Chalcogenide glasses for optical brazing

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Protective coatings of CVD diamond have been bonded to infrared-transmitting optical windows of ZnSe with As-Se-S system chalcogenide glasses of which the refractive index is made to closely match that of diamond by the "optical brazing" process. To select optimal composition in the As-Se-S system, the T_g, T_s, reflective index and infrared-transmittance of the glass samples were measured. Measurement of transmittance with a Fourier transform infrared spectrometer after the brazing process confirmed that scattering losses were greatly reduced. Infrared transmittance of ZnSe windows with a thin film diamond coating bonded to chalcogenide glass was about 63%.

1. Introduction

Zinc selenide is widely used in infrared optical materials because of its optical transmittance property in the infrared region. However these materials, which easily get damaged by abrasion, chemical attack, rain and dust, are limited for use in windows or domes in electro-optic systems. Accordingly, the search for a thin film material with good mechanical strength and infrared optical transmittance is proceeding to protect these infrared optical materials [1]. A bulk diamond is a thin, protective coating of diamond on a bulk window of zinc selenide, zinc sulfide or other infrared-transparent material. The purpose of the diamond would be to protect against rain and particle erosion. The alternative of depositing a thick layer of zinc selenide on top of a thin layer of diamond would probably be unsuccessful due to the mismatch in thermal expansion between the diamond and the other material. One possible approach to this problem is to deposit a layer of intermediate thermal expansion between the diamond and the zinc selenide. A successful scheme for attaching diamond to zinc selenide is based on an "optical brazing" process. This method begins with growth of a thin diamond layer on an optically smooth silicon substrate. The diamond facing the substrate is also optically smooth, but the growth surface of the diamond is very rough and therefore scatters a great deal of light. Ordinarily, this surface would require polishing before it could be used in an optical system. A sandwich is then made, in which a glass bonding layer is placed between the rough surface of the diamond and the smooth surface of a zinc selenide window. The bonding layer is an arsenic-selenide-sulfur glass whose refractive index is close to that of diamond and zinc selenide [1–3].

The aim of the present study was to select optimal composition in the As-Se-S system, of which the refractive index is made to closely match that of diamond and zinc selenide. Then the T_g, T_s, infrared transmittance and brazing temperature of the optimal composition and the transmittance of the optical brazed disk were measured.

2. Experimental procedure

Glasses were prepared from high purity As (Aldrich, 60 mesh, USA), Se (High Purity Chemicals, 200 mesh, Japan) and S (High Purity Chemicals, 50 mesh, Japan) powders. The glass batch, approximately 30 g, was weighed into a fused silica ampoule of 19 mm internal diameter. The ampoule with the contents was evacuated and sealed under a vacuum of 4×10^{-6} torr. The sealed ampoule was heated in a tube furnace at 800 °C for 24 h. The melt was quenched in cool water to obtain the glass.

The refractive index of the glass was measured using an Infrared Reflective Spectrometer (1800-FT/IR, Perkin Elmer, Germany). The infrared transmittance of the glass and optical brazed disk were measured using a Fourier transform infrared spectrometer (model FT-IR-300Z, Jasco, Japan). The glass transition temperature (T_g) and softening temperature (T_s) were investigated using a differential thermal analyzer (TG/DTA92, Setaram, France). The variation of $\Delta l/l$ of the samples with temperature were recorded using a thermal mechanical analyzer (model GM 13 K, Motoyama, Japan).

3. Results

The glass forming regions in the system As-Se-S were previously reported [4, 5]. The glass forming regions are wide; among them, the compositions with good properties are $As_{25}Se_{60}S_{15}$, $As_{35}Se_{45}S_{20}$ and $As_{40}Se_{20}S_{40}$.

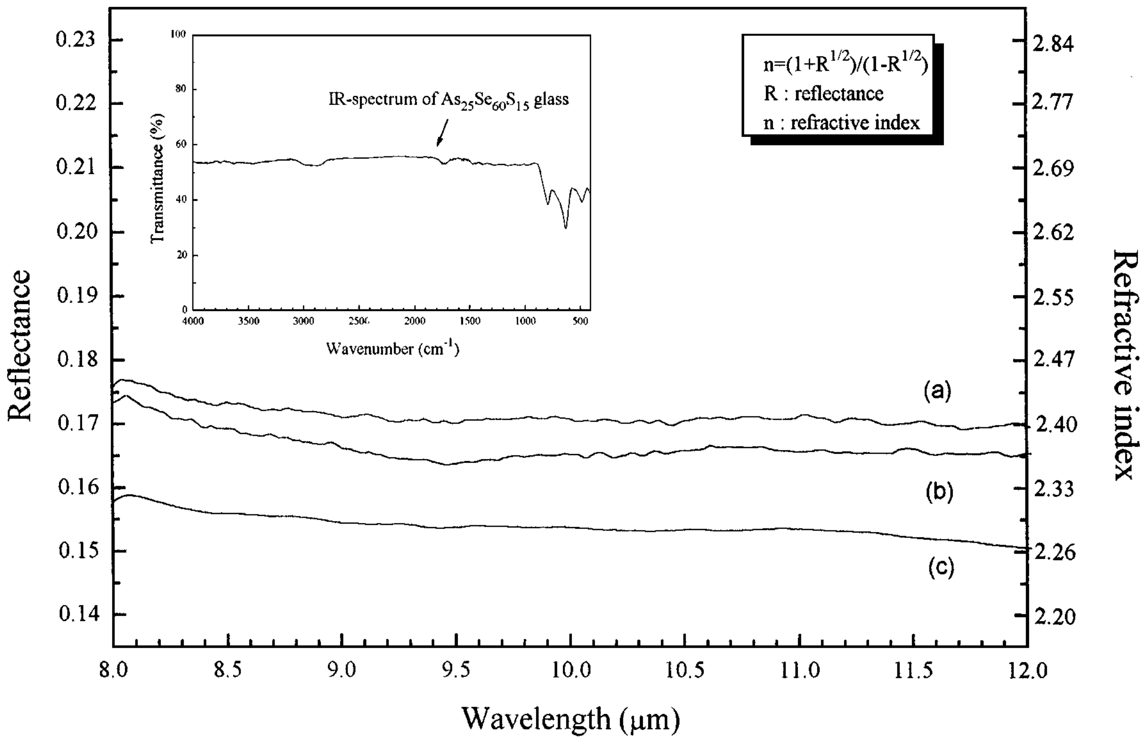

Figure 1 Refractive indices in the glass system As-Se-S; (a) $As_{25}Se_{60}S_{15}$, (b) $As_{35}Se_{45}S_{20}$ and (c) $As_{40}Se_{20}S_{40}$.

Variation of the refractive index with wavelength for glass $As_{25}Se_{60}S_{15}$, $As_{35}Se_{45}S_{20}$ and $As_{40}Se_{20}S_{40}$ is shown in Fig. 1. The indices were about 2.41, 2.35 and 2.28. Also, the small graph in Fig. 1 shows infrared transmittance of the $As_{25}Se_{60}S_{15}$ glass of which the refractive index is made to closely match that of diamond and zinc selenide. It was about 50%.

Typical DTA traces of $As_{25}Se_{60}S_{15}$, $As_{35}Se_{45}S_{20}$ and $As_{40}Se_{20}S_{40}$ glass obtained at a heating rate of 10 K/min, are shown in Fig. 2. Two characteristic

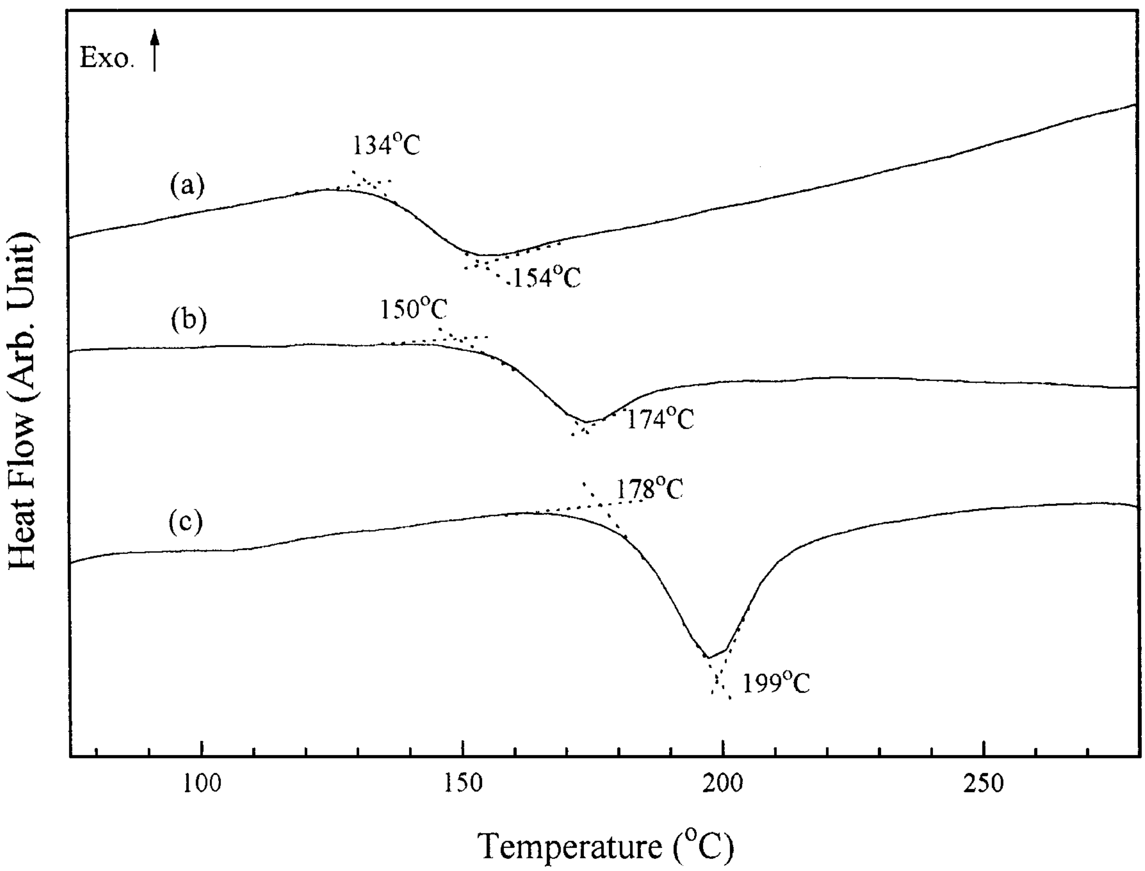

Figure 2 Typical DTA traces in the glass system As-Se-S at a heating rate 10 K/min; (a) $As_{25}Se_{60}S_{15}$, (b) $As_{35}Se_{45}S_{20}$ and (c) $As_{40}Se_{20}S_{40}$.

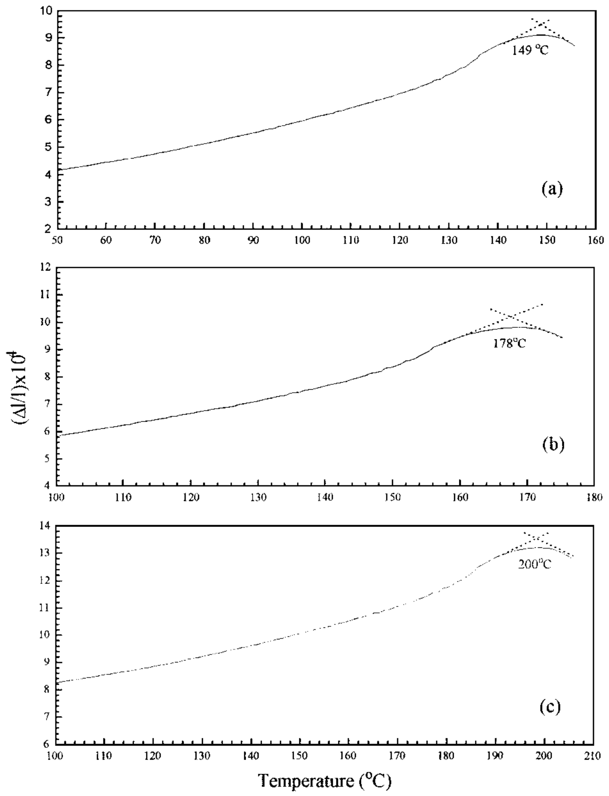

Figure 3 Typical data of α as a function of temperature in the glass system As-Se-S; (a) $As_{25}Se_{60}S_{15}$, (b) $As_{35}Se_{45}S_{20}$ and (c) $As_{40}Se_{20}S_{40}$.

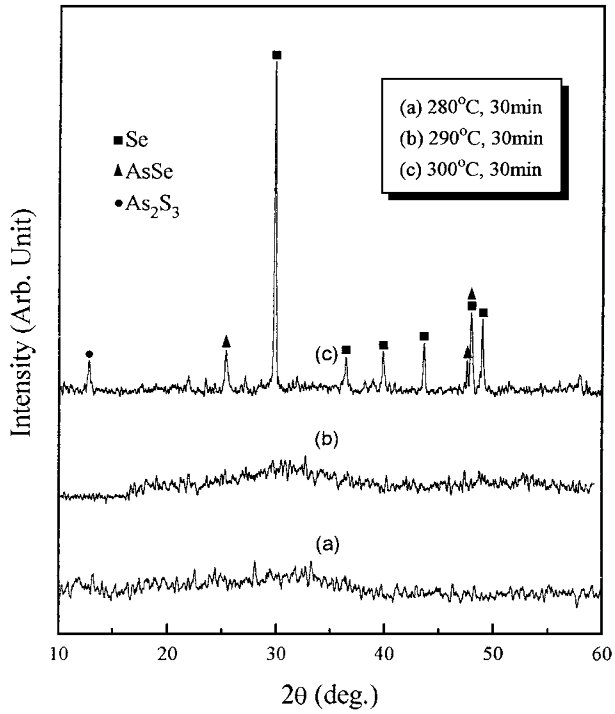

Figure 4 XRD patterns for glass $As_{25}Se_{60}S_{15}$ with temperature.

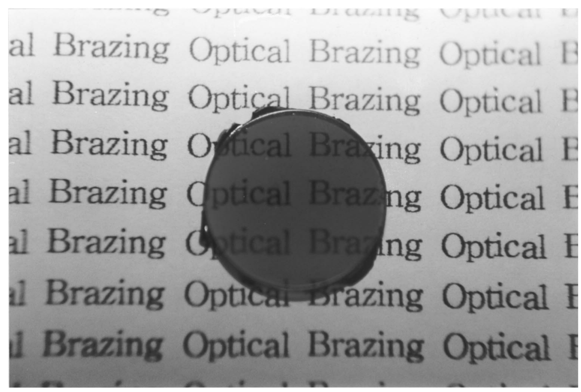

Figure 5 Photograph of a ZnSe window with a fine-grained diamond coating bonded to $As_{25}Se_{60}S_{15}$ by the optical brazing process.

curves are clear in the temperature region. The first corresponds to the glass transition temperatures (T_g) and the second corresponds to the softening temperature (T_c). The temperatures T_g and T_c of $As_{25}Se_{60}S_{15}$, $As_{35}Se_{45}S_{20}$ and $As_{40}Se_{20}S_{40}$ glass are 134 and 154 °C, 150 and 174 °C, 178 and 199 °C, respectively.

Fig. 3 shows the $\Delta l/l$ vs. temperature for $As_{25}Se_{60}S_{15}$, $As_{35}Se_{45}S_{20}$ and $As_{40}Se_{20}S_{40}$ glasses. They are about 149 °C, 178 °C and 200 °C.

The X-ray diffractogram indicates that the parent glasses exist in halo (chart a, b in Fig. 4.) and the heated glasses have three crystalline phases Se, AsSe and As_2Se_3 as shown in chart c in Fig. 4. By increasing the heat-treatment temperature, the crystalline phase forms at 300 °C.

A photograph of a 2 cm-diameter ZnSe window with a diamond coating bonded to $As_{25}Se_{60}S_{15}$ glass is shown in Fig. 5. The bonded ZnSe-glass-diamond window appeared translucent as can be seen.

Fig. 6 shows the visoble/near infrared (T_1) and mid/far infrared (T_2) transmission spectra of the bonded ZnSe-glass-diamond window. The T_1 and T_2 values for the bonded sample are 55 and 63%.

4. Discussion

The As-Se-S glasses are notable in their ability to wet and bond to ceramics, plastics and silicate glasses [2]. They have been found to be chemically durable and to exhibit extremely low water solubility. They have shown no tendencies toward devitrification. The structures may be based on long chains involving polymeric $(\text{-S-S-})_n$ linkages. Arsenic is thought to enter into the chains and is strongly bonded to sulfur. Selenium might enter the chains as a weak link, the rupture of which produces high melt fluidities at moderate temperatures [5].

The main aim of the study was to select chalcogenide glass in the As-Se-S system of which the refractive index is made to closely match that of diamond and zinc selenide. There was no significant difference between the forms of the curves for the glasses except $As_{35}Se_{45}S_{20}$. The refractive index at a given wavelength increases with the content of Se, which is the heaviest atom among the glass components. For diamond and zinc selenide the refractive index is 2.376 and 2.40 at 10 μm wavelength. For three compositions, therefore, the optimal composition was to select $As_{25}Se_{60}S_{15}$. IR-transmittance of the $As_{25}Se_{60}S_{15}$ glass was about 50%. There are impurity absorptions at 800, 645 and 500 cm^{-1} which could be assigned to the molecular As_4O_6, As-O and As-Se, in terms of [6].

The T_g of these glasses obtained by DTA is seen to increase with decreasing Se content. Also, the values of T_s obtained by dilatometry agree to within ± 5 °C

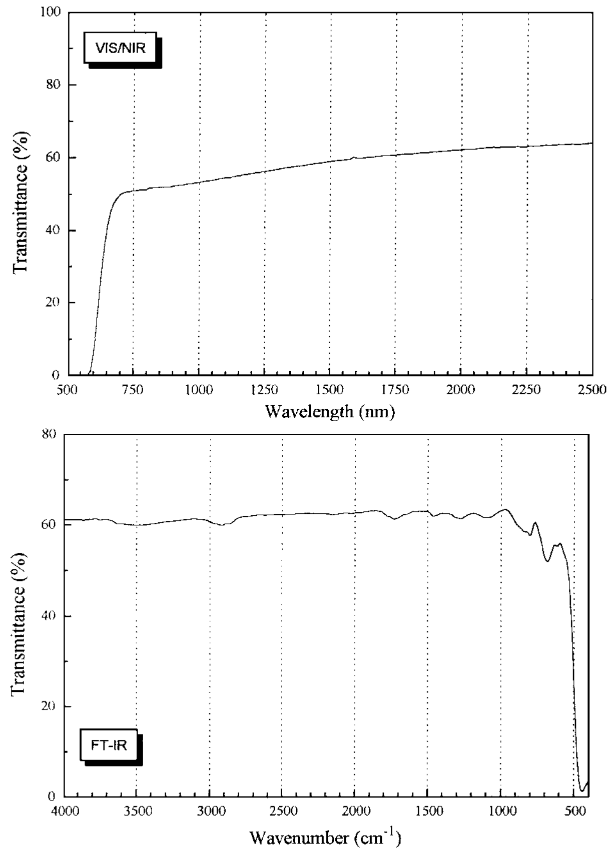

Figure 6 Transmittance versus wavelength for glass $As_{25}Se_{60}S_{15}$ glass brazed diamond-ZnSe.

with the value obtained by DTA for these glasses. The T_s decrease with increasing Se content in the glasses.

A 0.5 mm slice of $As_{25}Se_{60}S_{15}$ chalcogenide glass is inserted between diamond and ZnSe to form a sandwich. The assemblage is heated to about 260 °C. As the glass is transparent. From the magnitude of the transmittance in the absorption-free region, about 63%. Because the growth surface of the diamond is very rough and therefore scatters a great deal of light, IR-transmittance of the diamond is less than 45%. But if the diamond is bonded to a ZnSe substrate with chalcogenide glass, the transmittance values in the mid/far IR range and the VIS/NIR range for the bonded sample are about 63% and 55%, respectively, except of course where ZnSe absorptions are present below 700 cm and in the C-H absorption band in the diamond at 1750 and 2900 cm^{-1}.

5. Conclusions

The optimal composition of the study was to select $As_{25}Se_{60}S_{15}$ chalcogenide glass of which the refractive index is made to closely match that of diamond and zinc selenide as 2.47 at 10 μm wavelength. The IR-transmittance, T_g, and T_s of the $As_{25}Se_{60}S_{15}$ glass were about 50%, 134 °C and 154 °C respectively. The heated $As_{25}Se_{60}S_{15}$ glass has three crystalline phases: Se, AsSe and As_2Se_3 at 300 °C. The optical brazing process is an effective way to obtain diamond-coated infrared windows, having IR-transmittance significantly better than those obtained from the rough surfaces that are characteristic of CVD diamond. The diamond bonded to a ZnSe substrate with chalcogenide glass, the transmittance values in the mid/far IR range and the VIS/NIR range for the bonded sample are about 63% and 55%, respectively.

Acknowledgements

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