Negative Surface Tension as a Formation Factor of Nanoscale Porous Structures

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The surface tension plays the major role in systems with the developed surface. Most clearly its influence is shown, when the surface is formed by mobile phases - in emulsions and foams. However at solid phases it plays a considerable role, and its contribution to the general energy balance cannot be neglected. Chemisorption and formation of a double electric layer result in downturn of a surface tension. Management of a surface tension value is widely used at chemical and electrochemical reactions.

However chemical and electrochemical abnormal systems are known. At such systems the specific surface is extremely increased and the value of a surface tension should play a determining role. While dissolution of solids rather regular nanoscale porous structures are formed. It is possible to note porous aluminum oxide, porous nickel, but most clearly the effect is shown in case of porous silicon formation by anodizing in a fluoric acid solution, since base material is a practically perfect monocrystal.

The extremely large surface of porous silicon has allowed carry out measurements of mechanical strain in it and reveal convertible change of the strain sign due chemisorption on the surface (fig. 1) [1]. As mechanical strain in porous structure are connected to a surface tension, it is possible to calculate, that chemisorpted surface of silicon is characterized by σ = -0,104 N/m, and in electrolyte due to formation of a double electric layer, it will be even more negative.

On fig. 2 the schematic image of pore and specific (per dissolved volume) change of surface energy for pore's spreading and lengthening is shown. For negative σ the lengthening is more favorable, the cylindrical wall may be in thermodynamic balance and the hemispherical bottom is nonequilibrium and to be dissolved [2]. Calculated deviation from equilibrium potential at the bottom is given on fig. 3 and is rather significant for electrochemical process. Such approach allows explaining the directed growth and stability of porous structure.

For calculation of the size and density of pores in structures on p-and n-type silicon, the system of kinetic and transport equations was solved, the satisfactory consent with experimental data is received. The opportunity of a negative surface tension is discussed for formation of emulsions, porous oxides and metals.

1. Sugiyama H., Nittono O. /Journal of Crystal Growth.- 1990.- Vol. 103.-P.156
2. La Monica S., Jaguiro P., Ferrari A. / Proc. Electrochem. Soc. – 1997. – Vol. PV 97-7 P.140

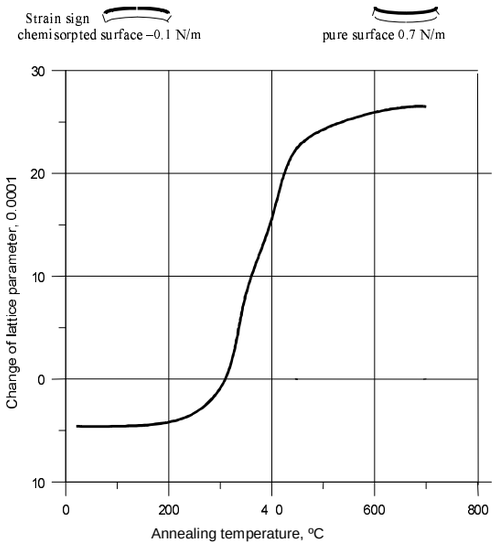
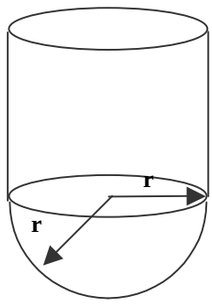


Fig.1



spreading $dS \cdot \sigma/dV = \sigma/r$

lengthening $dS \cdot \sigma/dV = 2\sigma/r$

Fig. 2

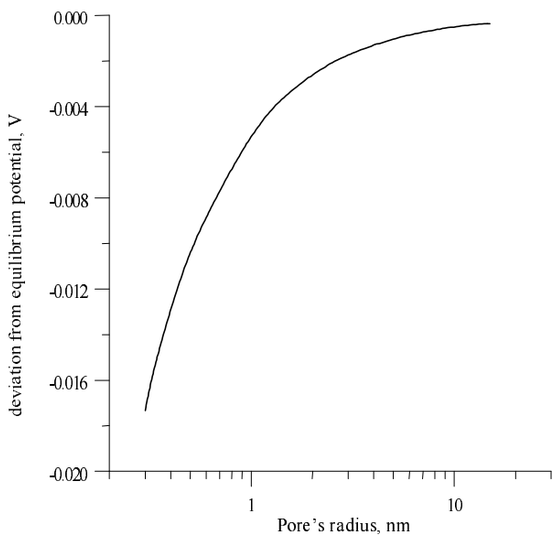


Fig. 3