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Antimony selenide core fibers

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ABSTRACT

A new type of thermally sensitive fibers with an antimony selenide (Sb_2Se_3) core and phosphate glass cladding is demonstrated. The fibers were fabricated by a molten core method and maintained overall diameters ranging from 250 to 800 μm and core diameters of 35–200 μm. A 2.8 cm long Sb_2Se_3 core fiber, electrically contacted to external circuitry through fiber end facets, exhibited a four orders of magnitude change in conductivity after the whole fiber was heated from 25 to 195 °C. In addition, the fiber exhibited enhanced photoconductivity under illumination. These results indicate that Sb_2Se_3 core multimaterial fibers have promising applications in temperature sensing, optical switches and photodetectors.

1. Introduction

Since the 1980s, optical fibers have been developed in many areas, including light generation using fiber lasers, nonlinear optics, medicine and remote and distributed strain- and temperature-sensing in environmental and infrastructure monitoring [1–7]. Considerable efforts have been devoted to these specialized optical fibers, which provide greater or enhanced functionality in the aforementioned areas. To date, multiple materials with disparate photonic, optoelectronic, acoustic, piezoelectric and thermo-mechanical properties have been monolithically integrated into fibers, which are paving the way to a new generation of multi-material fibers endowed with unique functionalities delivered at optical fiber length scales and costs [8–11].

Recently, a new fiber material, which can sense heat along its entire length and generate an electrical signal, has been demonstrated [12]. Specifically, a macroscopic preform, which contains conducting material (96% Sn–4% Ag alloy), semi-conducting material ($Ge_{17}As_{23}Se_{14}Te_{46}$ semiconducting glass) and insulating material (polysulfone film), was thermally co-drawn into long multimaterial fibers. This is in contrast to all previous work on thermal sensing using fibers, which require the use of optical probing signals [13]. However, considering that this multimaterial fiber is drawn at a temperature of 270 °C, it will be restricted to use at relatively low temperatures (<230 °C), likely to be lower than the melting temperature of the composition of the materials. In addition, superconductivity at liquid helium temperatures of approximately 4 K has been demonstrated in a glass-clad lead core multimaterial fiber [14]. However, only a few reports have focused on a thermally sensitive multimaterial fiber that can be used at relatively high temperatures.

Several approaches have been developed to successfully fabricate multimaterial fibers, including high pressure chemical vapor deposition (HPCVD), the molten core or reactive molten core method, the pressure-assisted physical filling (PAPF) technique and the low temperature drawing (LTD) method [9,15,16]. However, HPCVD is limited by its slow deposition rate, thus it is not possible to fabricate long lengths of fiber [17]. Similarly, one of the main drawbacks of the PAPF technique is that the lengths of the fibers are restricted by the short device lengths [15]. The LTD method has

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been used to integrate amorphous chalcogen-semiconductors, low melting temperature metals and polymers into multimaterial fibers [10]. However, there is no clear method to extend the LTD method to allow for significant amounts of traditional, technologically relevant semiconductors (such as groups II, II-VI and III-V) to be incorporated into the fiber devices [15]. Compared with the above methods, the molten core or reactive molten core approach is very useful for applications where long lengths of low loss fiber are required. Therefore, the molten core technique was chosen here to fabricate long lengths of thermally sensitive multimaterial fibers. The main criteria for successfully drawing glass-clad multimaterial fibers by the molten core approach are as follows [9,11]: (1) The glass cladding that makes the preform and holds the assembly together must be drawn at a relatively high viscosity (typically between 10^4 and 10^7 Pa s) and resist devitrification during thermal drawing. (2) The drawing temperature must be higher than the melting temperature of the core constituents and lower than the boiling temperature of the core materials. (3) The difference in thermal expansion coefficients between the materials should be small in the temperature range extending to the drawing temperature to avoid mechanical fractures resulting from thermo-mechanical mismatches. In addition, care must be taken to avoid fluid instabilities that may occur when the viscosity of the materials is lowered and the transverse dimensions are reduced.

Antimony selenide (Sb_2Se_3) is a naturally p-type V_2-VI_3-layered chalcogenide semiconductor with an orthorhombic crystal structure and a space group Pnma (No. 62) [18]. It has a direct band gap of 1.0–1.2 eV [18], a high Seebeck coefficient [19] and a fast amorphous-crystalline transition [20], making it an attractive candidate to use in photovoltaic [21], thermoelectric [22] and phase-change memory devices [23]. Recently, Sb_2Se_3 has attracted much attention as a new absorber material for thin-film photovoltaics due to its high absorption coefficient ($>10^5$ cm^{-1}) at short wavelengths, non-toxicity and low cost [21,24]. In addition, silicon core multimaterial fibers as microwire radial-junction solar cells and light trapping materials in horizontally aligned microwire solar cells have been reported [25,26]. Therefore, semiconducting Sb_2Se_3 is a very intriguing core material for temperature sensing, photodetecting and even solar cells in multimaterial fibers. In our previous studies, phosphate glass, which has excellent optical and mechanical properties, was used to fabricate glass-clad semiconductor core multimaterial fibers by the molten core method [16]. Therefore, according to the mentioned main criteria for successfully drawing glass-clad multimaterial fibers by the molten core method, phosphate glass was identified to be the suitable glass cladding to fabricate Sb_2Se_3 core multimaterial fibers.

2. Experimental

In this study, we demonstrate a multimaterial fiber with a Sb_2Se_3 core and phosphate glass cladding, fabricated by a molten core method [27]. A bulk multi-component phosphate glass ($55P_2O_5$–$18K_2O$–$13BaO$–$14Al_2O_3$ wt%) was fabricated using the conventional melt-quenching method and then processed to a cylindrical preform with a diameter of 22 mm. The phosphate glass preform had a diameter of a 3 mm cylindrical hole with one end closed. The other end of the cylindrical hole in the preform was sealed after the Sb_2Se_3 powder of 99.999% purity (Alfa Aesar Corporation, USA) was filled in under vacuum conditions. The continuous Sb_2Se_3 semiconductor core fibers were drawn using a commercial fiber drawing tower under an argon atmosphere. The drawing temperature of the phosphate glass cladding is ~660 °C, which is higher than the melting point (608 °C) of Sb_2Se_3 powder [21], assuring that the glass cladding draws directly into the fiber and that the molten of the core precursor phase also follows and ultimately solidifies as the fiber cools [28].

The polished fiber cross section and the distribution of elements spatially across the core/clad interface were characterized by an electron probe X-ray micro-analyzer (EPMA-1600, Shimadzu, Japan). The phosphate glass cladding can be removed by etching in HF acid. The crystalline phase of the fiber core was identified by an X-ray powder diffractometer (XRD) (X'Pert PROX, Cu $K\alpha$). The micro-Raman spectra (532 nm excitation) were collected on the fiber core using a Renishaw RM2000 instrument. The currents of the Sb_2Se_3 core fibers between dark and illuminated (under illumination from a 200 mW/cm^2 808 nm HeNe laser) states were recorded using a Keithley series 2400 source meter. The whole length of the fiber sample was heated by a crystal oven (TC038-PC, HC Photonic Corporation) to characterize the thermal sensitivity of the fiber. The current-voltage curves for the fiber sample were recorded using a Keithley series 2400 source meter.

3. Results and discussion

Fig. 1 (a) shows the polished cross section of the Sb_2Se_3 core fiber. It is clear that the fiber has good circularity and uniformity with an outer diameter of ~250 μm and an inner diameter of ~35 μm. There are no discontinuities at the core/clad interface and no cracks and bubbles, indicating good wettability and well-matched coefficients of thermal expansion between the Sb_2Se_3 core and phosphate glass cladding. The fiber core shows a bright white color due to the high refractive index contrast between Sb_2Se_3 and phosphate glass. The core/clad boundary is very clear. EPMA measurements were performed to examine the distribution of elements spatially across the core/clad interface. The two-dimensional energy-dispersive X-ary (EDX) mapping distributions of P, O, Se and Sb are illustrated in Fig. 1(b)–(e), respectively. The distributions of P and O are mainly in the cladding region, while the core is mainly composed of Se and Sb. The distribution boundary of each element forms a circle, however, some oxygen diffused into the core region. According to the color bar, it can be seen that Sb has a higher concentration than that of Se in the core region. These results indicate that the core-clad structure of the fiber is preserved completely and that some diffusion occurred during the fiber drawing process.

Fig. 2(a) comparatively presents the XRD patterns of the Sb_2Se_3 powder and fiber core. All the diffraction peaks of the Sb_2Se_3 powder agreed well with the orthorhombic Sb_2Se_3 structure (JCPDS 15–0861). It can be seen that there is excellent agreement between the diffraction peaks of the Sb_2Se_3 powder and those of the fiber core, indicating that the fiber core exhibits phase purity and that no obvious secondary phase is present. The narrow linewidth of the X-ray reflections further verifies the high degree of crystallinity in the fiber core. Fig. 2(b) provides the micro-Raman spectra from the Sb_2Se_3 powder and fiber core. Only two Raman bands, centered at 187 and 251 cm^{-1}, were observed, corresponding to the heteropolar Sb–Se and nonpolar Sb–Sb vibrations, respectively. These Raman bands are characteristic of crystalline Sb_2Se_3 [18,29]. The significant similarities between the Sb_2Se_3 powder and fiber core imply a high degree of crystallinity and phase purity. As noted above for Fig. 1(c), there is some diffusion of oxygen in the core region. However, the XRD and micro-Raman spectra were unable to observe oxide-related impurities, indicating that the content of oxygen in the fiber core is relatively low or that the oxygen in the core region is present as amorphous oxide precipitates.

The elemental (Sb, Se, O, P) profile across the core/clad interface of the fiber is shown in Fig. 3. The zero relative distance represents the middle of the core. The core possesses a composition of nearly 48.1 Se-49.7 Sb in weight percent, which is ~60 Se-40 Sb in mole percent and is reasonably consistent with the core precursor. It is