

AFM and XPS investigations of silica films manufactured by sol-gel method and ion sputtering

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Thin silicate films are of major importance in computer and communication engineering. The features of film microstructures will considerably affect service characteristics of such devices. Therefore, essential is the question of correlation between microstructure and film preparation technique. The films investigated here have been prepared by means of widely known ion sputtering and sol-gel techniques.

Non-doped silicate films were prepared by cathode sputtering of silicone in oxygen in vacuum chamber (residual vacuum was 10^{-6} Pa). To obtain double and multicomponent silicate films layers of partial oxides of corresponding elements were applied onto a substrate. Simultaneously or after that they were subjected to homogenization at the temperature less than 500°C . In sol-gel technique silicate films were prepared from tetraethoxysilane. The films obtained were deposited onto a substrate of polished silicon monocrystal and subjected to thermal treatment at $t=450^{\circ}\text{C}$ in nitrogen.

Surface morphology has been investigated by means of atomic force microscopy using a microscope Solver P-47 adjusted to semi-contact mode and probes from the NT MDT company. X-ray photoelectron spectroscopy was used to study chemical structure using a modernized spectrometer ES-2401. Experimental [1,2] correlations between chemical shifts of spectral lines in O1s- and Si2p-spectra and interatomic distances and bonding angles in Si-O-Si in silicates were taken as a base for X-ray electron analysis of chemical structure of silicate films.

Non-doped silicate films. In conditions of ion sputtering the films formed from nearly spherical primary nuclei (islands), which were uniformly distributed across the surface (Fig.1). The islands coalesced and after the thickness of 1000\AA had been reached they formed a continuous film (Fig.2). As the film thickness grows from 500 to 1000\AA , the number of islands increases (from ~ 100 to ~ 600 on the area of $1\times 1\mu\text{m}$) with decrease of their radii and heights as well as their size range. Such a change in topography is characteristic for an evaporation-condensation process dominant during the film growth. The silicon-oxygen film structure depends on the thickness of the deposited film: the thinner is the film the larger is the fraction of anions with large Si-O-Si angles. This is an evidence of the film density growth.

The thickness of a sol-gel film was no more than 100\AA . The surface topography of sol-gel manufactured films is essentially different from that of the films obtained by ion sputtering (Fig.3). The sol-gel film is formed from spherical structures with narrow size range: $300\text{-}500\text{\AA}$ in diameter and $\sim 10\text{\AA}$ high. Structures with this diameter appear on the surfaces of the deposited films when much larger thicknesses are reached. The films with similar thicknesses, but prepared by different techniques, have identical chemical structures.

Multicomponent lead-silicate films. Multicomponent lead-silicate films were prepared by depositing silicon oxides and metal oxides onto a substrate in proportion of 40 mol.%PbO + 60 mol.% SiO₂ and 64%SiO₂ +16,8%PbO+ 4,3%BaO+ 11%Na₂O+ 3,2%Al₂O₃. The film topographies change with thickness in the same manner as in non-doped silicate films, i.e. the process of evaporation-condensation dominates.

According to the phase contrast mode investigation the two-component films consist of only one phase (Fig.4). The surface layer of multicomponent lead-silicate films is inhomogeneous in phase composition, with spherical structures corresponding to different phases (Fig.5). Single-phase structure of double lead-silicate films is determined by high

glass-forming potential of a PbO-SiO₂ system in a wide concentration range of lead oxide. Since Na₂O – SiO₂ and BaO-SiO₂ systems tend to immiscibility, no complete interaction of sputtered oxides occurs in the multicomponent films under study.

According to XPS-analysis the film compositions differ throughout the thickness: surface layers are poor in lead, barium and sodium and rich in aluminum. Earlier, in the process of investigating surface layers of massive lead-silicate glasses we found thermostimulated changes in surface layer composition of multicomponent silicate glasses to follow the direction of liquidus curve minima on quasibinary phase diagrams for SiO₂ – metal oxide [3,4]. The thermostimulated diffusion processes in multicomponent silicate films obey the same laws. Another reason for the low PbO content in the film surface layers is high vapor pressure of this oxide: in the process of heating its major part volatilizes. As a result cells appear on the film surface, with the sizes comparable with those of the islands.

The X-ray electron analysis of the Pb4f-spectra have demonstrated the lead chemical state in double lead-silicate films to be similar to that in massive glasses, namely, modifier ($E_b=139$ eV) and netformer ($E_b=138.2$ eV) [3]. The ratio of lead atoms in the netformer and modifier is close to the ratio in massive low-lead glasses; namely, ~ 25:75 [4]. In contrast to the non-doped silicate films, no large changes in silicon-oxygen structure are observed with film thickness variations in the double lead-silicate films. The intensity ratio of Si2p-spectrum components that correspond to the silicon-oxygen structures of different sizes (102,4 eV, 103,2 eV, 104,1 eV) are close to the ratio which is observed in the case of the non-doped film ~200 Å thick and massive low-lead glass. In all probability, the silicon-oxygen structure forms at the initial stages of film growth when lead oxides interact with silicon. After lead oxide escapes from the film, slight structural changes are observed.

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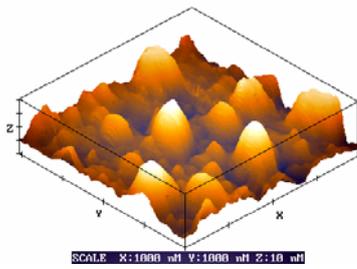


Fig.1 3D-image of non-doped sputtered silica films with the thickness of 500 Å, $S_q = 7,6$ nm

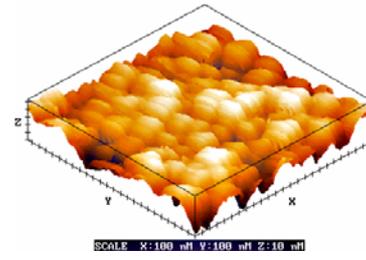


Fig.2 3D-image of non-doped sputtered silica films with the thickness of 1000 Å, $S_q = 6,2$ nm

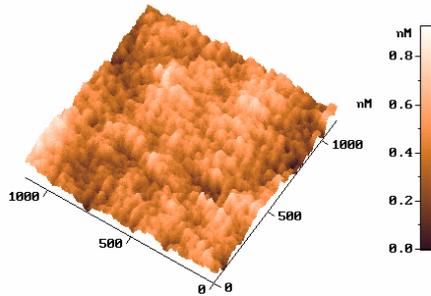


Fig.3 3D-image of non-doped sol-gel silica films with the thickness of 100 Å, $S_q = 0,5$ nm

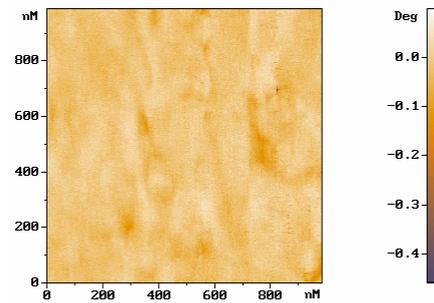
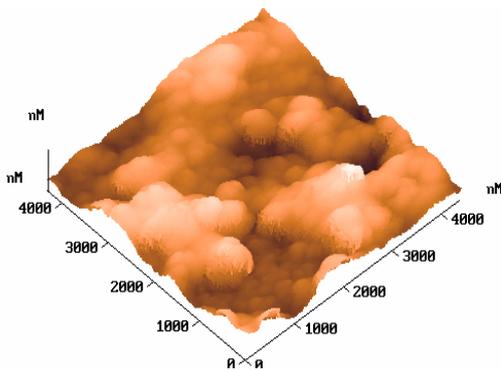


Fig.4 3D-image and lateral force image of binary lead-silicate films with the thickness of 200 Å.

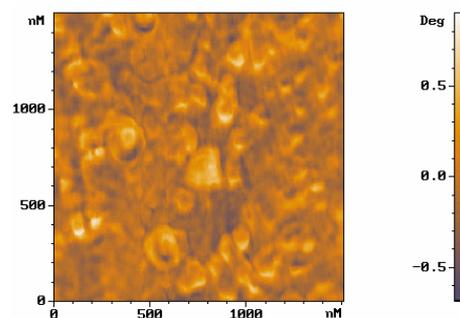
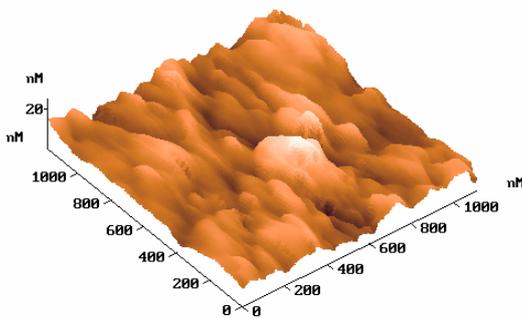


Fig.5 3D-image and lateral force image of multicomponent lead-silicate films with the thickness of 500 Å.