Photostructurable Glass for Microdevices

Development of Ag-Ce Doped Photostructurable Glass Ceramics for Microdevice Application

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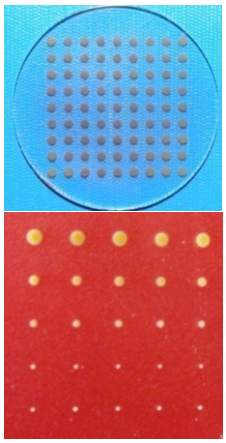

Glass Discs after UV Exposure and Heat Treatment (Scale: 0.2 to 1 mm diameter of holes)

ABSTRACT

In recent years glassy materials for micro devices fabrication are acquiring much attention over other materials for its excellent properties such as optical transparency, chemical inertness, thermal and electrical insulation, biocompatibility as well as ease of manufacturing. In this work we have utilized photolithography for micro structuring of glass. Ag and Ce doped Lithium Alumino Silicate glasses of composition (wt%):74SiO_2-6Al_2O_3-15Li_2O-5X (X=other additives) were prepared by melt quench technique and exposed to UV light for conversion of Ce^{3+} to Ce^{4+} and Ag^{+} into Ag^{o} metallic state for preferential nucleation/growth of metasilicate phase. XRD was used for phase identification in the heat treated glasses. DTA data revealed a lower crystallization temperature (T_p) at around 610°C for UV exposed glass as compared to unexposed base glass which is at around 627°C. UV Visible spectra confirm conversion of Ce^{3+} to Ce^{4+} ions in exposed glass samples. In the samples heat treated at nucleation temperature Ag agglomeration was confirmed from the band position at around 430nm. Heat schedule was optimized for the crystallization of Lithium metasilicate phase on UV-exposed glass. Activation energy calculation showed lower value after exposure under UV-light. The developed metasilicate phase was selectively etched in dil. HF for fabrication of micro devices. Different micro-patterns up to 200μ could be successfully prepared.

KEYWORDS: *Photostructuralable glass ceramic, Microdevice, LAS glass ceramics, Crystallization kinetics*

Introduction

Microfluidic devices find wide spread applications in various fields in the form of micro reactors, micro needles, micro sensors etc. These provide better thermal hydraulic and fluidic properties due to their large surface area to volume ratio than conventional devices[1]. They also provide large catalytic surface area and uniform temperature distribution which is most valuable for a number of reactions. Surface to volume ratio is key requirement in various applications and varies inversely with characteristic length. As characteristic length reduces surface to volume ratio increases and at micron size domain this value is significantly high owing to very small characteristic length. Small size of devices makes it portable and hazardous intermediates can be prepared insitu rather than storing them at isolated places. These can be fabricated using variety of materials such as metals, semiconductors, polymers, glasses, ceramics, etc[2]. Glass based micro devices have certain advantage over semiconductors and metals, thanks to its high/beneficial transparency in visible range, better thermal and electrical insulation, good corrosion resistance, biocompatibility[3]. As compared to polymer based micro devices the glass based devices are much more thermally stable and corrosion resistance and can withstand at higher pressures. In many places these materials are used as alternate to silicon based micro devices. Since glasses are isotropic in nature which makes these suitable for microstructuring in any direction in comparison to semiconductor such as Silicon. Different methods are reported for manufacturing of microdevices with complex shapes such as wet etching, dry etching, laser fabrication, sand blasting, mechanical machining, etc. Preparation of complex microstructures with high aspect ratio using mechanical methods is comparatively difficult due to poor machinability of glasses[4]. Photolithography is one of the popular and simplest methods for preparation of complex and high aspect ratio micro structures in glasses. Photostructurable glasses based on ternary Lithiumalumino silicate (LAS) system with small amount of Ag and Ce can be patterned with micrometer accuracy over large areas without use of photoresist[5].

In this study we report, fabrication of micropatterns/ microstructures on the glass by using photolithography. Ag and Ce doped Lithium alumino silicate glasses were prepared and characterized for selective growth of metasilicate phase. This phase has higher solubility in dil. HF than the base glass making them suitable for micro structuring. In this composition, Cerium is added to increase the glass photosensitivity and silver oxide to enhance the crystallization of the glass[6,7]. Micropattering down to 200 micron scale were carried out on these glasses using this process.

Methodology/ Synthesis

Ag and Ce-doped LAS glasses of composition (wt.%): 74SiO_2-6Al_2O_3-15Li_2O-5X (X=other additives) were prepared by melt-quench technique. Melting was carried in the temperature range of 1550-1600°C followed by annealing to remove thermal stresses. Cerium was used to provide the glass photosensitivity and silver oxide addition enhanced the photosensitivity of glass. All prepared glasses were

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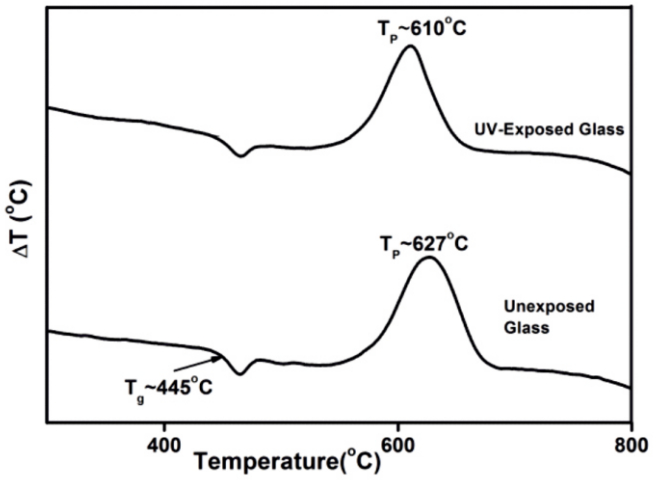

Fig.1: Merged DTA plots of unexposed and UV exposed Glasses.

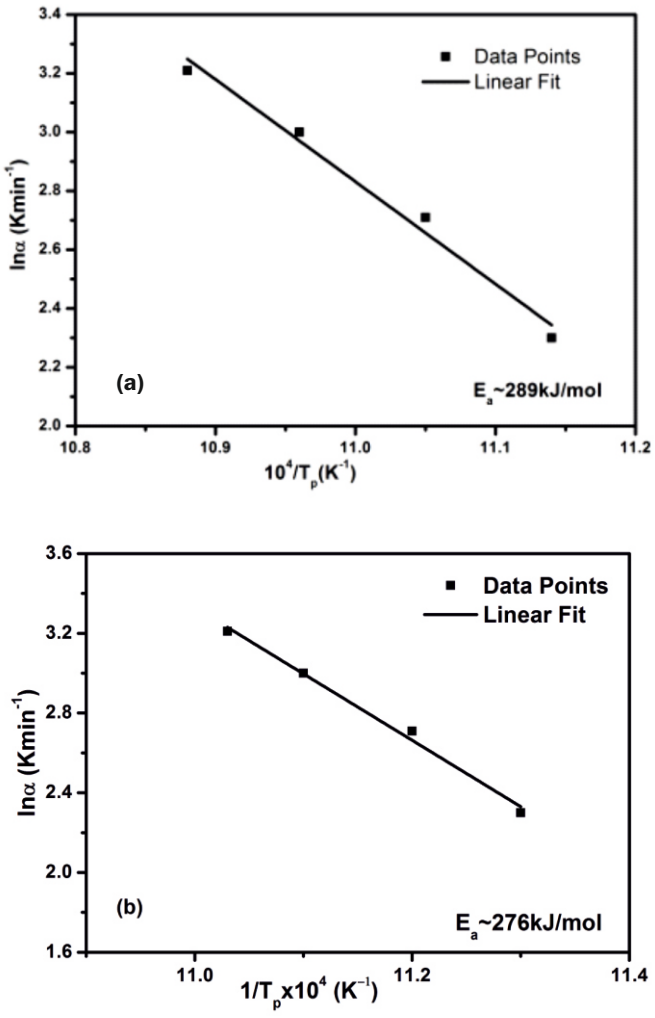

Fig.2: Marotta plot for activation energy of LASK (a) Unexposed (b) UV exposed glass.

transparent and bubble free. The glass samples were cut into thin pieces, polished and exposed under UV light at wavelength around 312nm (corresponding to Ce^{3+} absorption) for varying time periods (5 min to 4h). Based on the information by DTA data, heat treatment schedule optimization was carried for selective crystallization of Lithium metasilicate (Li_2SiO_3) phase. A two stage heat treatment was carried out on these polished and exposed glasses. In the first stage, sample was heat treated at nucleation temperature (in the range of 470-480°C)

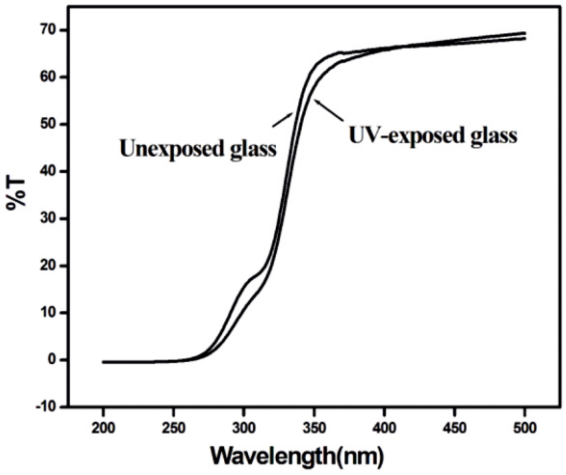

Fig.3: UV-Vis transmission spectra of unexposed and exposed Glasses.

in which formation of silver agglomerates is expected. In the second stage, sample was heat treated in the temperature range 500-550°C for required time period, for growth of Lithium metasilicate phase on silver agglomerates. To prepare pattern, glass piece was masked with a metal having desired pattern, UV exposed for pattern transfer, and then heat treated for Ag agglomeration and growth of Li_2SiO_3 phase. Finally this phase was preferentially dissolved in the 5-10% HF acid to leave the patterned glass.

Characterization

Differential thermal measurements (DTA) were performed on unexposed and exposed glass powder to determine glass transition temperature and shift in peak crystallization temperature using TG/DTA apparatus (Model: LABSYS). DTA experiments with varying rates of heating (10-25Kpm) were carried for activation energy calculations. XRD measurements were carried out to confirm the amorphous nature of the annealed glasses and to identify the crystalline phases in the exposed and heat treated glasses using Bruker D8 X-Ray Diffractometer.

UV-VIS spectrophotometer (Model V-670, M/s. JASCO, Japan) was used for absorption studies on unexposed and exposed glass samples, and on exposed and nucleated glass samples. Exposed and heat treated glasses were etched in dil. HF acid of different concentrations to dissolve metasilicate phase for time period in the range of 60-125 minutes.

Results/Discussion

Fig.1 depicts the DTA plots of unexposed and UV-exposed glasses with heating rate of 10 $Kmin^{-1}$. Both the glasses show broad endotherm at around 445°C indicating glass transition temperature (T_g). Data shows a lower exothermic peak temperature (Tp) at around temperature 610°C for UV-exposed samples as compared to unexposed base glass with peak temperature at around temperature 627°C. Non isothermal crystallization kinetics was carried on exposed and unexposed glasses by recording the DTA plots for different heating rates (10-25Kpm). Activation energy was calculated using Marotta equation which is as follows,

$$\ln(\alpha) = -\frac{E}{RT_p} + Constant$$

Here, E is the activation energy for crystallization, R is the gas constant, T_p is the peak of crystallization temperature, α is the heating rate ($K\,min^{-1}$).

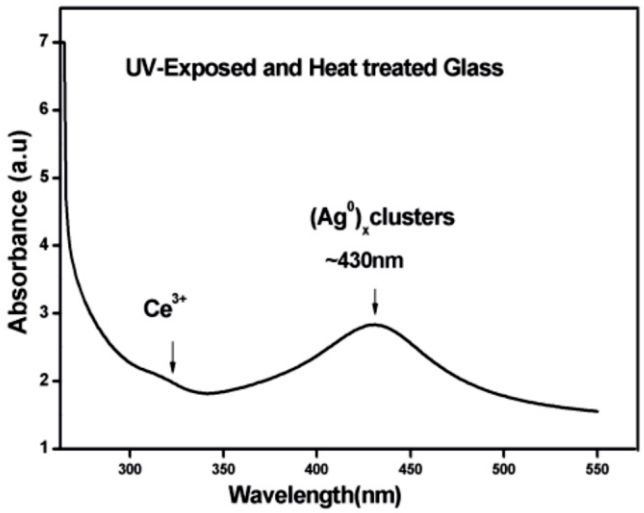

Fig.4: UV-Vis Absorption spectra of UV exposed and heat treated glass.

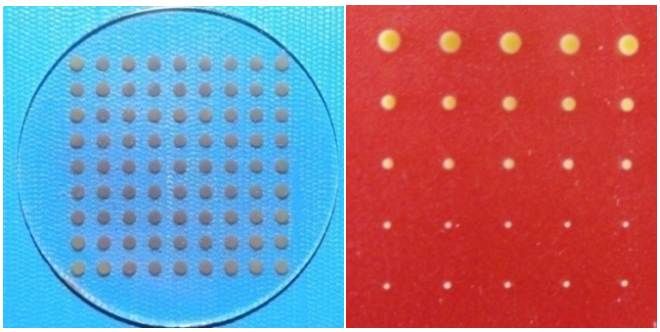

Fig.6: (a). Glass Discs after UV Exposure and Heat Treatment (Scale: 0.2 to 1 mm diameter of holes).

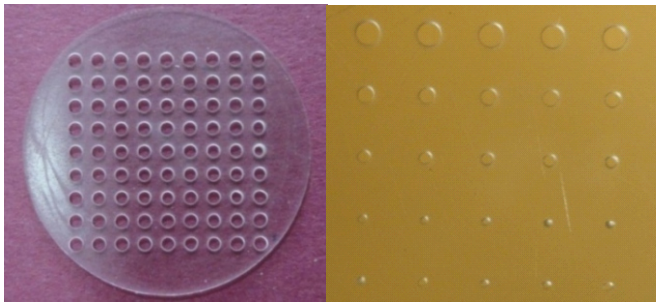

Fig.6: (b). Glass Discs after UV Exposure, HT and Etching in dil. HF (0.2 to 1 mm diameter of holes).

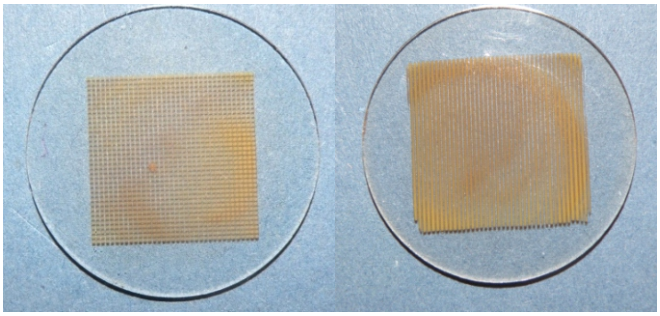

Fig.6: (c). Glass Discs after UV-Exposure, HT (0.2 mm holes and 0.2 mm line pattern).

Fig.2(a) & (b) showed Marotta plots for calculation of the activation energy for unexposed and UV-exposed glasses, respectively. Activation energy of crystallization for unexposed and exposed glasses were found to be 289kJmol^{-1} and

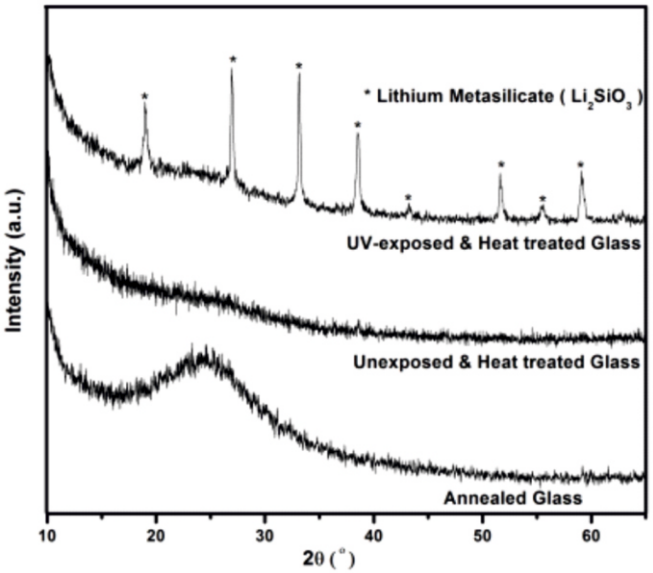

Fig.5: Merged XRD plots of heat treated, unexposed and UV exposed glasses.

276kJmol^{-1}. This reduction in activation energy after UV-exposure is due to the formation of silver nanoclusters, which provide heterogeneous nucleating sites for early growth of main phase.

Conversion of Ce^{3+} to Ce^{4+} state and Ag^{+} into Ag^{o} metallic state occurred after UV exposure.

Spectra in Fig.3 shows a broad band at around 305nm indicative of Ce^{3+} in base glass whereas in case of UV exposed sample the reduced peak intensity indicates conversion of Ce^{3+} to Ce^{4+} ions.

Fig.4 represents UV-Vis absorption spectra of nucleated samples which showed a broad band centered at around 430nm which confirms formation of Ag nanoclusters. These nanoclusters provide the heterogeneous nucleation sites for early growth of metasilicate phase in exposed sample, as compared to unexposed samples and helped for patterning in the glass.

X-ray diffraction patterns of annealed base glass, heat treated unexposed and heat treated UV- exposed samples are shown in Fig.5. XRD pattern of glass sample confirms its amorphous nature (broad hump in the region of 2θ≈20-30°). It also showed Lithium metasilicate phase (Li_2SiO_3) formation in exposed glass while no phase formation occurred in base glass/unexposed glass on subjecting to the optimized heat treatment. Early crystallization of this phase in glass after UV exposure is responsible for selective crystallization of glass, facilitating patterning/micro structuring.

Exposed and heat treated glasses were etched in dil. HF acid with varying concentration up to 10%. As the solubility of glass ceramic is more in the acid, it etched out from glass matrix leaving the matrix intact and thus desired pattern can be formed on the glass surface. Etching rate for metasilicate phase was found to be ~6µm/min. Etching ratio of glass ceramic to glass was found at around 10:1 in 10%HF.

Micropattering of LAS glass ceramics

Micropattering of different scales up to micron level were carried out using metal masking. Patterns with lines and holes up to size of 200µ could be prepared successfully with existing facility. Few photographs of microstructuring on Lithium Alumino silicate glass doped with Cerium and Silver are shown in Fig.6.

Conclusion

Ag and Ce doped LAS glasses were prepared, UV exposed and heat treatment process were fine tuned for selective growth of Lithium metasilicate phase. Shift in peak crystallization temperature in UV exposed samples to lower side was observed from DTA data. Kinetic analysis showed reduction in activation energy of crystallization after UV exposure which also indicates that silver is providing heterogeneous nucleation sites for early growth of metasilicate phase. Absorption spectra shows formation of silver nano clusters in the UV exposed and nucleated samples. Lithium metasilicate (Li_2SiO_3) phase formation was confirmed by XRD in exposed and heat treated glass while base glass showed no crystalline phase. Etching ratio of glass ceramic to glass was found ~10:1. Microstructures of dimensions up to 200μ could be prepared in these glasses using photolithography.

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