Journal of Non-Crystalline Solids 377 (2013) 245–249

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Formation of laser-induced SbSI single crystal architecture in Sb–S–I glasses

D. Savytskii [a], B. Knorr [b], V. Dierolf [b], H. Jain [a,*]

[a] Department of Materials Science and Engineering, Lehigh University, 5 East Packer Avenue, Bethlehem, PA 18015, USA
[b] Department of Physics, Lehigh University, 16 Memorial Drive East, Bethlehem, PA 18015, USA

ARTICLE INFO

Article history:
Received 16 October 2012
Received in revised form 23 December 2012
Available online 1 February 2013

Keywords:
Chalcogenide glass;
CW laser;
Crystallization

ABSTRACT

We report the successful fabrication of active single-crystal architectures in IR transparent Sb–S–I chalcogenide glasses using a CW 488 nm laser. Electron back scatter diffraction (EBSD) results reveal that the focal position of the laser spot with respect to glass surface is of paramount importance to the ability to grow long single crystals. Furthermore, by using a laser irradiated line instead of a spot as the seed for these architectures, overall reproducibility was significantly improved.

1. Introduction

Antimony sulphoiodide (SbSI) is a chalcogenide compound which exhibits high values of the dielectric constant, transparency in the infrared, spontaneous polarization, and pyroelectric as well as pyro-optic coefficients [1–5]. These characteristics set it apart from other ferroelectrics and make it suitable for use in uncooled pyro-optic and pyroelectric infrared detectors [6]. For such applications, arrays of crystalline ferroelectric pixels or other geometries are needed at reasonable costs.

Crystallization of glass by laser irradiation is a novel method which is recognized for its potential to construct active elements [7,8]. Thus far this technique has been applied primarily to oxide glass insulators [9–13]. By contrast, chalcogenide glasses are 'soft', wide bandgap semiconductors, which show strong electron–phonon coupling and photosensitivity. Consequently, laser-induced crystallization of chalcogenide glasses is expected to be significantly more complex [14].

In a previous work [15], 15 μm long single crystal lines of SbSI were 'written' on the surface of a glass containing 10 mol% of GeS_2 using a continuous wave (CW) laser. This method required fine tuning of various irradiation parameters including laser power, laser scanning speed, laser spot diameter and the focus of the laser spot. The main reason for the short length of the single crystal lines is undulations of the surface, which affect the focal point of the laser and make continued crystallization difficult to control as the sample is translated [15].

In this paper we report improvements in crystal size and quality stemming from a refinement of the experimental techniques reported previously [15] relating to the handling of sample surface variations as well as seed-crystal nuclei production. Unlike previous compositions that contained GeS_2 for stabilization of the glassy phase, in the present work no additional component was added, and it is the first demonstration of single crystal SbSI fabrication in the Sb–S–I glass system by a CW laser beam.

2. Experimental

For the preparation of Sb–S–I glass we used a similar method as for SbSI–GeS_2 glasses [15]. Glass samples of composition 82SbSI–$18Sb_2S_3$ were prepared directly from elemental Sb, S, and I powders. To obtain fast cooling rates, the inner diameter of the ampoules was reduced from 11 mm to 6 mm. To prevent explosion due to rapid volatilization, ampoules were slowly heated at 1 °C/s successively to 128 °C, 250 °C, 450 °C and 650 °C and kept at each temperature for 1 h and then heated to 730 °C for 12 h. Finally, the ampoules containing reacted melt were slowly cooled to 650 °C and quenched in cold water to form glass. The X-ray diffraction (XRD) analysis of the as-quenched glass confirmed its amorphous state.

XRD and differential scanning calorimetry (DSC) were used for identifying crystalline phases and for screening glass compositions, respectively. The XRD analyses were performed on a Rigaku "MiniFlex II" diffractometer. The glass transition (Tg), maximum crystallization (Tc) and melting (Tm) temperatures were determined with a Q2000 Thermal Analysis apparatus. The measurements were conducted with a heating rate of 10°/min using samples of different particle sizes from room temperature to 450 °C.

The samples' surfaces for laser-induced treatments were prepared using metallographic techniques. First, grinding using 600-, 1000- and 1200-grit SiC abrasive papers in conjunction with water was performed. Next, the samples were polished using Al_2O_3 suspensions with grain sizes of 3, 1, 0.3, 0.1 and 0.05 μm on cloth disks. Each grain

* Corresponding author. Tel.: +1 610 7584217; fax: +1 610 7584244.
E-mail address: H.Jain@Lehigh.EDU (H. Jain).

0022-3093/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jnoncrysol.2013.01.018

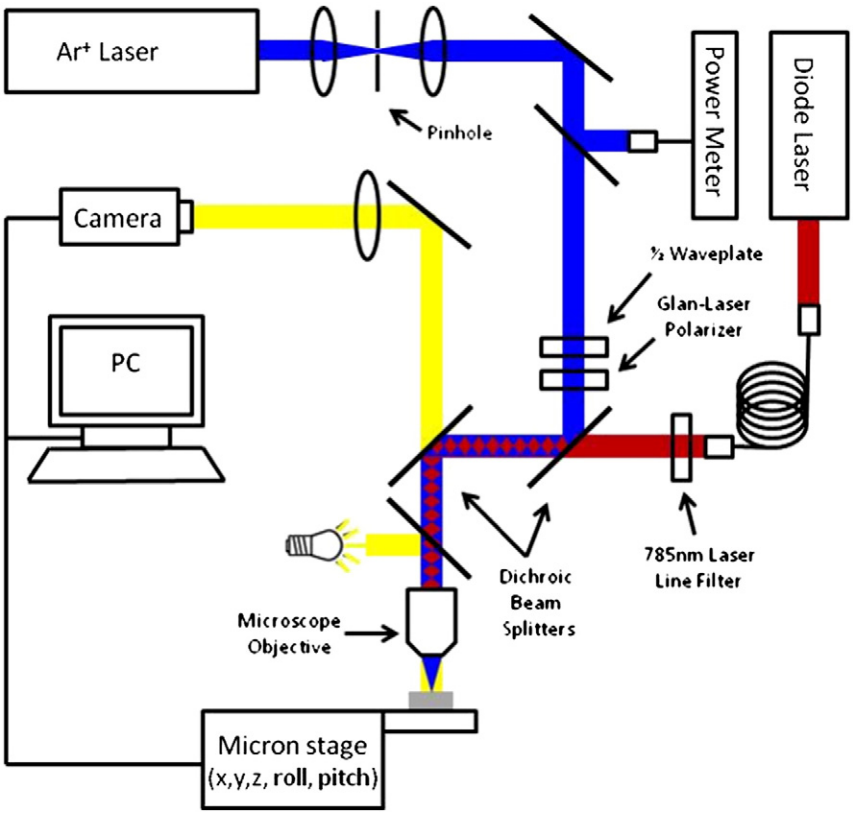

Fig. 1. Diagram of laser crystallization setup.

size was used for 10 min with a new cloth being used after the first 5 min.

Fig. 1 shows a diagram of the experimental setup. An argon ion laser operating at 488 nm is directed by mirrors and lenses through a pinhole to the microscope. A laser diode emitting at 785 nm is directed through a single mode fiber. The pinhole and fiber clean up the beams produced by the lasers, providing close-to-perfect Gaussian beam profiles. A waveplate and Glan-laser polarizer allow the orientation of the electric field (polarization) to be controlled as well as fine control of the intensity of the 488 nm laser at the sample. The sample sits on a glass slide which is placed on a custom-built stage consisting of 3 motorized micron-stages mated to a modified mirror mount. The former allow for translation in the x-, y-, and z-directions while the latter provides the ability to adjust the pitch and roll of the sample. A white light source illuminates the sample and in-situ monitoring of the sample is provided via a CCD camera. The CCD camera is also used to track the reflection of the 785 nm laser beam from the sample surface so that adjustments can be made to the focus, pitch, and roll of the sample in order to eliminate the effects of surface variations on the focal position of the 488 nm laser spot with respect to the sample surface. LabView software controls the positioning and movement of the sample stage.

Phases within the laser written lines were determined using a scanning electron microscope (SEM) (Hitachi 4300 SE) in low vacuum environment to eliminate charging effects. Crystallinity and orientation of the grains in laser created patterns were examined by electron backscatter diffraction (EBSD), in which Kikuchi patterns were collected by a Hikari detector inside the SEM specimen chamber. The accelerating voltage for the EBSD spot analysis and mapping was 20 kV and the probe current was 20 nA. A tilt angle of 70° and working distance of 15 mm were chosen. Chemical analysis of regions in the glass and laser-induced lines was performed using energy dispersive X-ray (EDS) spectroscopy simultaneously with EBSD. The spectra were collected using the EDAX-Genesis software package. The parameters for data acquisition (time, full scale for intensity, pulse processing time) were kept the same for all of the spots.

3. Results and discussion

The DSC thermograms reveal glass transition (Tg) at 130 °C and three different temperatures, where crystallization peaks are observed: 135–155 °C, 190 °C, 270 °C (Fig. 2). Using X-ray powder diffraction experiments (Fig. 3) the crystalline phases have been identified: the first and second peaks correspond to SbSI crystallization, and the third peak corresponds to Sb_2S_3 crystallization. The

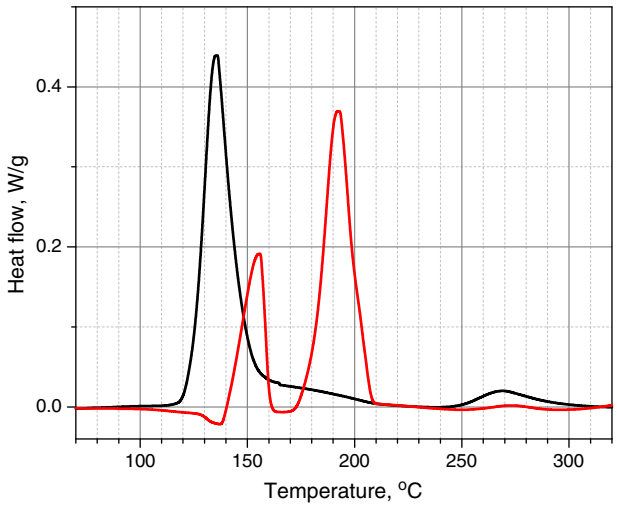

Fig. 2. DSC data (heating rate 10°/min) of the glass for 63–177 μm (black) and >1 mm (red) size particles.