. No reflections from SiC are observed in the drawn optical fiber.

4.3 Optical Transmission

The experimental setup shown in Figure 4.5 was used to characterize the fiber samples. Briefly, a single-mode tapered fiber, mounted on a three-dimensional translation stage, was used to couple light from a tunable laser, of 1.55 µm in wavelength, into the sample. Since the tapered fiber can focus the input laser light into a spot of approximately two microns in diameter, it offers an effective way to couple light into either the core or cladding of the “Si + SiC”-derived silicon optical fiber. The output end of the sample is placed in front of a near-infrared (NIR) objective (50˚) in order to form a magnified near field image in the infrared camera. The light intensity distribution at the sample output
facet can be obtained using this setup. A second optical path includes a white light source, a beam-splitter, a beam sampler, and a visible CCD camera and is used to image the output facet of this sample. The transmission of 1.55 µm light, incident on the center of fiber core, was low for both the “Si + SiC”-derived silicon optical fiber and a silicon optical fiber equivalent to that of the conventional silicon optical fiber of Ref. 1. For the conventional silicon fiber, a scattering pattern was observed in the cladding; i.e., light scattered out of the core and propagated in the cladding. However, for the “Si + SiC”-derived silicon optical fiber, there was no such scattering pattern in the cladding. This indicates, albeit qualitatively, that the core of the Si + SiC fiber scattered much less light; likely due to the reduced oxygen content. Since a considerable amount of light was confined in the cladding for shorter samples due to Fresnel reflection at the silica/air and silica/silicon interfaces, the attenuation of these samples was not able to be determined.

Figure 4.5 Schematic of the experimental set-up used for qualitatively evaluating transmission and scattering by the silicon optical fiber.
4.4 Thermodynamics and Phase Diagrams

Underlying these results are the technologically important thermodynamics of the Si-O-C system. The oxidation of SiC has been studied for over half a century [5, 6] and can be considerably more complicated than the simple stoichiometric reactions suggest. It was noted in Ref. 2 that the phase diagrams in the Si-O and Ge-O system offer insight into both the similarities and differences that are relevant to the fabrication of Si and Ge core optical fibers. This is equally true for SiC.

It is illustrative to discuss the Si-O-C phase diagram and, for this, an under-appreciated gem is Ref. [7]. As is shown schematically in Figure 4.6a, a ternary phase diagram having Si, O, and C at its apexes has a smaller ternary phase field comprising Si, SiO\(_2\) (along the Si – O binary), and SiC (along the Si – C binary). The tie line between the SiO\(_2\) and SiC and its phase dependence with temperature is critical to this discussion.

Figure 4.6b recasts the SiO\(_2\) – SiC phase diagram, based on Ref. 7, and, for consistency, uses the terminology from said reference as follows: G = gas (vapor), CR = crystalline SiO\(_2\) (either cristobalite or tridymite), SiC = silicon carbide (SiC), Si = solid silicon (Si), C = carbon (graphite; though presumed not present in the case treated in this work), LS = liquid salt, and LM = metallic liquid.
As suggested by the phase diagram, the SiO$_2$ + SiC = Si + SiO(g) + CO(g) stoichiometric reaction is more complex in practice. Table 4.1 provides a summary of the reactions and reaction temperatures that underlie the SiO$_2$ + SiC thermodynamics. As the mixture of Si + SiC in the core of the silicon optical fiber preform is heated towards the draw temperature (1925°C or, about, 2200K), the first reaction is the melting of the silicon at 1685K (1412°C). This liquid Si phase, further facilitated by the progressively higher temperatures, begins to dissolve the softened SiO$_2$ cladding above its glass transition temperature (about 1600°C or, about, 1873K). Amorphous silica, such as the cladding glass, does react more rapidly than crystalline SiO$_2$ with SiC [8]. If crystalline SiO$_2$ is either present or nucleates at the core/clad interface, then it melts at about 1996K (1723°C). Subsequently, any remnant SiC, which still is solid, is surrounded by a reactive melt that begins liberating vapors at 2086K (1813°C). Bubbles of these vapors should fine through the fluent melt at the draw temperature since the viscosity of silicon above
its melt is less than that for water [9]. The reaction continues until either the SiC is consumed by the SiO$_2$ or the fiber is drawn and cools, thereby hindering the thermal driving forces; ultimately the core crystallizes upon solidification.

This “road-map” behind the SiO$_2$ + SiC = Si + SiO(g) + CO(g) reaction, taken with the phase diagram of Figure 4.6b, suggests a specific non-stoichiometric route to gettering the oxygen out of the silicon optical fiber. The reaction noted above specifies equimolar quantities of SiO$_2$ and SiC. However, according to the phase diagram, such an equimolar ratio (50 mole % SiC in the Figure) will still have solid SiC as a thermodynamically stable phase at the draw temperature (denoted in Figure 4.6b as the dotted horizontal line). Ideally, the only phases present at the draw temperature are the metallic liquid and vapor, the latter evolving out of the molten core. Accordingly, as was done in this work, slightly less than an equimolar amount of SiC, with respect to the amount of oxygen (SiO$_2$) measured in the core of the silicon optical fiber, from Ref. 1, was used.

In this Chapter, the in-situ reactive molten core approach has shown to effectively remove any oxide phases in the core of the optical fiber through chemical reactions during the molten core fiber draw process. The addition of silicon carbide to the silicon core reduced the formation of oxide precipitates such that elemental analysis could not detect any measurable oxygen content in the core, and the resultant fiber core also was shown to be comprised of highly crystalline silicon. This realization, for the first time, of an oxygen-free silicon core optical fiber is an important advance in the field of semiconductor core optical fibers.
Table 4.1 Thermal progression of reactions in the SiO$_2$ + SiC system*

<table>
<thead>
<tr>
<th>Reactions in Order of Increasing Temperature</th>
<th>Temperature of Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon melts</td>
<td>1685K (1412°C)</td>
</tr>
<tr>
<td>[If free carbon present: SiO$_2$ + 3C = SiC + 2CO]**</td>
<td>1786K (1513°C)</td>
</tr>
<tr>
<td>Glass transition temperature of silica cladding: $\sim$1873K ($\sim$1600°C)</td>
<td></td>
</tr>
<tr>
<td>(Crystalline) SiO$_2$ melts</td>
<td>1996K (1723°C)</td>
</tr>
<tr>
<td>First vapor forms</td>
<td>2086K (1813°C)</td>
</tr>
<tr>
<td>Liquid forms vapor</td>
<td>2137K (1864°C)</td>
</tr>
<tr>
<td>Fiber draw temperature: $\sim$2200K (1925°C)***</td>
<td></td>
</tr>
<tr>
<td>$\alpha$$\rightarrow$$\beta$ SiC transformation</td>
<td>2250K (1977°C)</td>
</tr>
<tr>
<td>SiC melts</td>
<td>3082K (2809°C)</td>
</tr>
<tr>
<td>All vapors</td>
<td>3342K (3069°C)</td>
</tr>
</tbody>
</table>

* Compiled in part using data from Ref. 7.
** Presume no free carbon in the particular case treated here.
*** Reactions listed that proceed after the fiber draw (i.e.; reaction temperature is above the fiber draw temperature) are presumed not to occur but are noted for completeness.


CHAPTER FIVE

ON LOSS MECHANISMS IN CRYSTALLINE SEMICONDUCTOR CORE OPTICAL FIBERS

This Chapter focuses on identifying and beginning to understand the principal factors that contribute to attenuation in semiconductor core optical fibers. The sources of loss in these fibers can arise from a variety of mechanisms that fall into two main categories: absorption and scattering. Intrinsic absorption in semiconductors is mainly caused by free electrons and resonances associated with bound electrons and ions, while extrinsic absorption mainly comes from impurities and defect centers. Extrinsic scattering is presumed to come from stress birefringence, grain boundaries, precipitates, cracks and voids due to thermal expansion mismatch, surface roughness, and diameter fluctuations. Reduction of loss is of interest, as theory suggests that ~50 dB/km is possible [1]. While initial efforts to systematically address crystallographic [2, 3], impurity (specifically oxide) [4], and core/clad thermal expansion mismatch [5] have improved selected properties, including enhanced single crystallinity and reduces electrical conductivity, there has not yet been the revolutionary advance(s) that reduces measured losses to values (< 1 dB/m) where the advantages of optical fibers possessing a semiconducting core, particularly in nonlinear optics, can be most useful. Figure 5.1 provides a compilation of measured loss values for a variety of semiconductor optical fibers, with core size and citation specified. Regardless of the fabrication technique, furthering the fundamental understanding of loss in these novel semiconductor fibers, and subsequent work to reduce it, will help advance this growing field.
Fig. 5.1. Comparison of measured attenuation values and corresponding core sizes reported from various semiconductor optical fibers (silicon, Si; germanium, Ge; zinc selenide, ZnSe; amorphous hydrogenated silicon, a-H:Si. Abbreviations: Collaboration between the Pennsylvania State University and the Optoelectronics Research Center at the University of Southampton [PSU/ORC], Clemson University [Clemson]. Citations noted follow the following format (Journal name abbreviation volume, starting page number, year of publication), where “OE” is Optics Express, “JACS” is the Journal of the American Chemical Society, “APL” is Applied Physics Letters, “AM” is Advanced Materials, “JCG” is the Journal of Crystal Growth, “OME” is Optical Materials Express, and “OL” is Optics Letters.

As discussed in greater detail previously [6], a 3 mm in diameter by 30 mm in length silicon rod was sleeved into a 3.2 mm inner diameter by 30 mm outer diameter by 1000 mm in length high purity silica cladding tube and drawn into fiber with a preform feed of 4 mm/min. The cladding tube was pre-drawn to collapse and seal one end in order
to contain the silicon melt during the fiber draw, where the aforementioned molten core approach was used [4]. The fibers discussed in this work were drawn at a speed of approximately 12 meters/minute at a temperature of 1925°C, with a target fiber diameter of 1 mm and core size of approximately 100 µm.

In order to better determine the effect of core/clad roughness on attenuation and crystallography, and to more easily image the crystallographic microstructure of the core, samples of the silica-clad silicon-core fiber were cleaved and etched in HF acid (50% in deionized water) and stirred at room temperature overnight. Several pieces of the etched silicon core were mounted in resin and polished flat to a 0.5 micron finish in order to examine a cross-section of the core.

Microstructural and elemental analysis were performed under high vacuum secondary electron (SE) mode using a Hitachi SU6600 analytical variable pressure field emission scanning electron microscope (FE-SEM). Electron backscatter diffraction (EBSD) analysis was carried out using Oxford Instruments HKL Channel 5 software. Lattice-fringe imaging of the silicon core was obtained using a Hitachi H-9500 transmission electron microscope (TEM). Fig. 5.2 provides the scanning electron microscope (SEM) images on the silicon core samples, as well as an optical microscopy image. As can be seen, etching away the cladding glass provides direct access to the silicon core for analysis. These images were made in order to examine the core surface for cracks and microstructural features.
Fig. 5.2. Scanning electron and optical microscopy images of etched silicon core pieces.

Electron backscatter diffraction (EBSD) and what the authors believe to be the first direct lattice-fringe images of the silicon core are shown in Figures 5.3 and 5.4. The Fast Fourier Transform (FFT) is shown inset in Figure 5.4(a). Clearly resolved are highly crystalline regions, as well as regions of polycrystallinity. Grain orientations were determined using the Kikuchi line geometry patterns, which correlate to crystallographic Miller indices [7]. While several different grain boundaries are present in the EBSD and transmission electron microscopy (TEM) images, regions of well-defined local single crystallinity are also observed. Since silicon is a cubic crystal, it is optically isotropic and
scattering from grains of differing crystallographic orientation should not occur. However, differential density of gap states at grain boundaries can influence absorption [8, 9] as well as the electron density, which can influence scattering. The distribution of grain orientations can also yield a distribution of stresses, which can promote additional scattering via stress-optics effects [10]. Lastly, grain boundaries can serve as sinks for impurities to reside and, hence, can have locally different compositions which also could facilitate scattering. Towards this end, more highly single-crystalline fibers should contribute to a reduction in such perturbations that could help reduce loss in future fibers.

![Fig. 5.3. EBSD image of silicon core grain boundaries and crystallographic planes. The black scale marker on the bottom of Fig. 3(a) is 500 µm.](image)

The inter-planar lattice spacings, obtained directly from the TEM micrographs as shown in Figure 5.4(a), are in the range of 2.99-3.33 Å. Since \( a = 5.43\text{Å} \) for silicon, the only combination of \((hkl)\) in a cubic crystal for this range is the \((111)\) plane. These results, in combination with the silicon core grain boundary orientations shown in the EBSD data, corroborate well with known data that silicon has octahedral cleavage along the \(\{111\}\) faces. SEM micrographs (not shown) exhibit fissures emanating from the core interface with the cladding at an angle of 65°, corresponding to the \(\{111\}\) face,
suggesting that they could be a stress-induced cleavage originating at the core/clad interface due to the differential thermal expansion between the crystalline semiconductor (silicon) core and glass (silica) cladding. Most cracks do not propagate all the way across the core, so there may either be some self-healing during solidification or the stresses are sufficiently small at these core sizes so as to not catastrophically fail. Though not definitive, bright spots in the TEM images (and IR scattering images shown later) could be oxide precipitates. Oxygen is known to dissolve into the core as the molten silicon attacks the silica glass cladding at elevated temperatures during the draw process. The oxygen concentration, measured macroscopically via energy dispersive spectroscopy (EDX), and discussed previously in this Dissertation, is believed to yield nanoscale oxide precipitates that lead to scattering of light propagating through the fiber [1, 4, 6].

Fig. 5.4. Transmission electron microscopy (TEM) images of etched silicon cores. Regions of well-defined local single crystallinity are observed, though the samples are polycrystalline overall. The scale marker is 10 nm for Fig. 5.4(a) and 5 nm for Fig. 5.4(b).
Atomic force microscopy (AFM) was performed on the etched silicon core pieces using a Veeco Dimension 3100 Nanoman AFM; the data was analyzed using Gwyddion freeware. Additionally, a cladding glass tube was sectioned, and the inner surface was analyzed in order to determine if there were any effects of the cladding glass roughness on the post-drawn core. Measured root-mean-square (rms) roughness of the silicon core was approximately 2 nm. The rms values for the silica cladding tube inner surface ranged from 0.3-0.6 nm with a few spots of higher roughness (rms ~ 2 nm), possibly from incomplete cleansing of the tube after sectioning. This suggests that some of the surface roughness of the silicon core can be attributed to its conformation to the geometry of the silica tube during the molten core draw process. Previous analysis of surface roughness in silicon core optical fibers fabricated using chemical-vapor deposition processes [11] yielded rms values around 0.14 nm. At these levels of roughness less than 4 nm [11], surface scattering does not contribute significantly to loss in transmission (< 0.1 dB/cm) though may be an issue worth revisiting in the future should < dB/m attenuation levels be desired.
Fig. 5.5. AFM images of etched silicon core (a) and inner face of silica cladding tube (b).

In order to measure the infrared (IR) transmission and evaluate sources of scattering and loss, measurements were made using a setup equivalent to that previously detailed in this Dissertation [4]. Briefly, a single-mode tapered fiber, mounted on a three-dimensional translation stage, was used to couple light from a tunable laser (operating at a wavelength of approximately 1.55 µm) into the silicon fiber sample. The output end of the fiber is placed in front of a near-infrared objective (50×) to form a magnified near field image focused onto the infrared camera. A second optical path includes a white light source, a beam-splitter, a beam sampler, and a visible CCD camera and is used to image the output of this sample.

Images taken using an infrared camera are shown in Fig. 5.6. Specifically, Fig. 5.6(a) shows an image overlaid with the incident fiber taper, the bright spot where the pump light exits the taper, and the illuminated front face of the silicon core. Fig. 5.6(b) provides an infrared image of the output end of the silicon core showing a relatively uniform distribution of light across the diameter. Fig. 5.6(c) shows light scattering from
the side along the length of the silicon core. Clearly observed are bright bands which indicate a longitudinal heterogeneity. Whether these bands are associated with perturbations during the longitudinal solidification of the molten core, scattering from grain boundaries and possible oxide precipitates that would naturally segregate there, or small cracks is presently under further evaluation. Regardless, it is clear that side-directed scattering is easily observed along the length of the silicon core and likely causes much of the loss measured to date.

Fig. 5.6. (a) Infrared (IR) side-view image of the input end with regions noted. (b) IR image of output facet when IR light is coupled to the other end. (c) Longitudinal IR image of the silicon core. In all cases, the core-only (i.e., glass cladding etched away) samples were used.
At present, based mainly on the infrared images, the dominant loss in semiconductor core fibers appears to be scattering; either from cracks originating from the thermal expansion mismatch between core and clad, perturbations in the solidification leading to longitudinal variations in the fiber, and/or oxide precipitates that likely partition to the grain boundaries. Transmission electron microscopy (TEM), of the first lattice-fringe images of silicon core optical fibers, and electron backscatter diffraction (EBSD) showed regions of localized core single crystallinity, while surface roughness, using atomic force microscopy (AFM), was shown to be low and unlikely to contribute to the scattering losses. Methods for reducing loss in semiconductor core optical fibers, and leading to the development of higher quality optical fibers, should therefore entail a combination of tailored cladding glasses to both reduce dissolution of oxides into the molten core during fiber fabrication and to negate thermal expansion mismatches, in situ melt-phase chemical reactions to reactively getter oxide precipitates and other impurities or contaminants, and greater control of single crystallinity in order to reduce grain boundary scattering.


CHAPTER SIX

CLADDING GLASS DEVELOPMENT: THEORETICAL GLASS SCIENCE

As previously detailed in this Dissertation, the development of tailored cladding glass compositions is an obvious and necessary step forward in the advancement of semiconductor core optical fibers, due to the ability to match thermal expansion coefficients and negate mismatches, as well as reducing the dissolution of oxides into the molten core during fiber fabrication by drawing the fibers closer to the melting point of the semiconductor core. Vitreous silica has been used as the cladding glass for all of the silicon optical fiber efforts reported so far in this Dissertation and to date in literature [1-4] due to its commercial prevalence, well-known and characterized physical, optical, chemical, and thermal properties, and the corresponding familiarity and infrastructure of the optical fiber community. However, silica suffers from two main drawbacks. First, the draw temperature of silica, being about 2000°C, (Figure 6.1) is nearly 600°C above the melting point of silicon (1414°C), necessitating high fiber fabrication temperatures that promote the dissolution of the cladding glass into the core melt, leading to oxide precipitates and contaminants that can scatter and absorb light [2]. Second, there is a marked thermal expansion mismatch between silica (0.55 ppm/K) and silicon (2.6 ppm/K), which can lead to cracking and non-uniform internal stresses [5]. Other traditional glasses, such as sodium borosilicate (DURAN®) and conventional soda lime silicate window glass, possess neither the necessary viscosity/temperature behaviors, as evidenced in Figure 6.1, nor thermal expansion coefficients to address the aforementioned issues. Similar issues arise and are exacerbated for germanium core
optical fibers, where borosilicate glass has been employed [6], and the binary semiconductor InSb, where phosphate glasses have been used. Figure 6.1 shows that, as discussed above, silica glass is too refractory; melting too high (and expanding too little) to match the less refractory thermal properties of typical semiconductors: Si, GaAs, Ge, and InSb. Of these aforementioned synergistic properties, two important factors are: a tailored thermal expansion coefficient, in order to mitigate the formation of cracks upon cooling of the fiber, and a viscosity/temperature relationship that permits drawing of the glass cladding at a temperature above the melting point of the semiconductor core. These are specific requirements of the molten core fabrication method, which has proven to be the best approach for realizing long lengths of optical fiber at low cost and also fibers with the lowest optical losses measured to date. The most widely used viscosity (η) for fiber drawing is where η is approximately equal to $10^6$ Poise. More generally, though, thicker fibers can be drawn at higher viscosities and thinner fibers can be drawn at lower viscosities and higher temperatures. Stress-induced cracking, originating from the differential coefficients of thermal expansion (CTE), has proven to be one of the major obstacles in the consistent fabrication of high quality semiconductor core optical fibers. This should be eliminated by choosing a cladding glass with a similar thermal expansion coefficient as the semiconductor core. Thermal expansion mismatch additionally can create structural imperfections and residual stresses between the core and the glass cladding, which in turn can lead to heterogeneities and optical attenuation through scattering. Further, the cladding glass should be composed of a strong glass former that is
not prone to crystallization at the draw temperature, and should also be stable in air and humidity.

The purpose of this Chapter is to provide a glass science perspective to the identification and selection of glass families for semiconductor core optical fibers. Intentionally, this work largely is “theoretical,” based on known or interpolated glass properties, including thermal expansion coefficients and estimated draw temperatures. Initial experimental efforts will be detailed later in this Dissertation. More specifically, compositional families and specific suggested compositions are provided for a range of unary (Si, Ge), binary (InSb, GaAs), and ternary (InAlSb) semiconductor cores that either already have been fabricated using non-optimum cladding glasses (as is the case for Si, Ge and InSb), or are materials of particular interest given their optoelectronic properties (GaAs). It should be noted that while the focus is on cladding glasses which are amenable to the molten core fabrication method, these glasses should be equally well suited for CVD, core-suction, and/or high-pressure melt infiltration-derived semiconductor core optical fibers, the fabrication processes of which have been previously detailed in this Dissertation. For completeness, it is worth noting that while the tailoring of the glass cladding is important, it is one piece in a larger optimization process that likely also will include other considerations such as annealing, reactive melt chemical gettering, and control of core geometry to more fully advance optical fiber performance, as were previously detailed [7-9]. This Chapter addresses heretofore-unexamined issues associated with the cladding glasses, such that long lengths of optical fiber with low
internal stresses should reduce propagation losses and continue the practical advancement of novel optical fibers.

Figure 6.1. Approximate draw points for selected semiconductor core optical fibers, based on the semiconductor melting temperatures, compared with the typical viscosity-temperature curves for silica, DURAN®, and a typical soda lime silicate glass composition.

6.1 Compositional Development

Figure 6.1 shows that, for most of the semiconductors of practical interest, a glass cladding compositional space needs to be identified in which the glass is more refractory than the soda lime silicate but less refractory than vitreous silica. A generalized approach could be to select trivalent additives to silica, which are electron deficient in comparison
with silica, to decrease viscosity. A more refractory glass than borosilicate can be created by decreasing the amount of non-bridging oxygen in the glass while increasing the concentration of Al₂O₃. Accordingly, the compositional family x[Na₂O:Al₂O₃] + (100-2x)SiO₂ was initially selected as these glasses are relatively stable against crystallization and phase separation, while maintaining a relative ease in varying glass properties (such as viscosity) through slight compositional variations. Further, due to their geological similarity and relevance, some information and data is available about their preparation, characterization and properties.

Figure 6.2. Crosslinking of silicate glass structure.
Viscosity can be controlled by systematically varying the ratio of soda (Na$_2$O) to alumina (Al$_2$O$_3$); i.e., by tailoring the combination of bridging and non-bridging oxygen. Optimum values of Na$_2$O:Al$_2$O$_3$ will, therefore, be different for each selected semiconductor core in order to achieve the proper balance between core/clad CTE matching and cladding fiber draw viscosity. The structure and connectivity of the silicate glass network is defined by the number and arrangement, known as coordination, of bridging and non-bridging bonds that link each of the silica tetrahedral structural units to their neighbors, while maintaining charge balance. Figure 6.2 shows connectivity within such a silicate network. Since the concentration of alumina equals that of alkali oxide in the selected composition family, NaAlO$_{4/2}$ groups are created in the glass with very few non-bridging oxygen. Presumably there will be contaminate levels of non-bridging oxygen arising from slight off-stoichiometries in the Na$_2$O:Al$_2$O$_3$ ratio, impurities in all of the starting materials, and non-advantageous water. These effects can be quantified through a combination of infrared and NMR spectroscopies. Most of the aluminum will therefore occur in the structure in tetrahedral groups, charge compensated by Na$^+$ ions, which can substitute directly for silica tetrahedra. The AlO$_{4/2}$- groups are not as strongly bound as the SiO$_{4/2}$ groups. The 1Na$_2$O: 1Al$_2$O$_3$ ratio was selected specifically to achieve stability; insufficient alkali oxide content will cause some of the alumina to remain in trigonal coordination within the structure, allowing for the possibility of phase separation, which would lead to a significant weakening of the fiber strength. Additional alkali oxide beyond the 1:1 ratio would create excess structure-breaking non-bridging oxygen (Figure 6.3).
In order to identify specific compositions for various semiconductors of interest, the computational database SciGlass[10] was queried by selecting properties, such as viscosity at a given temperature and coefficient of thermal expansion, and selecting a temperature range where experimental data exists within the database. For example, to find a cladding glass that has an appropriate fiber draw viscosity at approximately 1450°C (for silicon, which melts at about 1414°C), the temperature range selected was 1300-1500°C. With these selected parameters, over a dozen glass compositions were identified. A similar search for CTE produced equally many results.

Figure 6.4a shows a plot of $T(\log_{10}(\eta) = 6)$, which is the temperature where $\log_{10}(\eta) = 6$, $\eta = 10^6$ Poise. As expected, this temperature decreases with added Na$_2$O+Al$_2$O$_3$, most quickly at initial additions and less quickly at higher additions. Figure 6.4b shows a plot of the average CTE against the same Na$_2$O+Al$_2$O$_3$ fraction and, in this case, the CTE increases. In both plots, there is less data in the region of interest for the more refractory properties of Si, but more data exists in the range of the less refractory Ge and GaAs. However, careful inspection of Figures 6.4a and 6.4b shows that none of the compositions possess both the desired temperature for fiber draw and CTE.
Figure 6.3. Ternary diagram of the $x[\text{Na}_2\text{O}:\text{Al}_2\text{O}_3] + (1-x)\text{SiO}_2$ glass compositional family.
Fig. 6.4. Estimated (a) viscosity and (b) coefficient of thermal expansion as a function of glass composition in the family $x[\text{Na}_2\text{O}:\text{Al}_2\text{O}_3] + (100-2x)\text{SiO}_2$. The compositional gap between $x = 0$ and $\sim 10$ represents an opportunity for basic glass science research into the properties and structures of these very refractory glasses.
The biggest data gap appears, as discussed above, in the CTE data where no glasses appear so far to have been prepared and characterized in the low x region of ~ 5 mole percent where it appears such a glass would be a good match. More data exists for \( T(\log_{10}(\eta) = 6) \) and glasses appear to be available with good matches to the required draw temperatures. However, known changes in CTE and viscosity with additional additives can be used to fine-tune these compositions in order to obtain the necessary design criteria. The selected semiconductors are listed with their proposed cladding glass compositions in Table 6.1, along with their respective melting points and thermal expansion coefficients.

Table 6.1. Semiconductor and Glass Compositions and Properties

<table>
<thead>
<tr>
<th>Core Material</th>
<th>Melting Point (°C)</th>
<th>Core CTE* (ppm/K)</th>
<th>Proposed Glass Composition***</th>
<th>Estimated Draw Temperature (°C)**</th>
<th>Cladding CTE* (ppm/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1414</td>
<td>2.6</td>
<td>6Na_2O + 6Al_2O_3 + 88SiO_2</td>
<td>1434</td>
<td>3.3</td>
</tr>
<tr>
<td>Ge</td>
<td>938</td>
<td>6.0</td>
<td>10Na_2O + 6Al_2O_3 + 4B_2O_3 + 80SiO_2</td>
<td>1000</td>
<td>6.0</td>
</tr>
<tr>
<td>InSb</td>
<td>527</td>
<td>5.4</td>
<td>5BaS + 5In_2S_3 + 35La_2S_3 + 54Ga_2S_3</td>
<td>550-600</td>
<td>6-8</td>
</tr>
<tr>
<td>GaAs</td>
<td>1238</td>
<td>5.7-6.8</td>
<td>12.5Na_2O + 12.5Al_2O_3 + 75SiO_2</td>
<td>1250</td>
<td>7</td>
</tr>
<tr>
<td>GaAlSb</td>
<td>1210</td>
<td>3.6</td>
<td>13CaO + 17Al_2O_3 + 70SiO_2</td>
<td>1265</td>
<td>3.9</td>
</tr>
</tbody>
</table>

* CTE, coefficient of thermal expansion.
** Temperature where glass viscosity is approximately \( 10^6 \) poise.
*** All compositions given in mole percent.
6.1.1 Silicon Core

For a glass-clad silicon core optical fiber, the optimal $x[\text{Na}_2\text{O}:\text{Al}_2\text{O}_3]$ concentration for draw viscosity is approximately $x = 6 – 8$ mole percent, as is shown in Figure 6.4a, but $4 – 6$ mole percent for a matched CTE, shown in Figure 6.4b. While not exactly the same, the results give a good enough match to the silicon thermal expansion, $3.3$ ppm/K compared to $2.6$ ppm/K for Si and allow for acceptable draw viscosity at a temperature just above the melting point of the silicon, $1434^\circ\text{C}$ and $1414^\circ\text{C}$, respectively. Greater detail on this system is provided below, as well as in the experimental results of the following Chapter.

6.1.2 Germanium Core

Germanium melts at a much lower temperature than silicon (Table 6.1), and this was viewed as potentially advantageous since the lower processing temperature might reduce the potential for cladding glass dissolution and subsequent oxygen diffusion into the core. Commercial borosilicate glass provided the most convenient match to the draw temperature, and fiberization generally was successful [6]. However, there was significant attenuation and occasional cracks in these early fibers such that compositional tailoring of a more idealized cladding glass was worthy of exploration.

A greater incompatibility for CTE and draw viscosity temperature matching was found for germanium within the same sodium aluminosilicate glass family, $x[\text{Na}_2\text{O}:\text{Al}_2\text{O}_3] + (100-2x)\text{SiO}_2$. Figure 6.4a shows that an optimal viscosity and draw temperature suggests an $x$ value in excess of approximately $30$ mole percent, while the
CTE matches at approximately 11-13 mole percent (Figure 6.4b). Because these compositional ranges are so different, it is very likely that more compositional optimization is required and so further study was needed to fine-tune the composition to optimize both the CTE and viscosity incompatibilities. Figure 6.4a shows that the glass needs to have a significantly lower draw temperature, but Figure 6.4b shows that the CTE need not be reduced as significantly. The addition of boron is known to reduce the CTE through the formation of tetrahedral boron, BO$_{4/2}$, yet not significantly reduce viscosity, hence significantly reducing the draw temperature. It therefore appears useful for modifying a base composition that possesses a good match in draw temperature.

The base compositional family, x[Na$_2$O:Al$_2$O$_3$] + (100-2x)SiO$_2$, was therefore modified, for the inclusion of B$_2$O$_3$, to the selected composition of 10Na$_2$O + 6Al$_2$O$_3$ + 4B$_2$O$_3$ + 80SiO$_2$. This glass was arrived at by compositionally substituting B$_2$O$_3$ for Al$_2$O$_3$. The SciGlass [10] database and Glass Calculator suggest that this cladding glass composition possesses a CTE of approximately 6 ppm/K and T (log$_{10}$η = 6) of about 1000 °C. The computed viscosity curves for several glass compositions within the x[Na$_2$O:Al$_2$O$_3$] + (100-2x)SiO$_2$ family and for 10Na$_2$O + 6Al$_2$O$_3$ + 4B$_2$O$_3$ + 80SiO$_2$ are shown in Figure 6.5.
Fig. 6.5. Estimated viscosity-temperature curves for selected cladding glass compositions.

As can be seen, all three glasses show viscosity-temperature curves that pass directly through the appropriate melting point temperature for the appropriate core semiconductor. As the viscosity windows vary slightly depending on the processing techniques, the proper composition and temperature may be adjusted to fit the technique accordingly.

6.1.3 Selected Binary Semiconductor Cores

Binary semiconductor core optical fibers have recently been developed, including the molten core fabrication of InSb fibers [11] and chemical vapor deposition of ZnSe
fibers [12], to take advantage of the high second-order nonlinearities and increased optical transparency window of compound semiconductors. The potential for expanding the binary semiconductors to include the optoelectronically-meaningful GaAs should also be explored. For completeness it is worth noting that materials such as GaAs and ZnSe have fairly high vapor pressures at their melting points. As such, they are more appropriate for CVD-based fabrication approaches than the molten core method, since the high vapor pressure is not likely to be contained by the soft cladding glass during the fiber draw.

6.1.3 a. Gallium Arsenide (GaAs) Core

Cladding glasses for a GaAs optical fiber in the same \( x[\text{Na}_2\text{O}:\text{Al}_2\text{O}_3] + (100-2x)\text{SiO}_2 \) family as discussed above would favor an \( x \approx 11 – 13 \) mole percent for both draw temperature and CTE. Specifically, the cladding composition \( 12.5\text{Na}_2\text{O} + 12.5\text{Al}_2\text{O}_3 + 75\text{SiO}_2 \) yields a CTE of approximately 7 ppm/K, and a draw temperature where the viscosity equals about \( \log_{10} \eta = 6 \) poise is approximately 1250°C. This is well matched to the GaAs melting point of 1238°C and CTE of 5.7 – 6.8 ppm/K. In the case of this \( 12.5\text{Na}_2\text{O} + 12.5\text{Al}_2\text{O}_3 + 75\text{SiO}_2 \) glass composition, a series of experimental data over wide temperature and viscosity ranges does exist for this composition, and the experimental points and the SciGlass [10] calculated curves are shown in Figure 6.5. The excellent agreement over ten orders of magnitude of viscosity is quite impressive. The deviation is only significant at the lowest temperatures, which are far colder than the
range of temperatures used for the fiber drawing. Such excellent agreement, while perhaps optimum for this particular glass, will be explored for the other glasses.

6.1.3 b. Indium Antimonide (InSb) Core

Due to the low melting temperature of InSb, a non-oxide cladding glass, discussed in greater detail below, provides the closest match for both the draw temperature viscosity and CTE. However, an oxide cladding glass might be more feasible for large-scale productions. As shown in Figure 6.1, the soda lime silicate compositional family provides a reasonably close draw point for the InSb core. A glass composition of $15.56\text{Na}_2\text{O} + 14.07\text{CaO} + 70.37\text{SiO}_2$ gives a CTE of 8.9ppm/K, which is fairly similar to the CTE of the non-oxide cladding composition selected for InSb. The temperature at the draw viscosity of this oxide cladding glass is 864 °C, which is higher than the InSb melt temperature of 527 °C. Further optimization should be possible in this family.

6.1.4 Ternary Semiconductor Core

Given the initial successes with binary semiconductor core fibers, it is worth considering ternary core analogs. Numerous crystals in the InGaSb, InAlSb, and GaAlSb ternary systems melt below the draw temperatures of many oxide and non-oxide cladding glass compositions, and thus are reasonable prospects for future consideration. Additionally, there exists a wide range of acentric binary and ternary semiconductors, potentially enabling novel odd-order nonlinearities in optical fibers.
While fibers with ternary semiconductor cores have not yet been achieved, success with binary core fibers leads to the belief that ternary core fibers may be within the realm of possibility. The ternary GaAlSb is considered here with regard to cladding glass selection. With a melting point of approximately $1210^\circ$C, and extrapolating from the liquidus line in the GaSb-AlSb phase diagram [13], a draw temperature for the GaAlSb ternary semiconductor core fibers is estimated to be between $1250^\circ$C and $1300^\circ$C. Averaging the CTE of GaSb (2.4ppm/K) and AlSb (4.9ppm/K) gives an expansion coefficient of 3.6 ppm/K. For this system, the CaO-Al$_2$O$_3$-SiO$_2$ glass compositional family is proposed, with the specific composition of 70SiO$_2$-17Al$_2$O$_3$-13CaO yielding an estimated draw temperature of about $1265^\circ$C and a CTE of approximately 3.9 ppm/K, well-matched to that of the GaAlSb.

While oxide glasses generally are better known and more readily fabricated than non-oxide glasses, the non-oxides do possess the benefit of longer wavelength transparency. Less of an issue for a silicon core optical fiber operating in the 1.3 – 2 µm spectral range where many practical applications exist and oxide glasses are transparent, the principal added value of semiconductor optical fibers lies in the mid- and long-wave infrared where oxide glasses are opaque over reasonable distances. The transparency of the cladding glass is important since there inevitably is a component of the optical mode propagating in the fiber core that extends into the cladding. The extent to which this evanescence field is influenced by the cladding is mainly due to the number of modes supported by the waveguide, which depends on the refractive index contrast between the core and cladding, the wavelength, and the core dimension. Given the high refractive
indices of the semiconductors, the index contrast, or, more formally, the numerical aperture, is essentially unity, thus requiring low-moded infrared fibers to have core sizes on the order of a micrometer or less. In such low-moded fibers, which are important for nonlinear applications, a considerable amount of the propagating light is carried in the cladding, so reasonable transparency is critical.

As with the oxide glasses, non-oxide cladding glasses must possess a melting point slightly higher than that of the semiconductor core materials, must not be prone to crystallization or oxidation at the draw temperature, must be stable in air and humidity, and, ideally, are transparent to at least ten microns in the infrared to provide utility to CO$_2$ laser applications.

While infrared glasses generally are fairly low melting, such that most semiconductors are sufficiently refractory to not melt at the draw temperature, InSb has a low melting point of 527°C and, as such, allows reasonable compositional freedom to select a cladding glass. Two strategies were taken here: highly modified, low T$_g$, heavy metal oxide glasses in the PbO + Bi$_2$O$_3$ + B$_2$O$_3$ system, and covalently bonded As-Ge-Se glasses whose composition lies near the rigidity percolation composition, where the average coordination number, $<r>$ [14], is approximately 2.4, were taken. In the latter case, the glass with the $<r>$ value for the strongest network, hence the highest viscosity and lowest thermal expansion coefficient, in these otherwise low melting, low viscosity, and high thermal expansion glasses, was chosen. The lowest melting temperature cubic semiconductor is InSb, which has a melting point reasonably matched to glasses in both the PbO + Bi$_2$O$_3$ + B$_2$O$_3$ and As-Ge-Se, as is shown in Figure 6.6.
Fig. 6.6. Viscosity–temperature curves for cladding glass compositions in the Bi$_2$O$_3$ + PbO + B$_2$O$_3$ and As-Ge-Se compositional families in comparison to the draw point for InSb.

As with the oxide cladding glasses described above, a variety of additives can be used to further tailor the viscosity and the coefficient of thermal expansion. For a CTE ~ 6-8 ppm/K, and a draw temperature [T($\log_{10}\eta = 6$)] of ~ 550 – 600 °C, the specific glass cladding composition for InSb would be about 5Bi$_2$O$_3$ + 40PbO + 55B$_2$O$_3$ for the former heavy-metal oxide glass series and about 35As + 35Ge + 30Se for the latter non-oxide glass series. The PbBiBO glass has a T[$\log_{10}(\eta)=6$] value of ~ 560 °C and a CTE of ~ 4-7 ppm/K, whereas the AsGeSe glass has a T[$\log_{10}(\eta)=6$] value of ~ 530 °C and a CTE of ~ 8-12 ppm/K. In both cases, more compositional exploration and property measurements
will be required to more accurately determine these values and, hence, more accurately tailor them to the specific properties of InSb. It is likely that the PbO + Bi₂O₃ + B₂O₃ system can be tailored within just this system itself, whereas the As-Ge-Se system, and its slightly low T[log₁₀(η)=6] value and slightly high CTE value, probably could benefit from the addition of a more refractory glass additive to strengthen up the network. Substitution of S for Se might be considered the easiest and most compositionally direct route to achieve a slightly more refractory glass, where As-Ge-S glasses have CTE values as low ~ 7 ppm/K. However, their typical T[log₁₀(η)=6] values lie in the range of ~ 400 °C. Hence, other additives, of such refractory sulfides and selenides as Ga₂S₃ and La₂S₃ and Ga₂Se₃ and La₂Se₃, will be considered if compositional optimization fails within the ternary As-Ge-Se system alone.

While the aforementioned sulfide glasses may be suitable for the lowest temperature semiconductors (e.g., InSb), more refractory possibilities exist through “hybrid” glass systems such as oxysulfides. For example, there is complete solubility in the GeO₂-Ge₂S₃ glass family and the glass transition temperature increases sharply when GeO₂ is added to GeS₂. In similarity to the alkali silicate glasses, modifying alkali sulfides can be added to this oxysulfide glass to lower the isoviscous (10^{13} Poise) glass transition temperature. Similarly, trivalent intermediates such as La₂S₃ and Ga₂S₃ can be added to increase the viscosity and glass transition temperatures. Trivalent B₂S₃ and Al₂S₃ provide similar network cross-linking effects but at the cost of severe atmospheric reactivity, and for this reason are not further considered.
6.2 Experimental Work

Based on the considerations presented in Chapter Six, selected glass melts were performed in order to provide preliminary validation to the glass development. Silicon optical fiber was chosen given its relative maturity to that of other semiconductor core optical fibers. Two compositions in the $x[Na_2O:Al_2O_3] + (100-2x)SiO_2$ family, specifically $7.5Na_2O + 7.5Al_2O_3 + 85SiO_2$ and $12.5Na_2O + 12.5Al_2O_3 + 75SiO_2$, were melted in air by Corning Incorporated, using platinum crucibles, at a temperature of 1700°C for 8 hours. While a homogeneous glass resulted, there were remnant bubbles present. For these proof-of-concept experiments, it was decided that bubbles would be tolerable in order to determine if the designer cladding glasses could be drawn into fiber that possessed less oxygen in the semiconductor core. Following an annealing treatment at 1000°C, rods were core-drilled out of the resultant glass and subsequently processed by Kigre Incorporated into cladding tubes possessing an inner diameter of 3.5 mm and outer diameter of 20 mm. Silicon rods, equivalent to those used in Ref. 2, were sleeved into a cladding tube which had previously been drawn in order to close off one end of the tube. Approximately 2 meters of fiber with core size of about 80 µm was drawn at a speed of approximately 2 meters/minute at a temperature of 1450°C using a carbon resistance furnace purged with argon.

Elemental analysis was conducted under high vacuum, using energy dispersive x-ray (EDX) spectroscopy in secondary electron (SE) mode on a Hitachi S-3400 variable pressure scanning electron microscope (SEM). The operating variable pressure was 20kV and the working distance was about 10 mm. Prior to microscopic evaluation, samples
were polished to a surface finish of approximately 0.5 micrometer. The $7.5\text{Na}_2\text{O} + 7.5\text{Al}_2\text{O}_3 + 85\text{SiO}_2$ composition exhibited a coefficient of thermal expansion of 4.07 ppm/K and glass transition temperature of 890°C, as predicted by SciGlass [10] using the Priven-2000 method.

The $12.5\text{Na}_2\text{O} + 12.5\text{Al}_2\text{O}_3 + 75\text{SiO}_2$ composition exhibited a coefficient of thermal expansion of 6.269 ppm/K and glass transition temperature of 850°C, also as predicted by SciGlass. In this case, the cladding glass drew at about 1450°C yielding fiber. A cross-sectional image of the fiber is provided in Figure 6.7a. Characterization of the elements present across the core (Figure 6.8a) shows that the oxygen content in the core is about 6 weight percent, which is considerably lower than the approximately 17 weight percent oxygen found in the original molten core silicon optical fibers drawn at about 1950 °C [2]. This comparison of profiles is shown in Figure 6.8b. It is likely that the reduced oxygen content is due to the considerably reduced draw temperature (1450°C versus 1950°C) enabled by these designed cladding glasses, relative to the commercially available yet non-optimum expedients such as silica glass.

Figure 6.7. Scanning electron microscope image of the cross-section of the tailored glass-clad silicon core optical fiber (residual bubbles present in glass).
Fig. 6.8. (a) Elemental profile across the core of a silicon optical fiber drawn using an optimized cladding glass and (b) Comparison of elemental profiles across the core of the original silica-clad silicon core optical fiber [2] and that of the cladding glass designed and drawn in this work.
Based on the above results, it was determined that the tailored glass compositions did indeed provide improved results in these optical fibers, so the next obvious steps were to create larger and bubble-free rods of the cladding glass from which we could draw long lengths of high quality fiber. Efforts to try to remove the bubbles in the cladding were extended by using an elevated melting temperature for improved fining. Molybdenum, used extensively in the glass industry as submerged electrodes, was chosen as the crucible material (purchased from Triumph Northwest, 16 mm diameter and 55 mm tall) based on cost, ease of fabrication, and thermodynamic stability with oxide melts. The composition 7.5Na₂O + 7.5Al₂O₃ + 85SiO₂ was selected, and the batched glass powder was pre-calcined between 1000-1200°C to remove carbonates (Na₂CO₃). Several melting runs were made, in a helium atmosphere, ranging from 1600-2050°C in melting temperature. Thermal properties of the melted glass were confirmed using a differential scanning calorimeter/ thermogravimetric analyzer (DSC-TGA), and the thermal expansion coefficients were determined using a TA Instruments Q400/2940 thermomechanical analyzer (TMA). Improved fining of the melts was evidenced, along with little significant chemical dissolution of the crucible into the melt, as shown in Figure 6.9.
Characterization of the glass post-melt showed the glass composition to have shifted slightly, as shown in Figure 6.10, to $6\text{Na}_2\text{O} + 8.4\text{Al}_2\text{O}_3 + 85.6\text{SiO}_2 \pm 1\text{-}2\text{ mole\text{%}}$. The coefficient of thermal expansion, measured as previously described herein, was 3 - 4 ppm/°C, and the glass transition temperature occurred at $830\text{-}850°\text{C}$. The viscosity $(T[\log_{10}(\eta)=6])$ was extrapolated to be 1400 - 1500 °C. While the composition suggested for the silicon core optical fiber in Chapter 6.1.1 was $6\text{Na}_2\text{O} + 6\text{Al}_2\text{O}_3 + 88\text{SiO}_2$, the experimental results of the $7.5\text{Na}_2\text{O} + 7.5\text{Al}_2\text{O}_3 + 85\text{SiO}_2$ composition proved to be a close enough match to continue further melts.
In order to further continue this study, a glass rod large enough to draw into fiber is necessary. To this end, a stepped molybdenum crucible of 200 mm depth and 35 mm diameter, with a tapered loading chamber of 60mm in height and 80 mm in diameter, was purchased from Engineering Services at Ames Laboratory at Iowa State University. The glass was melted at 2100°C, and annealed at a step rate to slow cool at approximately 0.25°C/min. Work is currently underway to core drill the glass from the crucible.
Cladding glass compositions have been proposed in this Chapter for several high-value semiconductor core materials. Specifically identified were cladding glass compositions that would eliminate thermal expansion mismatches with unary (Si, Ge), binary (InSb, GaAs), and ternary (GaAlSb) semiconductor core and should draw just above the melting point of the core minimizing issues with dissolution. Initial experimental results show considerably less oxygen content in the core of the fibers drawn with the tailored glass composition, with good matching of coefficients of thermal expansion, and suggest that continued efforts using this glass science approach should lead to the creation of more optimized semiconductor core glass-clad optical fibers.


CHAPTER SEVEN
SUMMARY/CONCLUSIONS

The molten core approach has been shown to be a practical method for producing optical fibers from unconventional materials over long lengths using scalable processes. Equally important is the rich materials science that can be conducted using this method, including fundamental studies of thermodynamics, kinetics, crystallization, and phase diagrams.

The principal sources of loss in present silicon core fibers were discussed and selected measurements reported to further identify whether cracks, grain boundaries (polycrystallinity), surface roughness, longitudinal perturbations, or oxide precipitates dominate in the drawn fibers [1]. Transmission electron microscopy (TEM) and electron backscatter diffraction (EBSD) results showed that regions of localized single crystallinity are present in the core. However, the overall polycrystallinity of the semiconductor core could possibly lead to scattering due to stress-optics effects [2] and absorption due to differential densities of gap states [3, 4]. Surface roughness was shown, via AFM measurements, to be relatively low, commensurate with previous measurements, and not likely to contribute significantly to scattering. Potential evidence for precipitates was shown in infrared transmission images. At present, the dominant loss in semiconductor core fibers appears to be scattering; either from cracks originating from the thermal expansion mismatch between the core and cladding, perturbations in the solidification leading to longitudinal variations in the fiber, and/or oxide precipitates that likely partition to the grain boundaries. Obviously, progressively higher purity source
materials could only be of additional benefit once the sources of scattering are more definitively identified and mitigated. With respect to each scattering source, presented here are comments on what has been done to date and what additional actions might be further taken.

7.1 Cracks and Stress-Optic Influences due to Core/Clad Differential Thermal Expansion

As the molten semiconductor cools from the draw temperature to its melting point, there is shrinkage that can lead to void formation. Once the solidification occurs, there will be either residual strain or, if this strain exceeds the fracture limit, cracking can occur. Transmission through a series of cracks can be modeled as multiple frustrated total internal reflections that can reduce transmission very quickly [5]. As detailed in this Dissertation, recent work has focused on cladding glasses with compositions specifically tailored to match the thermal expansion of the core phase to avoid such strain and cracking [6]. Stresses also are lessened at smaller core sizes, so methods to make smaller fibers, whether through tapering or drawing at reduced temperatures, also are worthy of further consideration.
7.2 Perturbations in the Solidification leading to Longitudinal Variations in the Fiber

Whether from inevitable (though small) perturbations in draw speed or diameter or presently unknown flow dynamics of the molten core prior to and during solidification, Fig. 5.6(c) quite clearly shows longitudinal striations and side scattering that originates from them. The most reasonable approach to lessening such striations is annealing, which has been tried on silicon optical fibers using both (photo)thermal [7] (as detailed herein) and laser annealing [8] processes. In both cases, enhancements in the quality of the crystallinity and properties were observed though deeper understanding of the annealing mechanisms that influence crystallographic reorientation is needed. Regardless, annealing – perhaps in-situ during the draw – has shown promise and should be further explored and optimized. Accordingly, this work serves as an example of how various fiber processing techniques can influence the crystalline details of these semiconductor core fibers.

7.3 Polycrystallinity and Oxide Precipitates

As has been well characterized, the as-drawn semiconductor core fibers are polycrystalline with single crystalline grain sizes on the order of several millimeters to centimeters [9]. Since grain boundaries are, by definition, regions of disorder between crystals of differing orientations, they tend to be regions where impurities can segregate
and can have differing dielectric, hence refractive, properties. While the aforementioned lengths over which single crystallinity is developed during the solidification of the fiber might be useful for selected applications, such as mid-IR light sources based on Raman shifting [10], generally, longer lengths would be preferred. Towards this end, the previously discussed annealing methods have proven effective in enhancing the degree of single crystallinity. In fact, the longest single crystalline semiconductor optical fiber (> 1 cm) was realized following photo-thermal annealing [7]. Tapering has also proven effective in controlling single crystallinity [11], as has the use of a square core rather than the more conventional round core [12]. There does not seem to be any one process that best enhances single crystallinity so future advances might further consider annealing, tapering, and fiber geometry (which might include some residual stresses to facilitate stress-induced crystallization). For completeness, it is noted that the optical attenuation of the annealed or tapered fibers was not measured, as the work herein focused on maintaining or controlling the fiber crystallinity and crystallography. However, analogous glass-clad crystalline germanium core optical fibers have been realized using the molten core method employed here with attenuations below 1 dB/cm [13], which are approaching levels required for practical optoelectronic application.

With respect to oxide precipitates, it has been conjectured, since the initial molten core silicon optical fiber [14], that the measurable presence of oxygen in the core is associated with oxide precipitates that arise from dissolution of the cladding glass by the core melt during the high temperature processing of the fiber. There are two principal methods to reduce the level of cladding glass dissolution: (a) reduce the processing
temperature, since dissolution is a thermally activated process, or (b) reactively remove (i.e., getter) the oxide phases through chemical means. With respect to reducing the draw temperature, the aforementioned designer cladding glasses [6] can be selected such that they, in addition to being expansion-matched, draw at a temperature just slightly above the melting point of the core semiconductor phase. This would then constitute the lowest temperature that a molten-core-derived optical fiber can be fabricated and has shown some initial success [6]; though more development is necessary.

With respect to the use of a reactive chemistry, the molten nature of the core phase during the fiber draw process enables a convenient and versatile route to control the core composition and crystallography. Molten core silicon optical fibers suffer from dissolution of the cladding glass by the core melt. This dissolution brings oxygen into the core, which presumably leads to oxide precipitates which scatter light and generally degrade performance. Since dissolution is a thermally driven process, the high draw temperatures of silica glass-clad silicon-core optical fibers further aggravate this issue. Efforts to reduce the formation of oxide precipitates have involved using in-situ reactions by adding silicon carbide (SiC) to the silicon core, in sufficient quantity to react with all of the diffused oxygen [15]. Employed here, for the first time, to the best of our knowledge, is a reactive molten core approach whereby silicon carbide (SiC) is incorporated into the silicon core such that the reduction of SiO$_2$ getters oxygen at the draw temperature. Such “Si + SiC”-derived silicon optical fibers were fabricated and were found by elemental analysis to exhibit no measurable oxygen in the core of the resultant fiber. Further, x-ray diffraction showed the SiC to be consumed during the draw
and that the fiber core was comprised only of highly crystalline silicon. Scattering was determined to be reduced as a result of the greatly lessened oxygen content. This work shows that the high temperature processing of optical fibers can be judiciously employed to take advantage of various chemical reactions to yield counter-intuitive results. Exemplifying this is the realization here of an oxygen-free silicon core optical fiber drawn in an oxide glass cladding at 2000°C; an important advance in the continued evolution of these crystalline semiconductor optical fibers.

It is likely that future progress towards the reduction in loss of these novel fibers will require a combination of (a) tailored cladding glasses to negate expansion mismatches and reduce cladding dissolution during fiber fabrication, (b) in-situ melt-phase chemical reactions to reactively getter oxide and other impurities/contaminants, and (c) greater single crystallinity in order to reduce grain boundary scattering though annealing, tapering, or core geometric control. Methods for reducing loss in semiconductor core optical fibers, as discussed herein, should lead to the development of higher quality optical fibers to expand the growing field of silicon photonic waveguides.


While there are applications for multimode semiconductor core optical fibers (e.g., IR power delivery), single mode analogs would be far more interesting to the community at large, particularly as relates to these fibers’ use in nonlinear optics. Accordingly, for completeness, it is appropriate to discuss the technological limits of the fabrication processes employed. Given the extraordinarily high refractive index contrast between the semiconductor core and glass cladding, which can approach about 2.5 in the case of InSb core and borosilicate clad (larger than air/silica used in many photonic crystal fiber designs), core sizes for single mode operation are in the range of 500 nm or less in the infrared spectral region. As shown in Fig. 3.3, the core radius has been reduced to ~3 µm and so the fiber is still multimoded; thus more extreme tapering will be required [1]. Such tapers are routinely fabricated using the same method described herein and so there are, in principle, no expected issues with extending this work to the single mode regime. While dissolution and diffusion are especially problematic at small core sizes, tapering results indicate that a reduced core size facilitates both a greater degree of single crystallinity and alignment of the principal crystallographic axis, relative to the fiber longitudinal axis, of the core phase [1]. There is, therefore, additional value in reduced core sizes beyond simply achieving a single mode crystalline semiconductor core fiber.

Though not yet attempted at single-mode core sizes, the aforementioned successes in employing melt-phase chemistry to reactively getter oxide phases that dissolve into the molten core from the cladding glass during fiber draw [2] is the most obvious initial path
forward. One disadvantage of the molten core approach is that the process would seem unable to permit a multi-semiconductor layer structure, as has recently been done using high pressure CVD approaches [3, 4]. Conceivably, semiconductors of reasonably similar refractive index could be deposited to create a core and inner cladding with sufficiently small numerical aperture so as to yield single mode operation at reasonable core sizes. Both molten core and CVD methods would have the previously discussed issues relating to optimized loss, crystallinity, and crystallography in common. It is hoped, therefore, that this work is more broadly applicable to the field than just for those fibers fabricated using the molten core approach.

For the future, analogous studies over longer lengths and with higher $n$ values (hypercircle exponents; see Appendix A) would be of interest. In addition to the expected and realized reduction in oxygen content in the silicon core optical fibers drawn using the cladding glasses developed in this work, one would expect a reduction in optical attenuation. Unfortunately, loss measurements could not be reliably made on these fibers due to the residual bubbles in the cladding that led to significant non-uniformities in core shape (Fig. 6.7). It would not be possible to deconvolve the components of loss associated with chemical heterogeneities (e.g., oxide precipitates) versus those from geometric perturbations. Efforts are underway to achieve bubble-free cladding glasses that will yield more uniform fibers on which accurate spectral attenuation measurements can be made.

Particularly at these extremely small core sizes, issues of diffusion are exacerbated. As a case in point, Fig. 1.4(b) shows that a (silicon) core will completely
oxidize during the molten core fiber draw process for core sizes below a few micrometers; i.e., while the fiber is still multimoded. Such core/clad reactivity is a limitation of the molten core process, provided additional measures are not taken to counter the chemical processes. Since dissolution, and the subsequent diffusion into the melt, is thermally activated this then suggests that a reduced processing temperature could significantly influence the oxidation of the melt and, as an important consequence, the formation of precipitates that cause scattering and limit the optical attenuation. Specialty cladding glass compositions have been developed; however, given the melt temperature for both silicon and germanium, these next-generation cladding glasses are necessarily still oxide compositions and, therefore, contribute to mid-infrared attenuation as more of the evanescent field propagates in the cladding as single mode conditions are reached. While, for example, some alkali- and alkali-earth silicates have been theorized to possess lower losses than silica [5, 6], a practical attenuation of 1 dB/m would limit single mode fibers to an operating wavelength of less than about 2.5 µm. This suggests that single mode semiconductor core fibers could enjoy a wealth of opportunities in the 1–2 µm spectral range though longer wavelength operation would necessitate multi-mode designs. The lower temperature semiconductors, such as InSb, may present better options for single mode operation, and should be explored further. Even though the core sizes would still be fairly small (several micrometers), there are refractory infrared glasses that can be drawn at temperatures above the semiconductor melting point and possess adequate transparencies at mid- and long-wave IR wavelengths as to be useful.


APPENDICES
Appendix A: Hypercircles

Hyperellipses, or sometimes called superellipses or Lamé curves [1, 2], represent a general class of curves defined by the following relationship: $x^n + a^n \cdot y^n = 1$, where $n$ is any positive real number and $a$ is a constant. “Hypercircles” occur when $a = 1$ and the $x$ and $y$ intercepts are equal such that $x^n + y^n = 1$ or $y = (1-x^n)^{1/n}$. When $y = x$, the radius vector makes a 45° angle with both axes such that $2x^n = 1$ and $x = y = (1/2)^{1/n}$.

At this 45° point, the radius vector, $R$ (a measured quantity, in this case measured using the SEM), has length: $R = \sqrt{2} \cdot x$, so $R = \sqrt{2} \cdot (1/2)^{1/n}$, from which follows $\log(R/\sqrt{2}) = (1/n) \cdot \log(1/2)$ and $n = \log(2) / \log(\sqrt{2} / R)$. So a direct microscopic (or micrographic) measure of the radius vector yields the exponential factor that defines the hypercurve. Figure A-1 provides several representative hypercircles for given values of $n$, which depend only on the measured value of $R$, as well as overlays of hypercircles that best fit the initial square-core silica glass preform and resultant round and square silicon core optical fiber.
Figure A-1. Schematic representations of one quadrant of selected hypercurves: $n = 2$ (circle), $n = 2.4$ (square core fiber treated in this work) and $n = 100$ (approximation to a square, $n = \infty$).

Fig. B-1. Elemental analysis of “conventional” silicon core optical fiber compared to “Si+SiC” silicon core optical fiber.
Fig. B-2. Screenshot of SciGlass computational software [1].
Fig. B-3. Screenshot of SciGlass computational software [1].
Fig. B-4. Molybdenum crucible loaded with calcined batch powder.

Fig. B-5. Molybdenum crucible and glass post-melt.
Fig. B-6. Glass melting run profile.
Fig. B-7. Differential scanning calorimetry/ thermogravimetric analysis (DSC-TGA) plot of the glass transition temperature of post-melted glass.
Fig. B-8. Thermomechanical analysis (TMA) plot for the thermal expansion coefficient of post-melted glass.
Fig. B-9. Thermogravometric analysis (TGA) plot for the weight loss of uncalcined sodium aluminosilicate batch powder.
Fig. B-10. Thermogravometric analysis (TGA) plot for the weight loss of the calcined sodium aluminosilicate batch powder.
Fig. B-11. Drawing of molybdenum crucible for large scale melt.
Fig. B-12. Molybdenum crucible for large scale melt.