Formation of fresnoite-type Ba$_2$TiGe$_2$O$_8$ crystallites in BaO–TiO$_2$–GeO$_2$ glass thin film and its optical nonlinearity

Ryoh OGAWA, Hirokazu MASAI, Yoshihiro TAKAHASHI and Takumi FUJIWARA

Department of Applied Physics, Graduate School of Engineering, Tohoku University, Sendai 980–8579

We report on fabrication of the BaO–TiO$_2$–GeO$_2$ glass thin films on a fused silica substrate by RF sputtering, and investigation of the crystallization behavior, surface texture and the optical non-linearity in the glass thin film by means of AFM, XRD, Raman and Maker fringe techniques. Although the Ba$_2$TiGe$_2$O$_8$, hereafter abbreviated to BTG, phase with second-order optical nonlinearity was mainly crystallized, the precipitation of the sub-phase of BaGe$_2$O$_6$ was also confirmed in the heat-treated glass thin films. In the glass thin film heat-treated at heat-treatment temperature ($T_{HT}$) = 730–750°C, the (211) preferential orientation of BTG phase and an upheaval about 300–400 nm were confirmed at the surface. These transparent crystallized glass thin films indicated a clearly Maker fringe patterns, demonstrating a second-order optical nonlinearity, and the effective second-order nonlinear optical constant, $d_{33}$, was estimated to be ~0.8 pm/V.

Key-words : Glass, Thin film, Crystallization, Fresnoite-type crystal, Optical nonlinearity

1. Introduction

In the area of photonics, nonlinear optical crystals, e.g., LiNbO$_3$ and KTiOPO$_4$ with large optical non-linearity, are significant materials because they enable us to switch an optical signal and convert the fundamental laser light into the light with twice frequency. On the other hand, the transparent glass-ceramics consisting of nonlinear optical crystals have been also considered to be a candidate for the photon material because precursor glass possesses high formability, which is a characteristic of amorphous material, and the optical functional crystal can be crystallized by a selecting glass-system and its composition. For example, reported the transparent LiNbO$_3$ and BaTiO$_3$-crystallized glasses showing second-order harmonic generation (SHG) are fabricated in the Li$_2$O–Nb$_2$O$_5$–SiO$_2$ and BaO–TiO$_2$–TeO$_2$ system, respectively. Recently, the transparent fresnoite-type BTS, BTG, and STS-crystallized glasses with high orientation from the corresponding glasses were successfully fabricated, and large second-order optical nonlinearity was confirmed in these materials. Moreover, Honna et al. succeeded in patterning BTG crystal line with a width of approximately 5 μm in the BaO–TiO$_2$–GeO$_2$ system glass by transition metal atom heat (TMAH) processing. Thus, the transparent BTG glass/glass-ceramics have a great potential for the advanced photonic device component. However, in practical use of this material as the device component, e.g., photonic circuit, fabrication of the thin film of the precursor glass/glass-ceramics should be demanded for the purpose of its miniaturization and integration.

Very recently, Ogawa et al. succeeded for the first time in fabricating the BaO–TiO$_2$–GeO$_2$ glass thin films using an RF magnetron sputtering and the BTG crystalline thin film showing a clear second-harmonic generation (SHG) was obtained by crystallization of the glass thin film. In addition, the thin film possesses a possibility for the form of novel glass composition because it has high flexibility of the glass composition compared to the bulk glass. Since Takahashi et al. reported that the crystal morphology and second-order optical nonlinearity of the BTG-crystallized glasses are considerably affected by their glass compositions, it is quite important to examine those issues in the BaO–TiO$_2$–GeO$_2$ glass thin films in order to apply them to the photonic devices with high optical performance. Therefore, the aim of this study is to clarify the crystallized phase, surface texture and estimation of its nonlinear optical constant in the BaO–TiO$_2$–GeO$_2$ glass thin film.

2. Experimental procedures

The BaO–TiO$_2$–GeO$_2$ glass thin film was fabricated by RF magnetron sputtering (ULVAC MNS–2000–RF2F) on a fused silica substrate. A detail procedure for preparation of the thin film is described in elsewhere. After sputtering, the as-prepared glass thin films were heat-treated at various temperatures, $T_{HT}$, for 3 h in order to obtain the transparent BTG-crystallized glass thin films.

The thickness of as-prepared thin films were measured by a surface texture measuring instrument (Tokyo Seimitsu SURFCOM–480A) and surface roughness of crystallized glass thin films were examined using an atomic force microscope (SII NanoTechnology Nanopics2100). After heat-treatment, the identification of the crystalline phase in the heat-treated thin films were characterized by X-ray diffraction (XRD) analysis (Rigaku RINT 2000) and Raman spectroscopy (Horiba Jobin Yvon T64000). Second-harmonic (SH) intensities of the crystallized glass thin films were measured by a surface texture measuring instrument (Tokyo Seimitsu SURFCOM–480A) and surface roughness of crystallized glass thin films were examined using an atomic force microscope (SII NanoTechnology Nanopics2100). After heat-treatment, the identification of the crystalline phase in the heat-treated thin films were characterized by X-ray diffraction (XRD) analysis (Rigaku RINT 2000) and Raman spectroscopy (Horiba Jolbin Yvon T64000). Second-harmonic (SH) intensities of the crystallized glass thin films were measured by the Maker fringe technique. The fundamental wavelength of a Q-switched Nd$^{3+}$:yttrium–aluminum–garnet (YAG) laser at a wavelength of 1064 nm was used as the incident light. Z-cut α-quartz with a thickness of 0.6 mm was used as a reference. As the polarization condition in...
Maker fringe measurements, the combination of p-excitation and p-detection was used.

3. Results and discussion

Although the glass thin films subjected to heat-treatment were slightly opaque, they possessed a sufficient transparency and homogeneity for optical measurements. Figure 1 shows the AFM image of the surface of the as-deposited thin film and the thin films heat-treated at \( T_{HT} = 730–750\)°C. One can see that heat-treated samples have an upheaval of approximately 300–400 nm, implying the formation of crystallites at the surface. The relationship between the heat-treatment temperature, \( T_{HT} \) and the root-mean-square value (RMS) for the surface of the thin film, which is a criterion of surface roughness, is shown in Fig. 2. The value of RMS in the as-deposited thin film was estimated to be 1.41 nm, indicating a smooth surface of the thin film. Although the values of RMS were almost constant (~50 nm) in the \( T_{HT} = 700–740\)°C, the sudden increase in the RMS was observed in the \( T_{HT} = 750\)°C. This is probably due to an abnormal growth of crystallites by higher heat-treatment temperature. It is also suggested that the decrease in transparency is due to the scattering of light by the large crystallites presented in the heat-treated glass thin films.

Figure 3 shows XRD patterns of the surface region in the as-deposited thin film and the samples heat-treated at \( T_{HT} = 730–750\)°C for 3 h, together with the diffraction pattern of \( \text{Ba}_2\text{TiGe}_3\text{O}_9 \) referred to the ICDD data (No. 000440560). Although the diffraction peaks could not be observed (i.e., a halo pattern) in the glass thin film heat-treated at \( T_{HT} = 700\)°C, indicating the amorphous state, the thin film heat-treated at higher temperature, i.e., \( T_{HT} = 710–750\)°C revealed sharp diffraction peaks associated with the crystalline phase, meaning that nucleation and crystal growth occurred in the \( \text{Ba}_2\text{O}–\text{TiO}_2–\text{GeO}_2 \) glass thin film by the heat-treatment technique. By comparison with the ICDD data, the diffraction peaks at \( 2\theta \sim 26.6^\circ, 28.6^\circ \) and \( 32.6^\circ \) are attributed to the BTG phase, and these peaks are assigned to the (201), (211), and (420) planes. In addition, it is found that the crystallized glass thin film obtained by heat-treatment shows the (211) preferential orientation of the BTG phase. This crystallization behavior is quite different from that of the 30BaO·15TiO2·55GeO2, which is hereafter called BTG55, bulk glass, i.e., the c-orientation. On the other hand, the additional diffraction peaks also appeared at \( 2\theta \sim 24.0^\circ \) and \( 30.8^\circ \). According to the Takahashi et al., it is difficult to distinguish the formation of the \( \text{BaTiGe}_3\text{O}_9 \) phase and the \( \text{BaGe}_4\text{O}_9 \) phase in the BTG55 glass because the crystal structure of both phases and their lattice constants are similar. Although it is considered that either of the crystalline phases is formed in the crystallized thin films, it was necessary to check the formation crystalline phase by another technique in this study.

Raman spectroscopy for the as-deposited thin film and the thin film heat-treated at \( T_{HT} = 730\)°C are shown in Fig. 4, together with the \( \text{Ba}_2\text{TiGe}_3\text{O}_9, \text{BaTiGe}_3\text{O}_9 \) and \( \text{BaGe}_4\text{O}_9 \) phases synthesized by a solid state reaction. It is observed that two Raman peaks e.g., 490, 600 cm\(^{-1}\) attributed to a fused silica substrate are confirmed (solid triangle in Fig. 4) in the as-deposited thin film. On the other hand, the glass thin film heat-treated at \( T_{HT} = 730\)°C indicates the additional bands, e.g., 250, 710, 845, and 910 cm\(^{-1}\). These Raman bands could be assigned to the BTG phase by comparison with Raman spectrum of the BTG phase (solid circle in Fig. 4). Markgraf et al. reported that Raman peaks around 290 cm\(^{-1}\) and 518 cm\(^{-1}\) are due to \( \nu_1(\text{Ba–O}) \) and \( \nu(\text{Ge–O–Ge}) \) modes, respectively. The bands in the range of 700–900 cm\(^{-1}\) are assigned to the stretch of the short Ti–O\(^{\prime}\) (apical oxygen of the pyramidal TiO\(_2\) unit) bond, the Ti–O\(’\) (non-bridging oxygen) bond, and terminal GeO\(_2\) groups. The Raman band observed at 911 cm\(^{-1}\) is attributed to the anti-symmetric stretch of the pyrogermanate groups. The Raman band observed in the crystallized thin film at \( T_{HT} = 730\)°C also correspond to that of Markgraf’s report. In addition, the shoulder peak around 550 cm\(^{-1}\), weak and broad bands at 844 and 882 cm\(^{-1}\) are also observed in the spectrum. By comparison with the spectra of the \( \text{Ba}_2\text{TiGe}_3\text{O}_9 \) and \( \text{BaGe}_4\text{O}_9 \) phase, the position of this shoulder is close to that of the main bands of the \( \text{BaGe}_4\text{O}_9 \) phase. Furthermore, weak and broad bands correspond to that of the \( \text{BaGe}_4\text{O}_9 \) phase. Therefore, it is considered that the \( \text{BaGe}_4\text{O}_9 \) phase is precipitated in the glass thin film. Thus, we have concluded that the peaks at \( 2\theta \sim 24.0^\circ \) and \( 30.8^\circ \) in the Fig. 3 could be ascribed to the \( \text{BaGe}_4\text{O}_9 \) phase. In the previous study, the formation of the \( \text{BaTiGe}_3\text{O}_9 \) crystallite is necessary for homogeneous crystallization of the BTG phase in the BTG55 glass. However, we already confirmed that the glass thin film heat-treated firstly crystallized the BTG phase at \( T_{HT} = 710\)°C, and then the sub-phase of \( \text{BaGe}_4\text{O}_9 \) was formed at higher temperature. It was demonstrated that crystallization mechanism of BTG phase in the thin film was different from that in the BTG55 glass.
The Maker fringe patterns for the BTG-crystallized thin film obtained by heat treatment at \( T_{HT} = 730–750 \) °C for 3 h are shown in Fig. 5. One can see a clear fringe patterns in these heat-treated glass thin films, meaning that these samples have the optical nonlinearity. The SH intensity is increased with increasing the heat-treatment temperature. It is probably due to increase of the volume fraction of BTG phase in the glass thin film. According to Lu et al.,\(^{20}\) effective second-order nonlinear optical constant, \( d_{eff} \), in the crystalline thin film is expressed by following formula:

\[
d_{eff} \sim \frac{l_{c,Q}}{l_s} \left( \frac{n^2(2\omega)\bb{n}{(\omega)}}{n^2(2\omega)\bb{n}{Q}(\omega)} \frac{l_{s,\text{Max}}}{l_{Q,\text{Max}}} \right)^{1/2} d_{11,Q} \tag{1}
\]

where \( l_s \) is the film thickness, \( l_{c,Q} \) is the coherence length of the quartz (~20 μm), \( n(\omega) \) and \( n(2\omega) \) are the refractive indices of \( \omega \) and \( 2\omega \), respectively (the subscript of \( Q \) and \( S \) denotes the values for the quartz and sample, respectively), \( I \) is the maximal value of SH intensity, \( T \) is transmittance of sample, and \( d_{11,Q} \) is the \( d_{11} \) of the quartz (0.55 pm·V\(^{-1}\)). Figure 6 shows the relation between the value of \( d_{eff} \) and the heat-treatment temperature, \( T_{HT} \). It is found that the value of \( d_{eff} \) is increased with increasing the heat-treatment temperature, \( T_{HT} \). Although the \( d_{33} \) value of transparent BTG surface-crystallized glass is estimated to be 24 pm·V\(^{-1}\),\(^{11}\) the thin film obtained in this study showed the considerably lower optical nonlinearity (\( d_{eff} \sim 0.8 \) pm·V\(^{-1}\)) compared to the surface-crystallized glass (i.e., the BTG55 glass ceramics).

It is considered that the \( d \) value is largely affected by the (1) volume fraction, (2) homogeneity and (3) orientation of the BTG phase in the corresponding glass. For example, Takahashi et al. reported that the BTG crystalline layer in the crystallized glass is ~10 μm of thickness,\(^{10}\) and the second-order nonlinear optical constant, \( d_{33} \), of the BTG-crystallized glasses is increased as the surface-crystalline layer of BTG phase on the glass phase became homogeneous.\(^{15}\) On the other hand, the as-deposited film has about 500–600 nm of thickness. Therefore, the volume fraction of the BTG phases in the crystallized thin film is smaller than that of surface-crystallized glass in the BTG55 reported so far. In addition, the results from the AFM observation in the crystallized thin film samples (refer to Fig. 1), we can see an upheaval at the surface of samples, which is caused by the heat-treatment, indicating the inhomogeneity of BTG phase due to crystallization. Furthermore, the formation of the sub-phase of BaGe\(_4\)O\(_9\) was confirmed by XRD and Raman spectroscopy in the heat-treated glass thin films. This crystallization tendency is quite different form the case of surface-crystallized glasses with BTG55 composition, i.e., precipitation of BaTiGe\(_3\)O\(_9\) phase and subsequent crystallization of BTG phase. In fact, although, the obtained fringe pattern was clear with increasing heat-treatment temperature, the estimated \( d_{eff} \) value in this study was low.
pared to bulk glass ceramics. It is considered that crystallized glass thin film heat-treated at $T_{HT} = 750$°C shows clear fringe pattern is caused by the volume fraction of the BTG phase in the thin film increases with increasing heat-treatment temperature. However, the impurity phase, such as BaGe$_4$O$_9$ also increases. Takahashi et al. estimated the SH intensity for the BTG crystalline and the BaTiGe$_3$O$_9$ crystalline by Kurtz method (powder state), and as a result, the SH intensity of the BTG phase was approximately 130 times as large as that of the BaTiGe$_3$O$_9$ phase. Since the structure of the BaTiGe$_3$O$_9$ phase is similar to that of the BaGe$_4$O$_9$ phase, the BTG crystal should have a large optical non-linearity compared to BaGe$_4$O$_9$ phase. Thus, it is considered that the decrease of the estimated $d_{33}$ value in the thin film compared to the bulk glass ceramics is caused by two reasons. One of them is low crystal volume in the thin film compared to the bulk glass ceramics. Another one is the precipitation of the sub phase, i.e. the BaGe$_4$O$_9$ phase. Moreover, it is known that 30BaO·15TiO$_2$·55GeO$_2$, 33.3BaO·16.7TiO$_2$·50GeO$_2$, and 40BaO·20TiO$_2$·40GeO$_2$ glass compositions show surface crystallization with high orientation to c-axis, which is the polarization axis in the crystalline phase. Masai et al. examined the relation between the $d_{33}$ value and degree of orientation of BTG phase in the surface-crystallized glasses. It was found that the $d_{33}$ value was increase with increasing the ratio of the diffraction peak intensity of (002) plane, $I_{002}$ to that of the (311) plane, $I_{311}$, in the XRD patterns, i.e., $I_{002}$ / $I_{311}$, (degree of orientation). This result indicates that the nonlinear optical coefficient depends on the c-axis orientation. On the other hand, the crystallized glass thin film in this study showed the preferential (211) orientation. Therefore it might be expected that the large optical nonlinear constant is achieved by increase of the volume fraction of BTG, decrease of impurities such as BaGe$_4$O$_9$ in the thin film and growth of the strongly c-axis oriented crystallites in the glass thin film.

4. Conclusion

The thin film of BaO-TiO$_2$-GeO$_2$ glass was fabricated by RF sputtering and the fresnoite-type Ba$_2$TiGe$_3$O$_9$ (BTG) crystallized glass was obtained by proper heat-treatment in glassy thin film. Surface roughness of the thin films heat-treated at $T_{HT} = 700$–750°C was examined by AFM. Crystallization behavior of BTG in the glass thin film was investigated by means of XRD analyses and Raman spectroscopy. The second order optical non-linearity was examined by Maker fringe method and their effective non-linear optical constant $d_{33}$ was estimated. The heat-treated glass thin films showed several different aspects in morphology and crystallization behavior from the bulk glass ceramics. The (211) preferential orientation of the BTG phase and an upheaval about 300–400 nm were observed. Although the BaTiGe$_3$O$_9$ phase is indeed important factor as a nucleation site for the growth of fresnoite-type BTG phase in case of the bulk glass, the precipitation of BaGe$_4$O$_9$ phase was confirmed in the thin film. Moreover the BTG phase was grown involving with precipitation of the BaGe$_4$O$_9$ phase. The SH generation in the crystallized glass thin film heat-treated at $T_{HT} = 730$–750°C was clearly observed and their effective optical non-linearity ($d_{33}$) was estimated to be $\sim$0.8 pm/V$^{-1}$.

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