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Dependence of Chemical Etching rate of PTR-glasses on Terms of Photo-thermo-induced Crystallization

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Etching kinetics of virgin photo-thermo-refractive glass and glassceramics (after photo-thermo-induced crystallization process at various terms) in aqueous hydrofluoric acid based solution has been investigated for the first time. It has been shown that the etching rate of the glassceramic is increasing with increasing of nanocrystalls number and size.

Keywords: Photo-thermo-refractive glass, Chemical etching, photo-thermo-induced crystallization

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1. INTRODUCTION

Photo-thermo-refractive(PTR) glasses have attracted considerable attention as a material for volume hologram recording. It is a sodium-zinc-aluminum-silicate glass doped with cerium, silver and antimony[1]. The process of ultraviolet exposure followed by heat treatment leads to precipitation of crystalline phase. It produces refractive index modulation and this phenomenon is used for phase volume hologram recording. One of the advantages of the material is a low level of scattering on the boundary between crystalline and glassy phases. Photo-thermo-refractive glass has small size of nanocrystalls (NaF-AgBr) that allows to record highly efficient volume Bragg gratings[2]. But the technical and industrial uses of PTR glass have increased in recent years. It has been found that the local nanocrystalline phase of PTR glass etches about ten times faster than the glassy one[3]. For that reason this materials can be used for fabrication of photonics and mechatronics elements.

The purpose of this paper is to describe a new PTR glass capable of being etched by an aqueous hydrofluoric acid based solution depending on characteristics of photo-thermo-induced crystallization process.

2. TECHNOLOGY AND EXPERIMENTS

Several photo-thermo-refractive glasses of approximate composition Na_2O-ZnO-Al_2O_3-SiO_2-NaF-KBr doped CeO_2, Sb_2O_3 and Ag_2O and based-on-it glassceramics were studied in this work. Polished samples of 1 mm thick and 7 × 7 mm lateral size were prepared for photo-thermo-induced crystallisation. Glass samples were ultraviolet exposed and heat treated. Nanocrystalls NaF were forming within UV-exposed area during the process of photo-thermo-induced crystallization. Ultraviolet exposure and heat treatment properties were varying depending on the aim of the experiment.

Samples were placed in 3N aqueous hydrofluoric acid based solution. During the measurement temperature and hydrodynamic were constant. Constant conditions were provided by magnetic churn with warm up and were controlled by mercury thermometer. The step heights between unexposed and exposed areas were measured using electronic micrometer. Sensitivity of the measurements was in the range of 1 μm.

3. RESULT AND DISCUSSION

The first set of samples were exposed to ultraviolet radiation with various durations. With increasing duration of ultraviolet exposure increases the number of nucleation centers. It leads to number of nanocrystals growth. Heat treatment was held within 10 hours at 489 °C. The dependence of etched layer thickness of glassceramics with various ultraviolet exposure duration on etching time in hydrofluoric acid based solution is shown in Fig. 1.

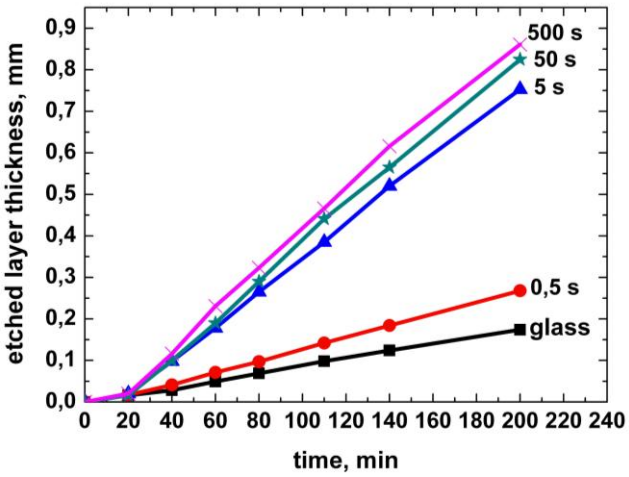

Fig. 1 – The dependence of etched layer thickness on etching time. Glassceramics with various ultraviolet exposure durations. 3N concentration. T = °C

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According to obtained curves, chemical etching rate rises with the increase of ultraviolet exposure duration and therefore the increase of nucleation centers number.

The second set of samples were exposed to ultraviolet radiation within 50 seconds each. Heat treatment temperature was 489 °C. Heat treatment durations were 3h, 5h, 10h and 20h. With increasing duration of heat treatment increases NaF-AgBr size. The dependence of etched layer thickness of samples with various heat treatment duration on etching time in HF solution is shown in Fig. 2.

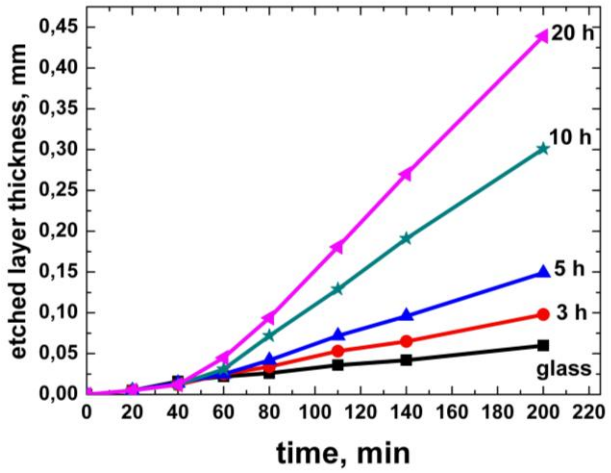

Fig. 2 – The dependence of etched layer thickness on etching time. Glassceramics with various heat treatment durations. 3N concentration. T = °C

The experiment showed that chemical etching rate increases with nanocrystall size growth.

The third set of samples were exposed to ultraviolet radiation as well within 50 seconds each. Heat treatment was held within 10 hours. With increasing temperature of heat treatment also increase nanocrystalls sizes. The dependence of etched layer thickness of samples with various heat treatment temperatures on etching time in HF solution is shown in Fig. 3.

The curves in Fig. 3 show the etching rate rising with increase of heat treatment temperature around 507 °C and following decreasing around 540 °C. The relationship between chemical etching rate and temperature of heat treatment is nonlinear.

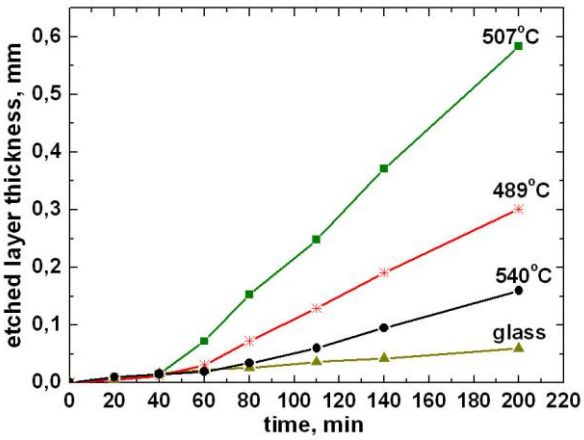

Fig. 3 – The dependence of etched layer thickness on etching time. Glassceramics with various heat treatment temperatures. 3N concentration. T = °C

4. CONCLUSIONS

The dependence or chemical etching rate on characteristics of photo-thermo-induced crystallization process has been investigated for the first time. It has been shown that number and sizes of nanocrystals influence on chemical resistance of the material.

According to the results of work, it was concluded that this materials are suitable for making elements and devices using the combination of chemical etching technology and photo-thermo-induced crystallization process.

AKNOWLEDGEMENTS

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