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Fabrication of Arsenic Selenide Optical Fiber with Low Hydrogen Impurities

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Arsenic selenide glass optical fibers typically possess extrinsic absorption bands in the infrared wavelength region associated with residual hydrogen and oxygen related impurities, despite using purified precursors. We report a purification process based on the addition of 0.1 wt% tellurium tetrachloride ($TeCl_4$) to the glass. During melting, the chlorine from $TeCl_4$ reacts with the hydrogen impurities to produce volatile products (e.g., HCl) that can be removed by subsequent dynamic distillation. The processing conditions have been modified accordingly to give very low H–Se impurity content. Consequently, the H–Se absorption band centered at 4.57 μm has been reduced from tens of dB/m to 0.2 dB/m.

I. Introduction

Infrared-transmitting chalcogenide optical fibers are being used for many applications[1–7] in the infrared (1–13 μm) from laser power delivery (CO at 5.4 μm and CO_2 at 10.6 μm) as well as in fiber optic chemical sensor systems using absorption, evanescent, and diffuse reflectance spectroscopy for environmental and facility cleanup.[3–6] These applications are made possible through the development and fabrication of stable low-loss arsenic sulfide based fiber ($As_{40}S_{(60-x)}Se_x$) and tellurium-containing fiber ($Ge_{30}As_{10}Se_{30}Te_{30}$) with minimum loss of 0.1 dB/m.[8–10]

Although purification has resulted in low fiber scattering losses, impurities related to hydrogen, carbon, and oxygen still leave discrete absorption bands in the infrared (H–Se at 4.57 μm, CO_2 at 4.3 μm, and O–H at 2.92 μm).[9] The majority of the impurity bands are associated with hydrogen-containing species. To minimize these impurities in the glass melt, it is necessary to getter the hydrogen using a reactive chlorine atmosphere.[10–12] This will create volatile species containing hydrogen, which allows for subsequent elimination through dynamic distillation of the glass. In our previous work,[12] in the arsenic sulfide glass we have successfully developed a glass purification/fabrication process to reduce the H–S absorption at 4.03 μm from 50 dB/m to 1.5 dB/m using tellurium tetrachloride ($TeCl_4$) as a getter for hydrogen impurity. This paper describes the results of the effect of $TeCl_4$ on arsenic selenide glass, which typically possesses intense impurity absorption bands associated with H–Se centered around 4.57 μm. The arsenic selenide fibers are of great interest because of many potential applications in the mid-IR.

II. Experimental Procedure

(1) Purification of Elemental Precursor (As, Se, and Te)

Commercially available six 9's purity arsenic (All Chemie), selenium (Johnson Matthew, Inc.), and tellurium (Kamis, Inc.) were purified by heating at 450°, 300°, and 475°C, respectively, for 8 h to remove oxide impurities such as As_2O_3, As_2O_5, SeO, SeO_2, SeO_3, Se_2O_3, TeO, and TeO_3. The arsenic, selenium, and tellurium were further purified by sublimation/distillation under dynamic vacuum at 500°, 500°, and 600°C, respectively, to remove scattering centers such as carbon, heavy elements, quartz particles, and other volatile species. High-purity tellurium tetrachloride ($TeCl_4$) was made inside an inert atmosphere glove box via chlorination of high-purity elemental tellurium at 240°C and collecting the $TeCl_4$ condensate. $TeCl_4$ was chosen over other halides (i.e., selenium tetrachloride ($SeCl_4$) or arsenic trichloride ($AsCl_3$)) because $TeCl_4$ is in solid form at room temperature, atmospheric pressure, and under vacuum, whereas both $SeCl_4$ and $AsCl_3$ are liquids under the same conditions.

(2) Fabrication of the Arsenic Selenide Optical Fibers

The core and clad compositions for the arsenic selenide fibers were $As_{39}Se_{61}$ and $As_{37}Se_{63}$, respectively. High-quality quartz distillation ampules were cleaned by etching with 50/50 mol% of HF/deionized water and then rinsed with deionized water. The ampules were dried in a vacuum oven at 115°C for 8 h and then baked out under vacuum at elevated temperature (~900°C) using an oxygen–methane flame. For comparison purposes, glass samples were made with and without the addition of $TeCl_4$ using purified chemicals. We describe the technique associated with the glass samples without $TeCl_4$ as a two-step process. For the glass samples made without the addition of $TeCl_4$, ~100 g batches of chemicals and 10 ppm of elemental Al were batched in ampules inside a controlled atmosphere glove box under nitrogen (<1 ppm H_2O, O_2). The ampules were evacuated at 2×10^{-5} torr, sealed with an oxygen–methane torch, and placed in a two-zone furnace for melting. The batch was melted above 700°C, distilled, and then remelted for homogeneity in a rocking furnace. The presence of aluminum in the glass melt getters the oxygen impurities during melting before distillation. The glasses were remelted in a rocking furnace and subsequently quenched from 400°C by immersion of the ampules in water for about 2 s, followed by annealing at 180°C.

For the glass samples prepared with the additions of $TeCl_4$ we describe this technique as a four-step process. In this four-step process, the first two steps are exactly the same as that of the above two-step process. The third step involves the addition of 0.1 wt% of $TeCl_4$ to the glass cullet. The samples were heated at 750°C for 24 h to allow melting and reaction to occur between the $TeCl_4$ and hydrogen impurities. Next, the ampules containing the melts were rapidly quenched in water from 650°C to preserve the integrity of the byproducts of the reaction with $TeCl_4$. In step three, the glass cullet containing $TeCl_4$ was subsequently distilled under dynamic vacuum at 550°C for 15 h to leave behind particulate matter

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impurities and eliminate any gaseous byproducts from the reaction with $TeCl_4$. Finally, in step four, the distillate was remelted at 750°C for 24 h followed by quenching from 400°C by immersion of the ampules in water for about 2 s and then annealed at 180°C.

The arsenic selenide glass cullet with a nominal core ($As_{39}Se_{61}$) and clad ($As_{37}Se_{63}$) compositions was drawn into optical fiber using a controlled double-crucible process. Over 250 m of fibers was drawn under inert atmosphere at a rate of ~5.0 m/min. The resulting fiber had an outer diameter of 200 μm and core size of 150 μm.

(3) Fiber Characterization

The fiber optical attenuation at room temperature was characterized using a FTIR spectrometer (Analect Diamond 20) and standard cutback technique.[13] The light source was a broadband NiCr wire and the detector was a liquid-nitrogen-cooled MCT (HgCdTe) detector. The fiber attenuation (dB/m) was determined from the following relationship:

$$\text{Attenuation (dB/m)} = [10 \log (P_0/P)]/(L - L_0) \qquad (1)$$

where P_0 and P are the measured powers at a given wavelength for the cutback length and the long length, respectively, and L and L_0 are the lengths of the fiber and the cutback section, respectively.

III. Results and Discussion

Figure 1 shows the attenuation spectra for the fibers fabricated from glasses made without and with the addition of $TeCl_4$ using the two-step or four-step process, respectively. Attenuation was measured by a standard cutback technique over a 5 m length. Figure 1(a) shows the attenuation for fiber fabricated from glasses made without the addition of $TeCl_4$. The minimum loss is 0.64 dB/m at 6.6 μm. At 4.57 μm, the attenuation due to the H–Se stretching vibration is approximately 10 dB/m. The three minor bands at 4.15, 3.55, and 2.32 μm are attributed to the combination and first overtone of the H–Se stretching vibration at 4.57 μm.[14] The fiber exhibits less than 1 dB/m loss in the region between 2 and 8 μm.

Figure 1(b) shows the optical attenuation of the fibers made from glass prepared with the addition of $TeCl_4$ using the four-step process. The minimum loss is 0.49 dB/m at 7.42 μm. The two small peaks at 4.3 and 4.57 μm are due to the stretching vibration of CO_2 and H–Se, respectively. The electronic and multiphonon edges are shifted to longer wavelengths. This may be attributed to Te, which is a heavier atom compared with As and Se atoms and is incorporated into the glass network while the chlorine is being removed as byproducts through dynamic vacuum. However, the magnitude of the shift in both edges appears high considering only 0.1 wt% of $TeCl_4$ was added. Further work is needed to elucidate the reason for this. The intensity of the H–Se peak at 4.57 μm decreases from 10 dB/m in Fig. 1(a) to 0.2 dB/m in Fig. 1(b). The higher temperature 650°C quench appears to be the most effective and lowers the H–Se intensity at 4.57 μm to 0.2 dB/m. Table I lists the H–Se impurity absorption band intensity and estimated concentrations. The H–Se concentration has been reduced from ~9 to less than 0.2 ppm.

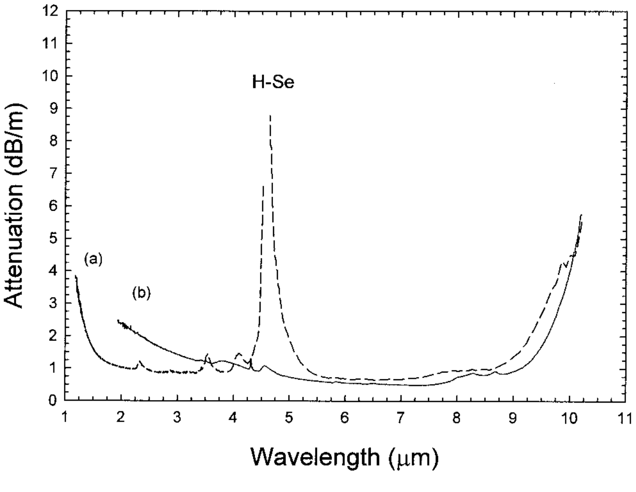

Fig. 1. Optical attenuation of arsenic selenide fibers. The core and clad compositions are $As_{39}Se_{61}$ and $As_{37}Se_{63}$, respectively. The fibers were made from glasses using purified chemicals with: (a) a two-step process, no $TeCl_4$ addition; (b) a four-step process, $TeCl_4$ addition.

Table I. Estimated Concentration of H–Se Impurity at 4.57 μm in the Selenide Optical Fiber†

$TeCl_4$ addition	Absorption loss (dB/m)	Impurity concentration (ppm)
No	10	9.07
Yes	0.2	0.18

†Extinction coefficient: H–Se = 1.103 dB/(m/ppm) at 4.57 μm. After Refs. 15 and 16.

As in our previous work[12] in this study we also propose that at high temperature $TeCl_4$ reacts with the H–Se species according to the following reaction:

$$TeCl_4 + 4H\text{–}Se_{(glass)} \rightarrow 4HCl_{(gas)}\uparrow + Te_{(glass)} + 4Se_{(glass)} \qquad (2)$$

The HCl formed is a gaseous product and is conveniently eliminated from the glass during dynamic distillation. The Te and Se become a part of the glass structure. We suggest that Te (also a chalcogen element with the same outer valence electron) is incorporated into the As–Se glass structure, along with the Se. The excess of Cl could also be incorporated into the glass structure as a network modifier.[17]

Considering that 0.1 wt% (0.14 mol%) of $TeCl_4$ was added, ideally all of the H–Se impurity should be removed since a large excess of chlorine was present in the glass melt. From Table I, there is only about 9 ppm of H–Se present for the fiber (Fig. (1a)) without $TeCl_4$ addition. After the four-step purification with $TeCl_4$ the H–Se concentration at 4.57 μm has been significantly reduced to 0.18 ppm (Fig. 1(b)), but not all of the H–Se has been removed. Melting for longer periods of time or using higher $TeCl_4$ concentrations may help to completely eliminate the H–Se absorption band.

IV. Conclusions

We have developed a four-step purification process to reduce the hydrogen-related impurities in the selenide fiber. This is facilitated by the removal of oxide in the first two steps and with the addition of $TeCl_4$ in the third step. This leads to the formation of HCl, a gaseous byproduct that can be removed by distillation. We have utilized this four-step purification process to obtain low loss and high-quality selenide optical fiber containing low hydrogen-related impurities (<0.2 ppm H–Se) and consequently a low H–Se absorption loss of 0.2 dB/m at 4.57 μm.

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