Laser-induced modification of glass–ceramics microstructure and applications

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Abstract

The laser-induced modifications in two kinds of glass–ceramics (GCs) with composition TiO₂–SiO₂ (Sitall ST-50) and Li₂O–SiO₂ (Fotoform) were investigated for fabricating optical elements. The laser-induced change of refractive index and surface relief constituted the first step of this task. The second stage was a chemical processing including ion exchange (Li ↔ Na, K, Rb, for “Fotoform” GCs) and etching of irradiated and non-irradiated areas. As a result of the above-mentioned processes, mini- and micro-optical components based on two GCs have been fabricated: lenses and lens arrays, waveguides and other waveguiding components, diffractive gratings, etc.
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1. Introduction

Photonics as a technology for fabrication of opto-informatic devices is just living in the first stage of miniaturization and integration that was reached in microelectronics 50 years ago. This stage is characterized by the formation of materials and components in a single process. Examples of such an approach could be the fabrication of thermo-photo-optical materials and components for holographic corrections of laser beam wave fronts [1], the fabrication of micro-optical components by laser densification of porous glasses [2], etc. Further development of miniaturization and integration in photonics should allow create photonics chips, combining different functions in a single monolithic block of specific material, whose structure is modified by different treatments. The most popular materials for such kind of investigations are semiconductors (InGaAs type), “photonics” glasses and optical polymers.

In the present work, a similar approach to glass–ceramics materials is performed. Glass–ceramics (GCs) have an amorphous structure with embedded micro-crystals that are responsible for their mechanical, chemical and optical properties. From the optical point
of view, GCs were not attractive until lately due to a strong scattering in the visible range produced by the embedded micro-crystals. The microcrystalline structure of GCs is the consequence of the tendency to crystallization of many oxides due to nucleation and growth processes during the heating–cooling cycle. Nucleation and growth of micro-crystals cannot be avoided in traditional thermal treatments of GCs due to the low cooling rate. But a high cooling rate after laser melting of GCs in definite zones could preserve the amorphous (glassy) structure, which is typical of melted GCs. This high cooling rate is given by the very effective thermo-conductive cooling in solids with respect to the natural air cooling, since the thermal conductivity coefficient of GCs is about 0.150 W/(m² s), two orders of magnitude higher than that of air, which is about 0.001 W/(m² s). To get such high cooling rates, only a local zone of material has to be irradiated. In this case, after the end of the laser action, the heat from the irradiated zone is very effectively transferred to neighboring zones of solid. This results in a change of physical and chemical properties of the irradiated area, like density, volume, viscosity, hardness, transparency, refraction index, etc. Most important, the optical transparency of GCs drastically increases in the visible and near-IR range due to the formation of a new glassy structure. Moreover, crystalline and glassy phases have different impurity diffusion coefficients and rates of etching. These properties allow modify the refractive index and the surface relief of optical elements. The other important feature is a difference in the density of ordered–disordered phases, which can be used to produce surface structures. Laser processing of GCs has already been realized and new amorphous structures at room temperature were fabricated [3]. The results presented in this paper on laser modification of two kinds of GCs, with composition TiO₂–SiO₂ (Sitall ST-50) and Li₂O–SiO₂ (Fotoform), show that the laser-produced new phases have new mechanical, chemical and, what is most interesting, optical characteristics. One can consider them as new materials—components created by the laser action.

2. Experimental details

In our experiment, we used two types of GCs. The first type, ST-50, has two crystalline phases, rutile α-

 TiO₂ and cordierite 2MgO·2Al₂O₃·5SiO₂. The second one is a photosensitive glass FS-1 [4], which is similar to “Fotoform” (Corning Inc.) having one crystalline phase, Li₂O·2SiO₂. Samples were prepared with thickness of 0.6–1.0 mm. The ST-50 ceramic samples were irradiated with a CW CO₂-laser (λ = 10.6 μm) at the power of 50 W with spot diameters of 0.5–5.0 mm. The FS-1 glass samples were irradiated with the same CO₂-laser beam and also with a pulsed N₂-laser beam (λ = 337 nm) at a pulse power of 1.6 kW, pulse duration of 10 ns and pulse repetition of rate 100 Hz.

The X-ray structural analysis (XRD) has been used to reveal structural changes in GCs after laser irradiation. Optical microscopy and micro-video-recording of the irradiated zones were used to study optical modifications during and after the laser treatments.

3. Experimental results and discussion

3.1. ST-50—structural changes

Initial GC materials had microcrystalline structure, as inferred from the appearance of peaks in the corresponding XRD spectra. Very different XRD spectra were recorded for the irradiated materials. Here, the peak intensities dramatically decreased, evidencing the disappearance (or considerable decrease in density and size) of micro-crystals. In the same spectra, the increase in the intensity of the amorphous background signals was observed. We conclude that the XRD investigation of GCs shows that laser action resulted in the formation of a new phase, an essentially amorphous structure, in which the size and density of the initial crystallites were noticeably decreased. From XRD investigations, we also inferred that after a successive laser irradiation of the new (mostly amorphous) material, it recovers again its initial polycrystalline structure.

3.2. ST-50—IR-laser photophysical action

The kinetics of the phase-structural changes can be understood from the temperature kinetics, especially from the heating and cooling rates, which are responsible for the formation of definite phases and
their optical stability. Temperature kinetics was investigated by a micro-pyrometer, as described in detail in previous publications [5,6]. The front of amorphization, which we identify as the transparent front, was studied by optical microscopy of sections and by micro-video-recording.

A typical view of heating—cooling curves of ST-50 GCs under CO$_2$-laser irradiation at two different power densities is shown in Fig. 1. In both cases, the laser heating produces a temperature of about 1500 K (the vitrifying and melting temperatures of this GCs are 1033 and 1473 K, respectively. In the region of laser power density of $3 \times 10^9$ to $1 \times 10^{10}$ W/m$^2$, initial temperature $T_0 = 700$ K; curve 2–2': $P \leq 0.3$ W, $q \leq 10^5$ W/m$^2$, $T_0 = 1000$ K; (b) development of the amorphized zone in the GC plate after the beginning of laser irradiation: 1–6, 2–6, 5, 3–7 s; (c) pictures of the surface of partially crystallized (non-transparent) areas after reverse crystallization of glass–ceramics.

3.3. FS-1—combination of UV photochemical and thermal action

In the photosensitive glass FS-1, a Li$_2$O–2SiO$_2$ crystalline phase is grown by a two-step process: exposure to UV radiation and thermal annealing. The first step is the exposure of the glass sample to UV radiation, which produces ionization of Ce$^{3+}$ ions. The electrons released from cerium ions are then trapped by silver ions. As a result, silver is converted from positive ion to neutral atom. This stage corresponds to a latent image formation and no significant coloration occurs. The next step is the thermal annealing, which is a process that in turn includes two stages. The first stage involves the high diffusion rate of silver atoms in the silicate glass (Fig. 2b). This diffusion leads to the creation of silver colloidal clusters at relatively low temperature (400–500 °C). A number of silver clusters grow in the irradiated zones of glass after aging at the above-mentioned temperatures. These silver clusters serve as nucleation centers for the growth of the crystalline phase Li$_2$O–2SiO$_2$. The micro-crystals Li$_2$O–2SiO$_2$ precipitate at a temperature of 550–650 °C. The large crystallites produce a yellow–opal coloration. Such GC areas are not transparent in the UV, visible, and near-IR spectral ranges. It was observed that the non-irradiated (amorphous) and the irradiated (crystalline) areas had significantly different specific volumes. We used this feature for fabrication of various optical elements (see Section 5). In our experiments, the polished samples were irradiated by a
pulsed nitrogen-laser. The irradiated samples were annealed at the temperature of 600 °C for 2–10 h. The crystallized zones return to the initial amorphous state when exposed to CW CO₂-laser radiation.

4. Changes of GCs properties due to laser irradiation

4.1. Optical transparency

Large changes in optical transparency of both ST-50 and FS-1 GCs were observed immediately after laser irradiation; transparent windows were created in the non-transparent materials. The absorption spectra of the initial and irradiated samples are shown in Fig. 2. Thus, using laser radiation one can transform GCs from a high absorptive material in the near-IR and visible band to a highly transparent material in the same wavelength bands. The optical loss decreased 10 times in the near-IR and 100 times in the visible range.

4.2. Surface morphology modification

The polycrystalline phase is much denser than the amorphous one. We have observed also the reverse effect, i.e., an increase in volume, after laser amorphization of GCs. Fig. 3a illustrates the surface relief change (shrinkage) of FS-1 GC as a function of the pulsed N₂-laser fluence. After UV radiation, the sample was annealed at 600 °C for 6 h. The UV irradiation results in the reduction of volume of the GC area and shrinkage (8–9 μm) takes place. Fig. 3b shows the increase in the surface relief in the irradiated zone under successive IR laser amorphization.

4.3. Modifications of chemical properties

Structural modifications change also the chemical properties of the irradiated materials. We studied the influence of the amorphization on the rate of chemical etching. New results about etching rates of the virgin and irradiated GC samples in HF and HF + HNO₃ acid solutions were measured and described earlier [7].
In the case of ST-50, the etching rate for the glass phase is higher than the one for the crystalline phase. The cause of the low etching rate of crystalline phase is that rutile and cordierite phases are not readily soluble in HF and HNO₃ acids. In the case of FS-1, we found a reverse situation, i.e., the etching rate for the crystalline phase is higher than that for the glass by a factor of 10⁷. Different etching rates create different surface relief on the sample surface.

4.4. Ion-exchanging properties

The FS-1 virgin glass contains lithium ions. Li⁺ in glass can be exchanged by other alkali ions, for example Na⁺, K⁺, etc. from salt melts (NaNO₃, KNO₃, etc.). The ion-exchange technique can be applied to optical elements fabrication, e.g. waveguides, lenses, etc. [1,8,9]. We observed that the exchange of lithium ions in the Li₂O·2SiO₂ crystalline phase obtained after N₂-laser exposure and thermal annealing is not possible. This crystallized area can thus play the role of a local mask, which blocks the ion-exchange process.

We applied the ion-exchange technique in an amorphous FS-1 sample. The sample was treated in KNO₃ melt at 450 °C. Lithium ions in a glassy phase were exchanged by potassium ions from the melt: \( 	ext{Li}^+_{\text{glass}} \leftrightarrow \text{K}^+_{\text{salt}} \). Due to the big difference of the ionic radii of \( \text{Li}^+ (0.65 \text{ Å}) \) and \( \text{K}^+ (1.33 \text{ Å}) \), the change of the macroscopic volume and surface relief of glass occurs. Fig. 4 shows the value of swelling as a function of time.

5. Applications of laser-induced structural and morphological changes in GCs

Since laser beams can be focused into a spot of very small size down to the diffraction limit, it is possible to modify locally the structure of the GCs to create miniature optical devices and components. We created, thus, optical planar waveguides by scanning the laser spot over the surface of a ST-50 GC sample. As demonstrated above, under laser action, the original GC is locally transformed to a glass phase with very low optical losses in the visible and near-IR range. Soaking then the sample into an HF solution due to the different etching rates of irradiated and initial GC, we obtained micro-channels on the surface of the GC samples (the irradiated GC has a higher etching rate than that of the initial GC ST-50), which can be used in microfluidic devices. Another important application of laser-induced structural changes is the fabrication of miniature lenses. The lens fabrication technique includes the following simple steps: (i) GC samples are fabricated with different thickness (the thickness of the samples defines the range of diameters of the lenses); (ii) the samples are then laser irradiated (the laser spot size can be controlled by a diaphragm); (iii) as a result of laser irradiation, optically transparent “windows” are opened in initially non-transparent media. Due to the difference in specific volumes of the polycrystalline (more dense) versus amorphous (less dense) phases, various optical components can be created: lens and lens arrays, diffraction optical components and diffraction gratings, in particular. Some examples of planar optical component production, such as lens arrays and microspheres by scanning a laser beam can be found in our previous publications [1,3,10]. In this work, we illustrate applications of laser techniques to the fabrication of diffractive gratings.

5.1. Diffractive gratings

We have applied the photo-thermo-induced crystal- lization process for fabricating diffraction gratings. A periodical mask with spatial frequency of 60 mm⁻¹ has been produced by UV N₂-laser irradiation of the FS-1 virgin glass. After thermal annealing, we obtained the surface relief shown in Fig. 5a. The highest achieved modulation amplitude of the induced
surface relief was 0.2 μm. The high light scattering in the volume glass–ceramics in the visible and near-IR spectral range did not allow us to use the gratings as transparent optical elements. Thus, the gratings were covered with an Al film, about 100 nm thick, and their characteristics were measured. Fig. 6 presents the diffraction efficiency of a reflective grating produced by photo-thermo-induced crystallization of glass as a function of laser fluence. The increase of fluence results in an increase of the diffraction efficiency up to 24%. Further increase of fluence results, however, in decrease of diffraction efficiency. This is because for high doses of exposure light scattering increases in the unexposed areas due to the growth of crystalline phase in these areas during the thermal annealing. Thus, overall, this reduces the contrast of the interference patterns.

The parameters of the gratings can be modified by etching and ion exchange. Fig. 5 illustrates the application of these technologies. Fig. 5a shows a diffraction grating fabricated by the photo-thermo-induced crystallization process. Fig. 5b shows that the modulation amplitude of the surface relief increases by HF etching; the etching rate for crystalline phase is several times higher than that for glass. Fig. 5c shows how the GC area plays the role of a mask, i.e., blocking the diffusion process. Finally, further increase of surface relief in the glassy area occurs as a consequence of the difference of radii of exchanging ions, for example Li⁺glass ↔ K⁺salt.

6. Conclusions

We have demonstrated that laser action can be tailored to create important structural changes in GCs. Due to the laser-induced structural changes, from polycrystalline to amorphous or vice-versa, the initial materials acquire new chemical and optical properties. Laser-induced amorphization or crystallization, in combination with chemical etching and ion-exchange processes, can be thus used to produce micro-optical components.

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