

Influence of thin glass films coherence on the Schottky and Rebinder effects in sensors

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Abstract. On the basis of the experimental study common property of three vitreous systems (SiO_2 , alumina borosilicate glass fiber and GeSe_2), which are two- or multilevel group of atoms presence capable of changing their electronic configuration in these systems under the influence of external influences has been established. The change in the structure of film glassy systems is accompanied by changes in the work electron function (Schottky effect). It was found that the strength of alumina borosilicate glass fibers was due to coherent domains that form a kind of surface film "cover". A sharp decrease in the strength of glass fibers from 400 to $\sim 250 \text{ kg/mm}^2$ (Rebinder effect) was established in a water-containing medium and heat treatment.

Physical glass nature is constantly at the center of scientific research attention, not only because of its practical importance, but also because of the fundamental problem importance of the vitreous state properties. Analysis of a large number of theoretical and experimental works [1–2] devoted to the structure and properties of Se, GeSe_2 , SiO_2 , SiSe_2 , AsSe, As_2O_3 , Sb_2O_3 , TiO_2 , GeO_2 , P_2O_5 , BeCl_2 , BeF_2 , ZnCl_2 allowed to create "concept of polymer-polymorphoid glass and glass-forming liquid". The basis of this concept is the provision in the glass-forming liquid existence at least two structural units – polymorphoids: low-temperature (LTPM) and high-temperature (HTPM), capable of transitioning from one polymorphic modification to another ($\text{LTPM} \leftrightarrow \text{HTPM}$) under certain conditions [3]. It can be considered and established that structure glasses is a system of two- (or multilevel) particles capable of transferring from one energy level to another under certain circumstances. It was known [4] that in such systems energy is released in the form of collective spontaneous emission or "super radiation Dicke". The cause of this radiation is the correlation between spatially separated emitters, interacting with each other through the radiation field. Thus, the main feature of the vitreous state can be considered the presence of multilevel molecular groups capable of performing a mutual transition (polymorphic transformation) under certain conditions (temperature, pressure), accompanied by a change in their electronic configuration.

The experimental results during the study of various glassy systems, such as (1) study of changes in the electron work function (EWF) of Si(100) plates in different oxidation states, (2) as well as the study alumina borosilicate glass fibers properties have been obtained during their heat treatment. The EWF values for silicon plate having a thick oxide film are close to the corresponding value for silicate glass, therefore, when discussing the processes occurring in glass fibers, the EWF data obtained for thick SiO_2 films were used. Oxidation of Si(100) plates was carried out thermally by the method



adopted in the electronics industry [5]. The samples were heat treated in a chamber oven (~ 1 h). The study results in the form of the dependencies $\phi = f(t^\circ)$ are shown in figure 1.

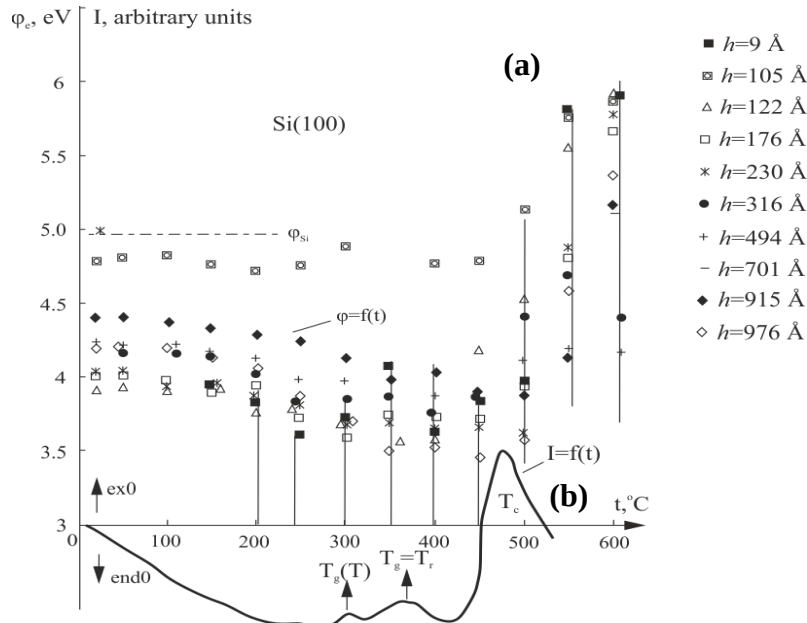


Figure 1. Dependence of the electron work function ϕ of Si(100) plates vs. heat treatment temperature (a), h is the oxide film thickness on Si (100); intensity (I) dependence of differential-scanning calorimetry (DSC) vs. annealing temperature of GeSe₂ (b).

Mechanical properties of industrial alumina borosilicate glass fibers samples (SiO₂ – 53.8; Al₂O₃ – 13.4; CaO – 13.4; B₂O₃ – 10.4; MgO – 4.5; other – 4.5 %) with average tensile strength $\sigma \approx 250$ kg/mm², average diameter of ~ 6.5 μm have been determined by standard techniques under atmospheric conditions at the length of all test samples 10 mm. The loading rate was constant and equal to 0.5 g/s. Density values (ρ_{gf}) were measured in addition to the mechanical properties of glass fibers. The measurement accuracy for ρ_{gf} was ~ 1 –3 %. The results are shown in figure 2.

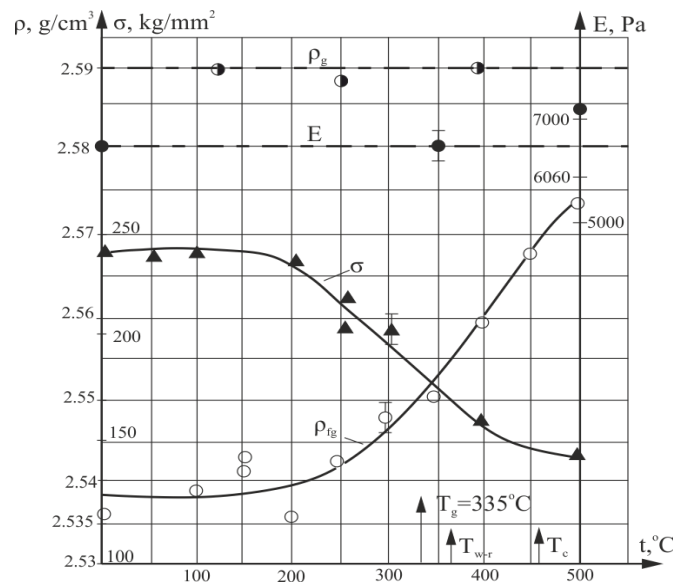


Figure 2. Dependence of tensile strength σ of alumina borosilicate fiber, elastic modulus E , glass fiber density ρ_{gf} and glass density ρ_g vs. annealing temperature t° .

The results of differential scanning calorimetry (DSC) obtained in the study of the structural relaxation of vitreous GeSe₂ in isothermal annealing have been used in this study to assess the energy effect that takes place at the restructuring of glass elements during their heat treatment. These data are shown in figure 1(b). If the change in the glass fiber strength is traced directly after its manufacture and in time, then the glass fiber strength during tension σ has two levels: a) high value closes to the theoretical (~ 400 kg/mm²) for so-called "untouched" fibers, i.e. measured immediately after drawing from a glass vessel with special precautions in the absence of contact with other glass fibers; b) working (industrial) value σ after fabrication (~ 250 kg/mm²), which is usually used for design development. Large difference σ between these levels is associated with non-reinforcing effect of the water-containing medium, which renders an adsorption ("wedging") effect on brittle bodies' strength (Rebinder effect). The mechanism of this phenomenon was investigated in [6]. It was shown, that sharp strength drop from 360 to ~ 200 kg/mm² when literally the first portions of water (relative humidity ρ/ρ_s from 0.001 to 0.03) occurs when precision weighting method has been used for measuring water adsorption on glass fibers (figure 3).

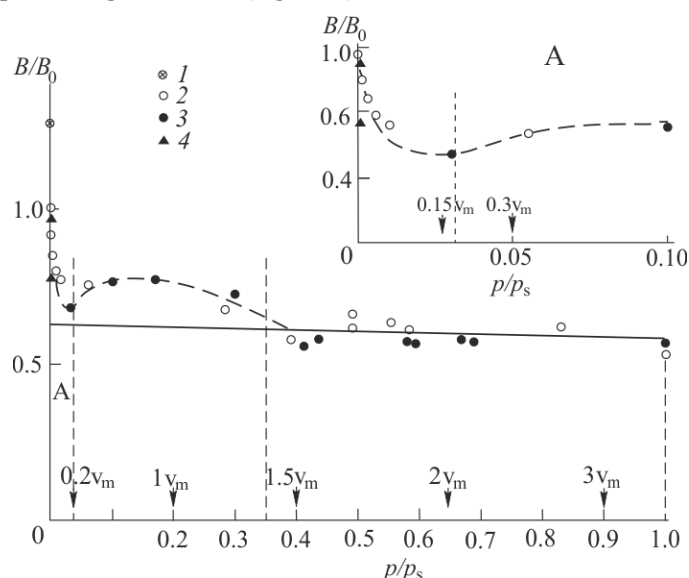


Figure 3. Dependence of the relative tensile strength B/B_0 vs. relative air humidity ρ/ρ_s (v_m – value of H₂O molecules monolayer) [6].

It is interesting to note (figure 1(a)) that the EWF value for oxidized Si(100) plates decreases sharply (~ 1 eV) when measured in atmospheric moist air medium (Schottky effect). The physical mechanism of this effect on Si(100) has also been investigated by authors [7] and explained by the presence in the structure of the sorbed H₂O coherent clusters having a large dipole moment. Sharp strength decrease effect in various materials has been explained in the scientific works of P A Rebinder [8] due to "a decrease in free surface energy, i.e. formation work of new surfaces". Thus, it is natural to assume that this kind of process must be accompanied by noted above a change in the electronic properties of the material. So, it can be concluded that: a) the main glass feature is the presence of two or multi-level groups of atoms in the system capable of changing their electronic configuration under the influence of external influences. The change in the structure of vitreous systems is accompanied by change in the electron work function (Schottky effect); b) during transition from liquid state to the brittle solid state at high cooling rate, which is realized in modern technology for the glass fibers production, structure of the liquid state was fixed, i.e. low-density fraction predominates, so the "untouched" glass fiber has a tensile strength σ close to the theoretical (~ 400 kg/mm²).

In the structure of such fiber, the main role is played by coherent domains, which form a kind of surface polymer "cover". The stay of glass fiber in the water-containing medium leads to a sharp decrease in its strength to ~ 250 kg/mm² (Rebinder effect); c) fiber heat treatment to ~ 500 °C is

accompanied by a further decrease in strength (up to ~ 150 kg/mm²) and increase in density (by 3.7 %). Main property changes were occurred in the range from 250 to 400 °C (to the crystallization temperature ~ 460 °C). Electron work function growth (by ~ 2.0 eV) has been observed in the same range of annealing temperatures, which indicates the destruction of coherent domains in the glass structure.

Acknowledgements

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