Laser-induced growth of oriented Sb_2S_3 single crystal dots on the surface of 82SbSI-18 Sb_2S_3 glasses

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Abstract

To produce ferroelectric single-crystal architecture on glass surface by laser irradiation, usually the starting structure is a dot. Therefore, we have investigated the formation of this basic element of laser-induced crystallization, as an example, on the surface of pseudo binary 82SbSI–18 Sb_2S_3 chalcogenide glass using a diode laser of wavelength $\lambda = 520$ nm. The intensity of the laser was chosen such that the temperature in the crystal growth region was kept below the melting temperature of the glass but high enough to facilitate solid state devitrification. The morphology, crystallinity and composition of crystallized dots were determined using Electron Backscatter Diffraction (EBSD) and Energy Dispersive X-ray Spectroscopy (EDS). We find that Sb_2S_3 single crystal dots with elliptic cross-section form with $\langle 001 \rangle$ direction parallel to the major axis of ellipse and the surface of glass matrix. On the basis of the presented results, we propose that laser heating can be exploited uniquely to grow oriented single crystals of solids.

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1. Introduction

Crystallization of glass by CW laser irradiation is a novel method which is recognized for its potential to construct active elements and devices. Thus far this technique has been applied primarily to oxide glass insulators [1, 2]. By contrast, chalcogenide glasses are ‘soft’, wide bandgap semiconductors, which show strong electron-phonon coupling and photosensitivity. Consequently, laser-induced crystallization of chalcogenide is expected to be significantly more complex [3]. Basic structural elements like zero-dimensional dots, one-dimensional (1D) lines and two-dimensional (2D) rectangles of single crystals have been written at or near the surface by selectively heating the glass with a laser beam that is absorbed by the glass matrix [1-3]. At present, a complete mechanistic understanding of this laser-induced crystal growth process is lacking. Obviously, one would benefit by answering the question: how does the simplest structure, viz. a dot, forms in or on glass upon exposure to suitable laser.

Antimony trisulfide (Sb_2S_3) is a promising material for photovoltaic cells since it shows high absorption coefficient ($\alpha > 10^3 \text{ cm}^{-1}$), and the band gap (1.7–2.5 eV) covers the maximum scan of the visible and near infrared ranges of the solar spectrum [4]. On the other hand, Sb_2S_3 has attracted attention for its applications in thermoelectric and optoelectronic devices operating in the infrared (IR) region [5, 6]. It is a highly anisotropic material with a layer structure and strong tendency to form 1-D structures. There is a great interest in preparing Sb_2S_3 nanostructures as nanorods, nanowires, and nanoribbons, among other morphologies, using a wide variety of procedures [7-9]. Therefore, we have selected to understand laser-induced formation of dots in this glass.

For forming single crystal of Sb_2S_3 in glass, it is important to choose a composition that satisfies two conditions: forms into glass easily and crystallizes in Sb_2S_3 phase when taken to

peak crystallization temperature. These requirements of chemical composition are well satisfied by 82SbSI-18Sb₂S₃. It corresponds to the edge of glass forming region within the Sb-S-I system. In this paper, we report results in the laser patterning of crystalline dots on the surface of the glasses of 82SbSI-18Sb₂S₃ under irradiation with a 520 nm CW laser diode in air. The wavelength 520 nm is above the bandgap of the selected glass composition, and is thus absorbed within a thin surface layer (several hundred nanometers) of the sample. Consequently, we can expect that the maximum temperature from laser heating will be located near the surface of sample.

2. Experimental

2.1. Sample preparation

We prepared glasses starting with a batch of elemental Sb, S and I powders in appropriate ratio, and following the ampule quenching method previously developed for the SbSI-GeS₂ system [10]. 82SbSI-18Sb₂S₃ glass, which is within the normal glass-forming region of the Sb-S-I system, was prepared. The glass of non-stoichiometric composition was prepared using ampules with 11 mm ID. X-ray powder diffraction (XRD) analysis of the as-quenched samples confirmed their amorphous state.

The sample surfaces for laser treatments were prepared using metallographic polishing techniques. First, plate-like samples were ground using 600-, 1000- and 1200-grit SiC abrasive papers in conjunction with water as lubricant. Next, the flat samples were polished using Al₂O₃ suspensions with particle sizes of 3, 1, 0.3, 0.1 and 0.05 μm .

2.2. Laser writing setup

We started with the fabrication of crystal dots using a $\lambda=520$ nm ThorLabs LP520-SF15 single mode fiber pigtailed laser diode. This laser provided the ability to precisely control the intensity

using ILK Lightwave LDX-3620 Ultra Low Noise Current Source with an analog control input. Using a microscope objective (numerical aperture 0.75) illuminated spots of 5 μm diameter were produced on the polished surface of the glass sample. Crystallized dots were created by slowly ramping the power density from 0 to 80 $\mu\text{W}/\mu\text{m}^2$ within a time period. Upon reaching final power (80 $\mu\text{W}/\mu\text{m}^2$), the laser was held in place at the same spot for an additional length of time.

2.3. Characterization of laser written structures

The laser-irradiated regions were analyzed with a Scanning Electron Microscope (Hitachi 4300 SE) in water vapor environment to minimize the charging effects. Chemical composition of samples was determined by an Energy Dispersive X-ray (EDS) spectroscopy detector attached to SEM. The parameters for data acquisition (acceleration voltage, time, full scale for intensity, pulse processing time) were kept the same for all the samples. The spectra were collected for separate points on a sample's surface and analyzed using EDAX-Genesis software package. A qualitative color map of the distribution of major elements as well as oxygen in the laser-irradiated regions was obtained using the same EDAX software.

Crystallinity and orientation of the crystal grains in laser created dots were examined by electron backscatter diffraction (EBSD) technique, in which Kikuchi patterns were collected by a Hikari detector inserted into the SEM specimen chamber. The crystalline grains and their orientation within selected areas were determined through EBSD mapping scans. The step size for these maps was 0.2 μm with a hexagonal sampling grid. EBSD scans were collected and indexed using TSL (TexSEM Laboratory) orientation data collection and analysis software. All patterns were indexed using SbSI and Sb_2S_3 crystal structure parameters. Indexing of diffraction patterns was achieved by a voting system and characterized by a number of parameters such as the image quality (IQ) value votes, the fit-factor, and the confidence index (CI). The orientation

imaging microscopy (OIM) software package was used to identify crystal grains and generate image quality, phase, and inverse as well as normal pole figure maps. All these maps were filtered for $CI < 0.1$.

3. Results

3.1. Thermally induced crystallization of glasses in the Sb-S-I system

In order to understand laser-induced crystallization, it is instructive to know how a given glass composition would transform upon simple heating. Therefore, ordinary temperature induced crystallization of Sb-S-I glasses within the $x\text{SbSI}-(100-x)\text{Sb}_2\text{S}_3$ pseudo-binary series was investigated in our group previously [11, 12]. The differential scanning calorimetric scans and X-ray diffraction measurements on the powders of these compositions of varying size particles allowed the identification of one-dimensional (1D) surface, and three-dimensional (3D) bulk crystallizations of the SbSI phase, which depended on the composition of glass [11]. Similar to the case of stoichiometric SbSI (G1) glass, SbSI phase devitrifies by the two crystallization processes in other glasses within $x\text{SbSI}-(100-x)\text{Sb}_2\text{S}_3$ [12]. This result is shown in Fig. 1. With decreasing SbSI concentration, x , we find that the two exothermal effects shift to higher temperatures and the temperature interval between them decreases. In contrast to the SbSI phase, the temperature of crystallization for the Sb_2S_3 phase does not depend on the size of particles and slowly decreases with decreasing x . For 63SbSI–37 Sb_2S_3 (G3) glass, which corresponds to eutectic composition, the temperature of SbSI bulk crystallization becomes higher than the crystallization point of Sb_2S_3 phase. Evidently, for the glass of 52SbSI–48 Sb_2S_3 (G4) composition Sb_2S_3 phase starts to crystallize first. This completely changes the conditions for nucleation and further crystallization of both the phases in glasses with the hypereutectic chemical composition.

Figure 1. Composition dependence of transformation temperatures: glass transition (circles), crystallization temperature of SbSI (squares) and Sb₂S₃ (diamonds) phases for four (G1-G4) different glasses within xSbSI-(100-x)Sb₂S₃ series [11, 12].

3.2 Laser-induced single crystal dots in 82SbSI–18Sb₂S₃ glass (G2)

We investigated structural and chemical changes induced by the 520 nm CW laser beam in a dot for different exposure conditions: ramping the power density from zero to 80 $\mu\text{W}/\mu\text{m}^2$ in 5 or 10 s with or without additional exposure for 5 s or 10 s. For comparison, we also produced a dot irradiated with 50 $\mu\text{W}/\mu\text{m}^2$ intensity at once for 5s.

Figure 2. SEM image of laser-induced dot created by slowly 5 s ramping the power density from 0 to $80 \mu\text{W}/\mu\text{m}^2$ and further 5 s exposure at the same power density. Scale bar corresponds to 5 μm .

Figure 2 shows typical morphology of dots produced on $82\text{SbSI}-18\text{Sb}_2\text{S}_3$ glass, where we see two different depressed or contracted regions: inner area (B) irradiated by the laser beam, and an area A that surrounds B and is separated from the glass matrix (G) by a sharp step like boundary. This morphology complicates structural investigation by EBSD method, which works well only on very flat surfaces. So, to obtain flat surface in areas of dots the samples were repolished using Al_2O_3 suspensions. The SEM images of 5 dots induced by different laser beam exposures are shown in Fig. 3, under the conditions mentioned in the caption, as typical examples in this study. We expect that polishing the sample after exposure removed a layer of 1-2 μm thickness, and hence possibly changed the appearance of corresponding regions somewhat. Notwithstanding, the inner region B in the *as irradiated* sample corresponds to the crater in the center of each dot after polishing. Evidently, region A due to higher hardness than glass matrix does not polish off as easily and therefore appears as an elliptic protrusion above the background of dots in Fig. 3.

Figure 3. SEM image of laser-crystallized dots created using 520 nm laser exposures at five different places separated by 15 μm : No. 1 - 10 s ramping of laser intensity from 0 to 80 $\mu\text{W}/\mu\text{m}^2$; No. 2 - 10 s ramping from 0 to 80 $\mu\text{W}/\mu\text{m}^2$ and 5 s exposure; No. 3 - 5 s ramping from 0 to 80 $\mu\text{W}/\mu\text{m}^2$ and 10 s exposure; No. 4 - 5 s ramping from 0 to 80 $\mu\text{W}/\mu\text{m}^2$ and 5s exposure; No. 5 - 5 s exposure at 50 $\mu\text{W}/\mu\text{m}^2$ applied at once. Scale bar corresponds to 5 μm .

Fig. 4(a) shows the SEM image of dot No.1 selected for EBSD analysis. Fig. 4(b) presents an IQ color map of the selected region. Here the black and blue pixels represent non-crystallinity. Thus the area around the laser-induced protrusion region with low (< 600) IQ-values indicates the absence of crystalline grains. By contrast, for majority of the raised area

(region A) the IQ values are high, indicating the presence of crystalline grains. But in some parts of region A, relatively low IQ-values are detected, which is presumably a result of surface roughness.

Figure 4. Crystallinity analysis of dot No.1 in Figure 3: (a) SEM image, (b) IQ map, (c) CI map, (d) colored orientation IPF map with reference vector in the direction of surface normal (ND), and (e) pole figure for <001> direction of Sb_2S_3 .

The observed high CI values (up to 0.914) for Sb_2S_3 phase (Fig. 4(c)) demonstrate that it is the phase that forms as the crystalline dot under laser exposure and not SbSI as was initially expected. Using TSL analysis software, the inverse pole figure is plotted for the normal (ND) direction in Figure 4(d). From this map it can be seen that a single crystal grain of Sb_2S_3 was produced under the laser writing in the shape of an ellipse. The blue colored pixels in this figure indicate <010> orientation of the grain in direction normal to the surface of the sample. From pole figure plotted for <001> crystallographic direction in Fig. 4(e), we conclude that <001> of the Sb_2S_3 grain is parallel to the sample surface as well as to the major axis of the elliptical shape of the raised part indicative of region A.

Single crystal grains of Sb_2S_3 were produced also in the other four laser-induced dots in Fig. 3. The results of the EBSD mapping for dots No. 2 and No. 5 are shown in Fig. 5. From

these images and maps it can be seen that single crystals of Sb_2S_3 with an elliptical shape were produced. The pole figures plotted for the $\langle 001 \rangle$ crystallographic direction in Fig. 5(c) indicate that this crystallographic direction is also parallel to the sample surface and the major axis of both the elliptical Sb_2S_3 crystals (No.2 and No.5). Similar results were noted for the remaining two laser-induced dots (No.3 and No.4). Only one difference was observed, however, for the spatial orientation of Sb_2S_3 single crystals: the dots 1-4 have $\langle 010 \rangle$ direction normal to the surface of the sample, whereas for the crystal of dot No. 5, the $\langle 100 \rangle$ crystallographic direction of Sb_2S_3 is parallel to the normal of the surface. The first four dots were created by slowly ramping the power density from zero to $80 \mu\text{W}/\mu\text{m}^2$, while dot No. 5 was produced by applying $50 \mu\text{W}/\mu\text{m}^2$ at once. Apparently, the way the laser intensity is applied and consequently the type of heat-profile that is dynamically produced determine the orientation normal to the surface.

Figure 5. SEM image (a), colored orientation IPF map with reference vector in the direction of surface normal (b) and pole figures (c) for the laser-induced dots No.2 and No.5. Scale bar corresponds to $2 \mu\text{m}$.

A comparison of the EBSD and EDS maps in Figures 5 and 6, respectively, confirms that Sb_2S_3 phase crystallizes in region *A* of the dots. Apparently, the material from region *B* was removed during the polishing of sample after crystallization. We suspect that *as grown* Sb_2S_3 crystal starts to oxygenate in the center of the dot where temperature is the highest. The EDS map for oxygen shows small grains of antimony oxide in this region, which corresponds to region *B* in the *as irradiated* dot (Fig. 2). It is noted that chemical composition around region *A* corresponds to the initial glass composition (Fig. 6).

Figure 6. SEM image and EDS color maps of dot No.2 for sulfur, antimony, iodine and oxygen.

4. Discussion

In our previous work irradiation with a laser of $\lambda = 488$ nm led to the evaporation of SbI_3 from the surface of SbSI glass due to a thermal runaway effect [3]. By switching to a semiconductor laser with a wavelength $\lambda=520$ nm which increases the absorption depth and allows for more precise intensity control, we are able to produce Sb_2S_3 crystals. It means iodine must have been rejected in some form from such crystals, for instance, through the evaporation of SbI_3 . At least some of the contraction of happening in regions *A* and *B* of Fig. 1 could be for this reason. So we did not eliminate the evaporation from laser heating, but instead shifted the chemical composition from SbSI towards Sb_2S_3 , as shown by EBSD and EDS maps for the dots on the surface of G2 glass (Figures 4-6). As a result of the enrichment of the supercooled liquid with Sb_2S_3 component, the temperature of Sb_2S_3 crystallization becomes lower than that of SbSI phase as predicted by Fig. 1. Naturally, such a change will preferentially “stimulate” the

formation of Sb_2S_3 crystals. This simultaneous use of temperature and chemical gradients is a unique feature and possibility in the laser induced crystallization process.

Very interestingly, our results indicate that the single crystal dots of Sb_2S_3 obtained from laser irradiation exhibit preferred orientations: in all cases the $\langle 001 \rangle$ direction is parallel to the glass surface. Furthermore, for the dots created using gradually increasing laser power the crystal has (010) crystallographic plane parallel to the sample surface, but (100) plane for the dot produced by instantaneous application of the laser. It has been shown recently that spontaneously formed crystals at the surface by simple furnace heating are also oriented in some oxide glasses as a result of oriented nuclei at the beginning [13-15]. Stress relaxation near the surface can be a reason for preferred surface nucleation [16-18]. Another explanation of the preferred orientation of the $\langle 001 \rangle$ direction parallel to the glass surface becomes plausible from the examination of Sb_2S_3 crystal structure, which consists of chains parallel to $\langle 001 \rangle$ crystallographic direction. It would seem that the chains should orient in the glass surface because longer Sb-S interatomic distances indicate weaker bonding perpendicular to the chains that form parallel to $\langle 001 \rangle$.

The large difference in covalent bonds within and between the chains [19, 20] predetermines higher crystal growth rate of Sb_2S_3 along the c-axis than along the directions normal to the chains. As a result, $\langle 001 \rangle$ -oriented needle-like Sb_2S_3 crystals were obtained in various attempts to grow synthetic Sb_2S_3 and were also observed in natural stibnite minerals [21-23]. Preference for the fastest crystal growth parallel to temperature gradient imposed by laser motion is a common observation [24].

In general, when considering crystallization on the surface, we may anticipate the process to be affected by the anisotropy of the rate of enthalpy change on one hand, and by the field gradients in kinetics on the other hand. Therefore, the minimum of enthalpy and the maximum in

kinetics will favor crystallization in some specific orientation [25]. Note that the latter part can be modified by external fields, such as temperature gradient during laser-induced crystallization.

Considering the details of the experiment, in principle it is possible that the intensity distribution within our laser beam was not exactly circular and isotropic. Consequently the temperature profile had elliptic shape at the glass surface. Such noncircular (axial) symmetry of thermal gradients can induce the nucleation and growth of Sb_2S_3 single crystal with the fastest growth direction $\langle 001 \rangle$ along the temperature of maximal growth rate in the laser-induced dot. Another possible explanation is that the crystallographic alignment of all single-crystal dots, i.e. the preference for in-plane c -orientation, is related to the polarization of laser beam [26]. At present we cannot be sure of what parameters determine the orientation of the laser induced single crystal spots of Sb_2S_3 formed in Sb-S-I glasses, but the observed reproducibility of crystal space orientation demonstrate its dependence on the parameters of laser-induced treatment (power distribution in the beam, polarization, shape, etc.). This statement concerns also the orientation of the normal direction of the single crystal relative to the glass surface, which depends on how the laser heating was implemented (gradually vs. abruptly, see section 3.3). To understand the mechanism of oriented nucleation and growth of Sb_2S_3 crystals, it is necessary to conduct additional investigations.

Turning our attention to region B , we note that Živković et al. [27] reported that Sb_2S_3 crystals can burn in the presence of oxygen to produce antimony oxide at temperatures as low as 190°C , and the process becomes rapid between 340 and 445°C . This temperature range corresponds to the crystallization temperature of Sb_2S_3 phase as detected by DSC for all the investigated glasses of the Sb-S-I system (Fig. 1). The presence of oxygen found in region B

confirms that this oxidation reaction indeed occurs during the formation of single crystal dots in G2 glass.

5. Conclusions

Facilitated by SbI_3 evaporation, oriented Sb_2S_3 single crystals were produced on the surface of SbSI-rich glasses of Sb-S-I system during laser irradiation. These single crystal grains were found to grow in $\langle 001 \rangle$ direction parallel to the glass surface. This demonstrates the possibility of controlling the orientation of a crystal formed by laser irradiation at the surface of glass matrix. Sb_2S_3 crystals form at 260°C and oxidize at $>340^\circ\text{C}$ in the presence of air. The reaction energy from the formation of Sb_2O_3 increases the temperature in the dot and thus stimulates further oxidation of the as grown Sb_2S_3 crystal. Despite this complication (that can be overcome by performing the laser irradiation in an oxygen-free environment), we demonstrated the possibility to control the single crystal orientation by laser beam. By combining precise control of heat and composition profiles using a laser as the heat source, a new possibility of crystal growth is introduced.

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