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## Production of porous films of silicate glass using a plasma focus setup

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Abstract. The aim of the work was to obtain and study films of porous silicate glass. The proposed method for producing porous films is based on the rapid cooling of the melt on the surface of a glass plate after exposure to short pulses of argon plasma generated on an electrodischarge installation of plasma focus type. Silicate glass films obtained by such method have the properties of both porous glasses and foam glass. The specific volume density of these films is ~ 0.4 g/cm<sup>3</sup>, their porosity and hygroscopicity correspondingly ~ 0.3 and ~ 30%

#### 1. Introduction

Currently, porous silicate glasses (PS) are used in chemistry as sorbents and molecular sieves, in chromatography and biology, quantum microelectronics, etc. [1-6]. Porous glasses are obtained from alkaline borosilicate glass by treatment with acid solutions [7-9]. With a high content of silicon dioxide  $(SiO_2)$  of the order of 50% or more, which is necessary for the formation of the PS frame, the removal of  $B_2O_3$  and  $Na_2O$  leads to the formation of pores with sizes of ~ 0.01 – 10  $\mu$ . However, the presence of various chemical elements in alkaline borosilicate glass breaks the continuity of the  $SiO_2$ grid and leads to the formation of crystallites with sizes  $\sim 1-2$  nm. The formation of crystallites leads to distortion of the uniform structure of the PS. The thickness of the PS obtained by this method is limited to  $\sim 0.2$  mm. At the same time, for optical microelectronics and in a number of other applications, it is desirable to have a PS of smaller thickness. In addition, the production of PS only from alkaline borosilicate glass greatly restricts the application scope of PS.

The aim of the work was to obtain thin porous films on the surface of ordinary silicate glass when exposed to the high-intensity plasma jets at the Plasma focus installation.

#### 2. Experimental technique

The source of the plasma jets was a Plasma Focus installation PF-4 at Lebedev Physical Institute (LPI) [10]. The stored energy in the electrical capacity of 48  $\mu$ F was ~3.6 kJ. The plasma – forming gas was argon (Ar) at a pressure of ~1 Torr in the discharge chamber. The duration of the plasma pulse was  $\leq$ 100 ns. The density of the energy flow on the surface of the plates was ~  $10^7 - 10^8$  W/cm<sup>2</sup> and it was adjusted by moving the sample holder relative to the installation anode. Glass plates were irradiated with plasma jets at a temperature of 300 K. Glass plates measuring ~  $35 \times 35$  mm and 3 – 4 mm thick were cut from ordinary silicate glasses ( $Na_2CaSi_6O_{14}$ ) of standard chemical composition [11]. Three glass plates were attached to the sample holder (Figure 1), which was inserted into the discharge chamber of the unit on a rod.

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Figure 1. Device for plasma irradiation of silicate glass plates on the PF-4 installation:  $1 - \operatorname{rod}$ ;  $2 - \operatorname{r$ sample holder; 3 - glass plate; 4 - copper cathode; 5 - copper anode.

Silicate glass films with a thickness of  $\sim 40 - 80 \,\mu$  and a size of  $\sim 5 \times 5 \,\mu$ m were separated from the surface of the plates using a razor blade. The structure of the films was studied using an optical microscope Leica DM ILM (Germany). The microscope allowed to automatically determine the linear dimensions of defects in the structure of films up to ~  $0.3 \mu$ . Optical transmission spectra of films were measured in the wavelength range of  $0.35 - 1.0 \mu$  on a SF-46 spectrophotometer at a temperature of 300 K. The film thickness was measured using an Ambios XP-200 Profiler (USA). The films were weighed using the VLR – 200 analytical balance. When determining пористость of silicate glass films, the methods [12] were used. The specific density of glass films ( $\rho_{\text{film}}$ ) was determined by weight using the formula:

$$\rho_{film} = P_1 \rho / \Delta P \tag{1}$$

where:  $P_1$  is the weight of the dry sample, g;  $\rho = 0.99671 \frac{g}{cm^3}$  – water density at 21.5°C;  $\Delta P = P_2 - P_1$  change in sample weight after wetting in water;  $P_2$  – weight of the wet sample, g. The apparent density of dry plates of porous glasses ( $\rho_d$ ) was calculated using the formula: (2)

 $\rho_d = P_1/V,$ V- volume of the dry sample, cm<sup>3</sup>.

Due to the small weight of individual films, 8 samples with approximately equal surface area  $(\sim 0.2 - 0.3 \text{ cm}^2)$  and thickness  $(\sim 40 - 60 \mu)$  were weighed, then averaging the measurement results, the main characteristics of the films were calculated.

The total porosity of glass films (W) was determined by the weight method using the formula:

$$W = W' / (W' + \frac{1}{\rho_{Si}})$$
(3)

where:  $W' = (P_2 - P_1)/\rho P_1$ ; W'- the value of the inverse specific density, cm<sup>3</sup>/g;  $\rho_{Si} = 2.18$  g/cm<sup>3</sup> the density of the silica frame (SiO<sub>2</sub>).

Moisture absorption ( $\beta$ ) of silicate glass films was calculated using the formula:

$$\beta = \Delta P / P_1 \tag{4}$$

It was found that there are water-soluble chemical compounds in the volume and on the surface of the films. At initial wetting of 8 samples of dry films weighing  $2.14\pm0.05$  mg, the weight of the films after drying at a temperature of ~ 70 °C decreased to 1.55±0.05 mg. During subsequent wetting and drying, the weight of the films did not change. The film characteristics were determined after repeated wetting and drying of the films at a temperature of ~  $60-70^{\circ}$ C for ~2 hours.

#### 3. Experimental result

Figure 2(a) shows a sample of silicate glass irradiated with Ar plasma 5 pulses at a distance of x = 50 mm from the installation anode. It can be seen that small splits of ~ 2–3 mm (light areas) are observed in the center of the plasma exposure area in Figure 2 (1). Glass films are formed on the surface of the plates at a distance of ~ 5 – 8 mm from the center of the plasma impact area, figure 2 (2).



**Figure 2.** (a) – Silicate glass irradiated with Ar plasma with a flux density of ~  $10^7$  W/cm<sup>2</sup>. The number of plasma pulses is 5, the distance from the glass plate to the anode is 50 mm, the thickness of the glass plate is 3 mm. *1* – the area of influence of the most intense part of the plasma flow; 2 – the area of film cleavage on the surface of the glass plate; (b) – a silicate glass film glued to the glass plate.

In this case, the optimal conditions for obtaining glass films on the PF-4 installation are the distances from the glass plate to the anode  $\sim 40 - 80$  mm. In Figure 2(a) it is seen that the films are exfoliated in a ring around the center of the plasma impact area. This characteristic structure is associated with an inhomogeneous distribution of energy in the plasma stream [10]. Figure 3 shows the structure of the surface of the silicate glass film. It can be seen that the film is covered with microcracks and consists of blocks of arbitrary shape, which is associated with rapid melting and cooling of the glass when exposed to an intense plasma jet. When viewed locally, (figure 3(1)) shows clusters of glass and metal droplets on the surface of the film (Figure 3(a)). At the same point (1), gas bubbles up to tens or more microns in size are visible (Figure 3(b)). At higher magnification (Figure 3(b)), clusters of small glass spheres of the order of units of microns in the form of a "flower rosette" are observed at point (1).



Figure 3. Structure of the surface of the silicate glass film: (a)  $-\times 130$ ; (b)  $-\times 300$ ; (c)  $-\times 1000$ .

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Figure 4 shows profilograms of glass films glued with Kontaktonol glue on a glass plate 1.5 mm thick. The thickness of the glass films is ~ 50 and 70  $\mu$ . As can be seen from the profilograms, the glue is almost completely absorbed by the films. The thickness and linear dimensions of the films depend significantly on the energy of the plasma flow and the geometry of the plasma impact area. The effect of the thickness of glass substrates ~3–5 mm on the formation of glass films was not observed.



**Figure 4.** Profilograms of silicate glass films: (a) – thickness  $\sim 50 \mu$ ; (b) – thickness  $\sim 70\mu$ . The peaks in the left part of the drawings refer to a film of silicate glass, in the right part to a drop of dried glue.

Figure 5 shows the transmission spectra of glass films (figure 4 (a), (b)) in the wavelength range of 350 - 1000 nm at a temperature of 300 K. Optical spectra of glass films were adjusted for light absorption and scattering in a thin layer of glue ~  $100 \mu$ .



**Figure 5.** Transmission spectra of films of porous silicate glass: 1 - initial plate of silicate glass with a thickness of 1.5 mm; 2 - film with a thickness of ~50 µ; 3 - film with a thickness of ~70µ; 4 - film of glue ~ 100 µ.

#### 4. Discussion of results

Below are the characteristics of silicate films calculated using the formulas (1-4). The specific density of films is ~ 0.4 g/cm<sup>3</sup>, which is about 2 times higher than for porous and foam glass – 0.1 - 0.25 g/cm<sup>3</sup> [7-9, 13]. The volume porosity of the films is ~ 0.4, which is noticeably less than for foam glass ~ 0.9 [13]. Films have a moisture absorption of ~ 30%, which is significantly more than in foam glass  $\leq 2\%$ . It can be seen that the film properties are closer to foam (sponge) glasses with open pores /13/. Compared to real porous glasses, the films have a volume porosity close to them and a high specific density. However, they have a fairly high transmittance (0.75 - 0.85) in the wavelength range of ~ 350 - 450 nm (Figure 5 (a), (b)), which is close to the transmittance of thin porous glasses (~ 0.9 ) obtained from the NBS [14, 15]. These properties of silicate porous films may be of interest for optical microelectronics [5, 6]. The high hygroscopicity films make it possible to create a miniature optoelectronic instruments for measuring humidity. The advantage of the proposed method is a

comparative prostate and the possibility of obtaining thin porous glass films on any glass, which allows you to expand the scope of application of porous films. The disadvantages of films obtained in this way include their fragility, heterogeneity of the structure and the presence of third-party impurities that come from the anode unit of the installation [16].

#### 5. Conclusion

Porous films of silicate glasses with thickness of ~  $40-80 \mu$  were obtained at the Plasma focus facility (PF-4, LPI). Films of porous silicate glasses have intermediate properties between real porous silicate glasses and the properties of foam glass.

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