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Effect of controlling recrystallization from the melt on the residual stress and structural properties of the Silica-clad Ge core fiber

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ABSTRACT

Effect of controlling recrystallization from the melt (1000 °C) on the residual stress and structural properties of a Ge core fiber via molten core drawing (MCD) method is investigated. Ge core fibers is investigated using Raman spectroscopy, scanning electron microscope (SEM), and X-ray diffraction (XRD). Compared with the as-drawn Ge fiber, the Raman peak of the recrystallized Ge fiber shift from 300 cm^{-1} to 300.6 cm^{-1} and full width at half maximum (FWHM) decreased from 5.36 cm^{-1} to 4.48 cm^{-1}. The Ge crystal grains which sizes are of 200–600 nm were formed during the process of recrystallization; the XRD peak of (1 1 1) plane is observed after recrystallization. These results show that controlling recrystallization allows the release of the thermal stress, and improvement of the crystal quality of Ge core.

1. Introduction

There has been growing interest in multi-material fibers that comprise semiconductors [1]. As a kind of semiconductor core fiber, Ge core fibers have a great potential for mid-infrared applications. The optical transparency of Ge extends even further into the infrared, with a low loss window of 2–15 μm, it has great potential for applications in the important mid-infrared wavelength regime [2]. It has a very high refractive index in the fiber core, allowing for tight mode confinement [3]. There is also a large third-order nonlinear susceptibility, which acts to enhance the nonlinear coefficient [4]. Attempts to fabricate crystalline Ge core fibers are tried all the time. Ballato [5] reported that the Glass-clad single-crystal Ge optical fiber was drawn by molten core drawing (MCD). Extensive studies by the Clemson team to determine the crystalline size and orientation of these fibers have revealed that MCD method can produce large grain sizes, with single crystalline regions of lengths ranging from 8 to 15 mm, and dominant growth directions of ⟨1 0 0⟩ and ⟨1 1 0⟩ [6,7]. Consequently, this method has produced the lowest loss Ge fibers to date, with a value of 0.7 dB/cm measured at 3.39 μm, albeit in a large 300 μm diameter core [8]. The HPCVD method can be used to fabricate both amorphous and polycrystalline Ge fibers in core diameters of only a few microns [9]. Losses for the HPCVD fibers have been reported for the a-Ge:H material, with the lowest loss being measured in a fiber with a 30 μm diameter of 4.8 dB/cm at 10.6 μm [10].

However, the development of the Ge core fiber has been hindered owing to the difficulties of performance further improvement. Similar with silicon core fiber [11,12], high residual stress and low crystal quality are two important problems in the development of Ge core fiber. Heat treatment is an effective approach to improve the quality of semiconductor core fiber. Incoherent light source based rapid photothermal processing (RPP) was used for the first time to anneal glass-clad silicon core fibers by Gupta [13]. Measurement results indicated that the RPP treatment increased the local crystallinity and therefore assists in the reduction of the local stresses in the core, leading to more homogenous fibers. Laser annealing of a fiber with an amorphous silicon core was demonstrated by Healy [14]. The annealing process produced a fiber that had a highly crystalline core, whilst reduced the optical transmission losses by ~3 orders of magnitude. Healy [15] annealed silicon core fiber by CO_2 laser, it could produce single crystal silicon cores which was 1.8 cm, thus greatly reduced the optical transmission losses. The fiber only had losses of only ≈2 dB/cm at 1.55 μm and 1 dB/cm at 2 μm. Chaudhuri [16] fabricated polycrystalline silicon core optical fibers by modified thermal annealing of amorphous silicon chemically deposited at high pressure, obtaining a low optical loss of less than 1 dB/cm at a wavelength of 2.2 μm. Ji [17] precisely scanned a continuous wave

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argon ion laser (wavelength of 488 nm) along the amorphous Ge core fibers deposited inside silica capillary fibers by HPCVD to uniformly crystallize them, obtaining the first small core diameter (5.6 μm) single-crystal Ge fibers, up to ≈9 mm long, and with optical loss down to 1.33 dB cm^{-1} at 2 μm. However, relative to Si core fiber, little is known about heat treatment of a Ge core fiber, especially heating treating at temperature higher than Ge melting point.

In this study, a Ge core fiber drawn via the MCD was heated treatment at 1000 °C which is beyond the melting point of single crystal Ge in a muffle furnace. After that, the fiber is cooled down slowly to room temperature with a rate of 2.5 °C/min. At the condition of cooling slowly, kinetically Ge atoms have enough time to choose the most preferable sites, and to be incorporated into the crystal. The effect of the controlling recrystallization from melt on the stress and structural properties of the Ge core fiber is mainly investigated.

2. Experimental section

The Ge core fiber was fabricated by the MCD method. Small crystals of Ge bulks with purity of 99.99% were packed into a silica tube having an inner diameter of about 3 mm and an outer diameter of 10 mm, which had been pre-drawn in order to seal one end of the tube. Fiber was drawn using a drawing tower at approximately 2000 °C. This is well above the melting point of the Ge core, and the molten Ge was then encapsulated by the viscous silica cladding. The drawing temperature and velocity were monitored and adjusted during the process to obtain fibers of different diameters. Approximately a Ge fiber of about 200–240 μm diameter was drawn, which yielded a core size of 50–80 μm. Fig. 1 shows the photograph and microscopic photograph of the as-drawn Ge core fiber. About 20 cm of this fiber was used for our research.

The fiber was heated from room to 1000 °C which is above the melting point of single crystal (938 °C) in a muffle furnace. The heating rate was 10 °C /min. Then the fiber was kept at 1000 °C for 10 min. After that, the fiber was cooled down to 400 °C at a rate of 2.5 °C/min. Then, the furnace was shut down to chill the Ge fiber naturally to room temperature.

3. Measurements section

The cross-section of the fiber was investigated using a CamScan Apollo 300 scanning electron microscope (SEM). The microscope was operated at 20 and 10 mm working distance. The cross-section of the fiber was mechanically polished with silicon carbide (SiC) emery paper. Energy dispersive X-ray spectroscopy (EDS) was used for elemental analysis to examine the distribution of elements. Elemental compositions were measured at several locations traversing the cross-section of the fiber, and the distribution of Ge, Si and O elements were examined.

Micro-Raman spectra were collect on both the Ge starting bulks and the center of the cross-section of the Ge core at room temperature using an InVia Raman spectrometer, with 20 mW power at 633 nm wavelength excitation.

X-ray diffraction analysis (XRD) was used to study the crystallization state of the Ge core. It was carried out in the cross-section of the Ge core using a 18 KW D/MAX2500V+/PC X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) and a solid-state Ge detector. Diffraction patterns were collected from 20° to 80° in 2-theta.

4. Results and discussion

Fig. 2 shows an SEM image of the cross-section of the Ge core fiber. The diameter is about 210 μm with an inner diameter of 50–70 μm, there is no obvious interfacial irregularities at the core/-cladding boundary.

Elemental analysis was performed on the cross-section of the recrystallized Ge core fiber in order to determine the extent of the elemental distribution. Fig. 3 shows the results of the cross-sectional elemental analysis using EDS. The results show that the Ge concentration of the core is almost 100% with negligible oxygen. The interface is well-defined.

To determine the stress and crystal quality of the fibers, micro-Raman measurements were carried on the cross-section of the Ge core. In order to compare the shift and broadening of the Raman peaks of the Ge core to that of the bulk Ge crystal, the Raman spectrum of a bulk Ge crystal was measured as a reference, as shown in Fig. 4. The peak position and Gauss full width at half maximum (FWHM) values of the samples are shown in Fig. 5 and Table 1, respectively. All fibers and Ge crystals exhibit a strong peak around 300 cm^{-1} corresponding to the transverse optical (TO) mode, and the peak position is slightly different in the different samples. The peak positions of Sample 1 (as-drawn Ge core), 2 (recrystallized Ge core), and 3 (Ge crystal) are 300.0 cm^{-1}, 300.6 cm^{-1}, and 301.2 cm^{-1} respectively. The different peak positions between the Ge core fibers and the Ge crystal means that tensile stress is formed in the Ge core [18]. The position shift of the phonon Raman peak may occur when the stress changes, because the phonon vibration frequency is related to the residual stress in the material. Relative to the as-drawn Ge fiber, when recrystallized, a red shift in the Raman peak position is observed. This indicates that the residual stress releases through recrystallization, most likely because

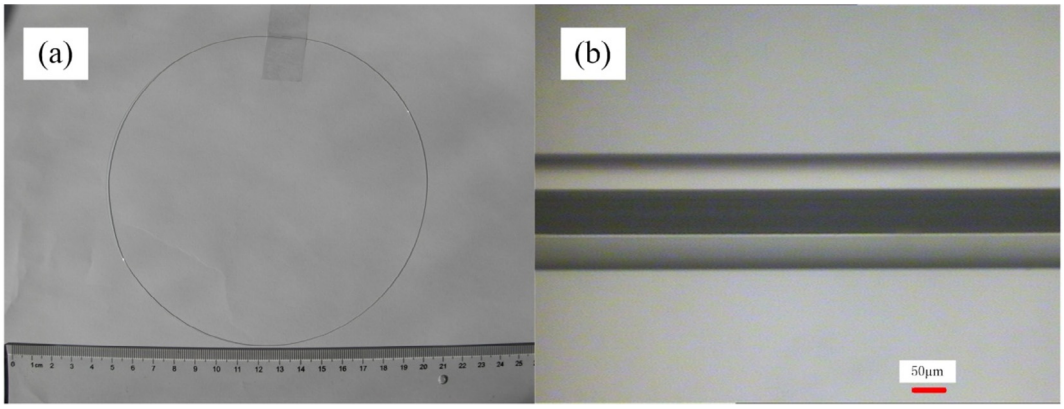

Fig. 1. (a) Photograph of a as-drawn fiber. (b) Microscopic photograph of a as-drawn fiber.