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PHYSICAL PROPERTIES OF ORGANOSILICATE POROUS GLASSES

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Abstract A novel material consisting of porous glass framework with carbon impregnations was fabricated and its physical properties were examined. This material can be considered as a specific organosilicate compound with the organic phase on the walls of voids in the rigid silica matrix. Incorporation of different carbon quantities results in the shift of the optical absorption edge. Local heating by illumination with power light sources leads to the increase of carbon - incorporating material transparency. The produced organosilicate solids can thus act as effective registration media.

INTRODUCTION

Organosilicate compounds are widely used in electronics and applied optics. These substances are generally obtained in amorphous or crystalline phases in the form of bulk materials or thin films. In this paper we propose a new compound fabricated on the basis of silica porous glasses. The walls of voids in these glasses are covered with amorphous carbon.

Porous glasses filled with different substances have been already examined in a number of papers. Their rigid sponge-like framework can be filled, particularly, with light sensitive materials to form high quality bulk photosensitive media. In the paper [1] it was proposed to cover the walls of porous glasses with photoresist and to use this material for hologram recording. The exposed photoresist acts as a mask in the etching process. The density of etched porous glass changes in regions previously subjected to illumination. Thus resulting in the effective change of the refractive index. The process of filling the porous glass with fine-grained photoresist is rather

difficult. The following many-stage chemical treatment is also rather complicated. In the present work we show that carbon can be used instead of the photoresist to avoid these difficulties. The obtained porous glass with carbon inclusions was also found to have specific optical properties. Optical filters with varying optical absorption edge were fabricated using porous glass specimens with different carbon content.

EXPERIMENTAL

Porous glasses employed in our experiments were fabricated according to the technology described in the earlier papers [2,3]. Sodium borosilicate glasses of a special content were etched in acid solutions. Phase separation initially existed in the studied glasses and was enhanced by thermal treatments at 660 ^{o}C. The phases had different chemical properties. After the etching process the mass of the studied samples descended below a value of 32%. The remainder of glass consisted of almost pure silicon dioxide. The rigid framework of porous samples retained geometrical dimensions of initial solid glass wafers. The thickness of our specimens was in the range from 0.5 to 2 mm. For purposes of diffraction gratings fabrication a thin (20 μm) layer of porous glass was formed on the surface of initial glass wafers. An infinitive percolation cluster formed by voids existed in the investigated samples. Porous glasses could be filled with water solutions to incorporate the molecules of necessary substances into the volume of almost all the voids. The dimensions of cavities were calculated from absorption-desorption isotherms according to Roberts [3] theory and from electron microscope photographs of porous glass splits. Typical dimensions are in the range from 2 to 10 nm, while large voids (compared in size with the wavelength of the visible light) occupy less than 20% of the whole volume of cavities. Filling with carbon was performed in the following way. Porous glass wafers were placed in sugar or glucose solutions with various concentration of organic compound. Extra solution was filtered away from the surface, the sample were dried and annealed at 200-220 ^{o}C for a few minutes. This resulted in the decomposition of the organic substance. Investigations of splits indicate that for high concentrations of

sugar solutions almost all the voids are filled with carbon, which is spreaded uniformly in the porous glass. It should be noted that carbon-containing wafers were much more strong than initial porous glasses. The absence of crystalline carbon inclusions was confirmed by standard X-ray difractometric investigations.

Optical absorption spectra were taken in the range from 200 to 1200 nm with the help of SF-46 spectrophotometer. The investigated wafers were filled with glyceryne which acted as immersion in case when not all the voids were filled with carbon. They were placed between two silica plates during optical absorption measurements.

To measure electrical properties conducting contacts were fabricated on both sides of the wafer with the help of special copper-containing conductive paste.

Heat treatments of obtained materials were performed by power visible light ($1.5 \cdot 10^2$ J/cm^2), by Quant-15 technological Nd-glass laser and in the furnaces at temperatures 700-750 °C.

To fabricate diffraction gratings only 20 μm thick layers of porous media filled with carbon were obtained on the surface of initial sodium-borosilicate glasses as it is shown in Fig.1. A nickel mask was put in contact with the porous organosilicate glass to copy the grating by power light illumination.

RESULTS AND DISCUSSION

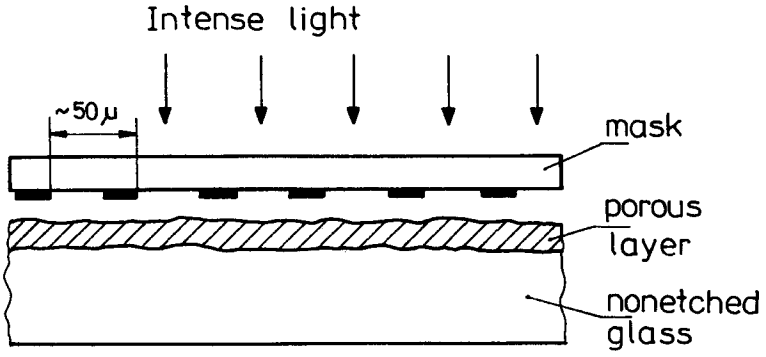

FIGURE 1 Fabrication of diffraction grating

The transmission spectra of the initial porous glass and porous glass wafers filled with carbon are shown in Fig.2. The high energy threshold depends upon the content of carbon in fabricated specimens. The data of Fig.2 correspond to organosilicate glasses obtained by the decomposition of glucose. 4%, 8%, 15% and 40% glucose solutions were used. It is evident that the increase of glucose concentration leads

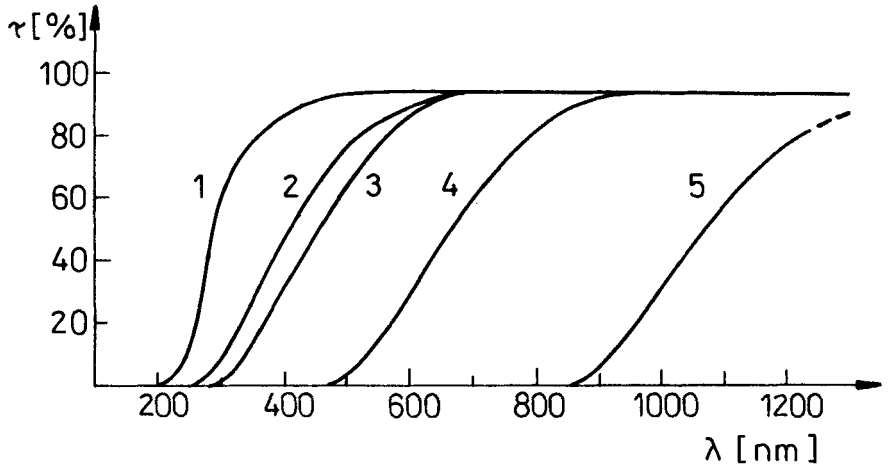

FIGURE 2 Transmission spectra of porous glasses with carbon. The density of carbon : 1-0, 2-$5\cdot10^{-3}$, 3-10^{-2}, 4-$2\cdot10^{-2}$, 5-$6\cdot10^{-2}$ (g/cm^3).

to the shift of the absorption edge to the long-wave region. The increase of optical density is not consistent with Buger-Beer low [4]. The optical density is not proportional to the concentration of carbon, which is true for equal absorbing particles in the transparent matrix. We argue that this is a result of filling large voids with the increase of glucose solution concentration. In this case the shift of the absorption edge can originate from the change of absorbing particles characteristic frequencies as it follows from Mie theory [5]. This explanation is in an agreement with the results of dc conductivity measurements. Up to glucose concentrations of about 40%-50% leakage currents between the electrodes on both sides of investigated wafers were very small (<10^{-12} A for the applied voltage 300V). A threshold like increase of conductivity was observed for

wafers fabricated in concentrated glucose solutions. This means that carbon does not cover the surfaces of all voids with a uniform layer. Small voids are filled first while the size of occupied voids increases.

Annealing of C-containing wafers at temperatures exceeding 700 ^{o}C in the air resulted in the oxidation of amorphous carbon. The annealed specimens restored their initial transparency. The same effect was observed when annealing was performed locally. This could be done by a focused power light beam (concentrated sun irradiation was used in our experiments as well as an infrared power laser). When this annealing was done through a mask as it is shown in Fig.1, the remainder of carbon acted as the lines of the diffraction gratings. It should be noted that carbon layers on the walls of voids are a good mask for chemical etching. Thus the mentioned above gradient-index glasses which are able to store optical information can be fabricate by etching in HF, particularly.

CONCLUSION

We have shown that porous glasses filled with amorphous carbon can be used as recording media and varying absorption edge optical filters. To make fabricated optical elements more precise efforts must be concentrated on the creation of highly uniform initial porous glasses with small size voids only and on the regimes of amorphous carbon fabrication.

REFERENCES

1. V. I. Sukhanov et.al. in Optical holography with registration in three-dimensional media, edited by Yu.N.Denisjuk (Nauka, Leningrad, 1989), pp 86-105 (in Russian).
2. K. Marczuk et.al, Proceedings SPIE, Int.Congress on Optics, Haque, 1991, in press.
3. S. Greg and K. Sing, in Absorption, Specific Surface, Porosity, (Mir, Moskwa, 1984), p. 310 (in Russian).
4. D. V. Sivukhin, in Optics (Nauka, Moskwa, 1985) p. 550 (in Russian)
5. P. Rouard and A. Meessen, in Progress in Optics, edited by E. Wolf (North-Holland Publishing Company, Amsterdam, New York, Oxford, 1977), vol.XV, p. 126.