AFM investigation of Pt-doped spin-on glass thin silica films

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Introduction

Tetraethoxysilane solution based films are used in semiconductor technology as sources for diffusing dopants into silicium. They are also used as catalyst coatings in thin film gas sensors. The catalyst film working characteristics are determined by their structure, general porosity, pore size, distribution through thickness and the chemical state of dopants.

Experimental results and discussion

The paper presented studies the surface layers and internal structure of spin-on glass films deposited on a silicium single-crystal. The films were obtained by sol-gel method from tetraethoxysilane (TEOS) doped by platinum salt. For comparison, dopant-free films were investigated. The films were applied by spinning, followed by heating for 15 min at 450^0C in nitrogen or air.

Atomic force microscope P47-Solver (NT MDT) was used to study the film surface in a semi-contact mode in air. Topography and phase contrasts were selected.

Changes in composition, silico-oxygen structure, and the chemical state of platinum were studied by X-ray photoelectron spectroscopy (XPS). The spectra were taken on a modernized spectrometer ES-2401 using nonmonochromatized MgK_{α}-excitation. Depth profiling was performed using ion gun (Ar^+, 900 eV). The pressure in a preparation chamber and an energy analyzer chamber was $5{\cdot}10^{-9}$ torr and $5{\cdot}10^{-9}$ torr, respectively.

Fig. 1 demonstrates the AFM-image (topography) of a dopant-free film annealed in nitrogen atmosphere.

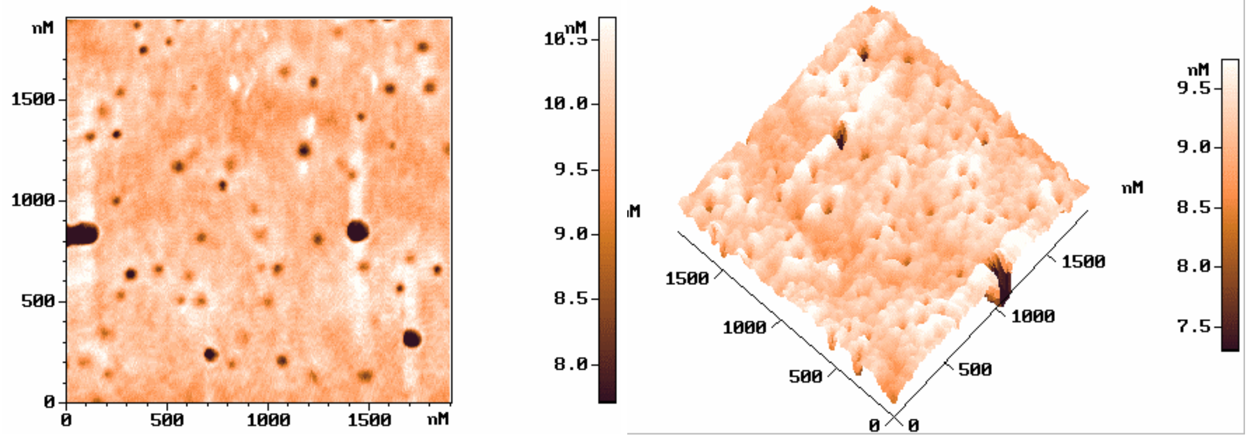

Fig.1. AFM-image of dopant-free spin-on-glass thin silica film.

Typical features of film surfaces doped with Pt and heated in nitrogen atmosphere are shown on Fig.2(a-d). It is seen that inclusions with typical sizes 500x500 nm are formed in the film. The phase-contrast imaging showed that these inclusions differed from the matrix in their characteristics, hence, represented part of some other phase. According to a three-dimensional inclusion image given on Fig. 1c, they have a fine substructure. A wide scan image of a film surface area (Fig.2d) evidences the uniform distribution of the inclusions across the surface. However, the apparently directed orientation of inclusions is observed, which can testify their formation in an already rather anisotropic matrix along elasto-soft directions. It should be mentioned that the film surfaces heated in nitrogen are very unstable, capable of enduring only three-four scans taken from the same area. Such a behavior is indicative of the incomplete tetraethoxysilane polycondensation, i.e. the uncompleted process of a glass-like matrix formation. The XPS data confirm this suggestion: degree of binding in the silicon-oxygen structure of the film surface layer is ~18% (the degree of binding was defined as the number of oxygen bridge atoms in Si-O-Si bonds relative to the total number of oxygen). Taking into account XPS data, one can deduce that the AFM-observed inclusions represent platinum compounds with different oxidation states, including a non-oxidized state (Pt^0, Pt^{2+}, Pt^{4+}).

Heating in air results in quite differently shaped inclusions (Fig.3 (a-d)) with typical sizes of 150x50 nm. The inclusions join into conglomerates of 4-5 particles with a clearly directed orientation. According to the XPS-data the inclusions are Pt^0, Pt^{2+} and Pt^{4+}-compounds. Heat treatment in air gives rise to the formation of a strength surface which endure a large number of scans. The probable reason is TEOS after-oxidation by the air oxygen, which results in more complete process of SiO_2 formation. The degree of binding in a matrix here (according to the XPS-data) is ~36%. However, a higher strength (higher degree of binding) is characteristic only for the outer film surface ~8 nm in thickness. The internal film structures, formed both in nitrogen and in air, are equal in structure. Thus, the variation in the heating environment only results in the variation of the film outer layer.

It should be mentioned, that in films, heated in nitrogen, the surface layers are three times richer in platinum in comparison with the bulk, while in films, heated in air, a uniform distribution of platinum through thickness is observed.

Conclusion

A combined investigation of the surface and internal structure of "spin-on glass" thin silica films, doped with platinum as a catalyst, has been performed by means of AFM and XPS. The conclusions are as follows:

1. Platinum doping of the nitrogen-annealed films results in the decrease of degree of binding of the film silico-oxygen structure. The degree of binding is defined as the relative number of oxygen bridge atoms in Si-O-Si bonds.

2. Heating atmosphere influences the mechanical strength of the doped film surfaces, sizes and shape of the inclusions, as well as degree of binding of the silico-oxygen structures, uniform thickness distribution of platinum inclusions.

3. The observed directed distribution of Pt-containing inclusions across the film surface implies structural anisotropy, which can result in the anisotropy of physico-chemical characteristics.

4. No correlation between the chemical state of platinum and the heating atmosphere has been found. Platinum was always present as Pt^0, Pt^{2+}, Pt^{4+}.

The AFM-investigations were performed using the equipment of The Centre of the Joint Usage of the Physical-Technical Institute UrBr RAS (Research Centre for the investigation of the surface and nanosized systems).

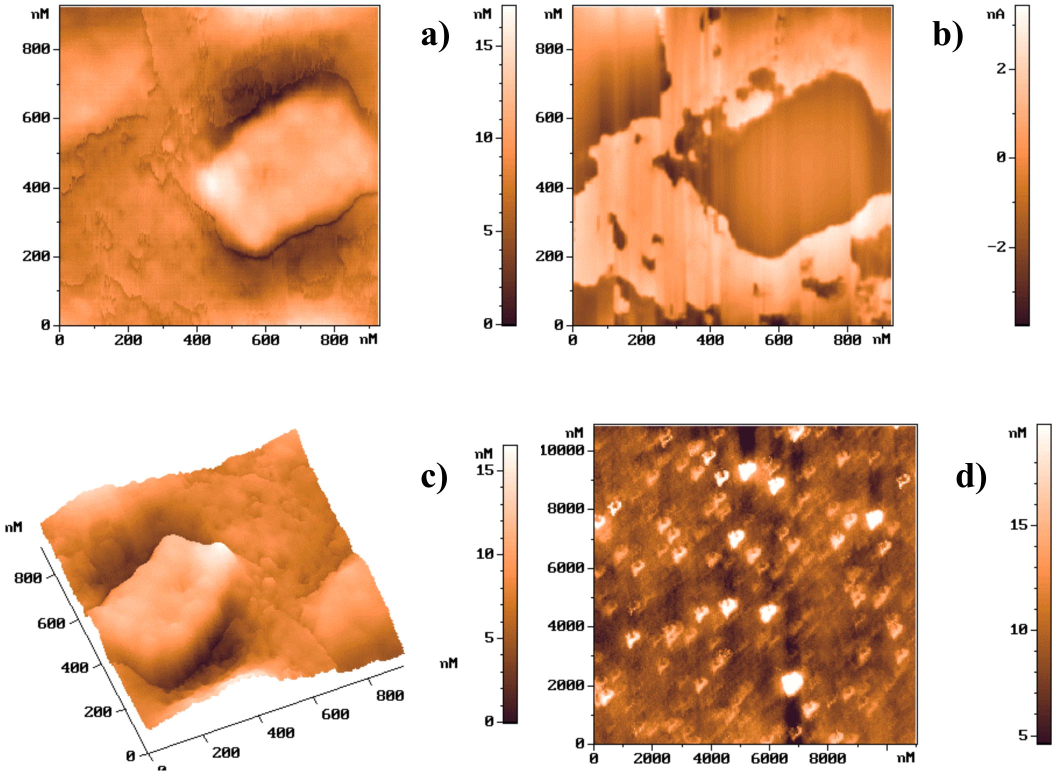

Fig.2. Surface of the film doped with Pt and heated in nitrogen atmosphere: a), c), d) – topography, b) – phase contrast.

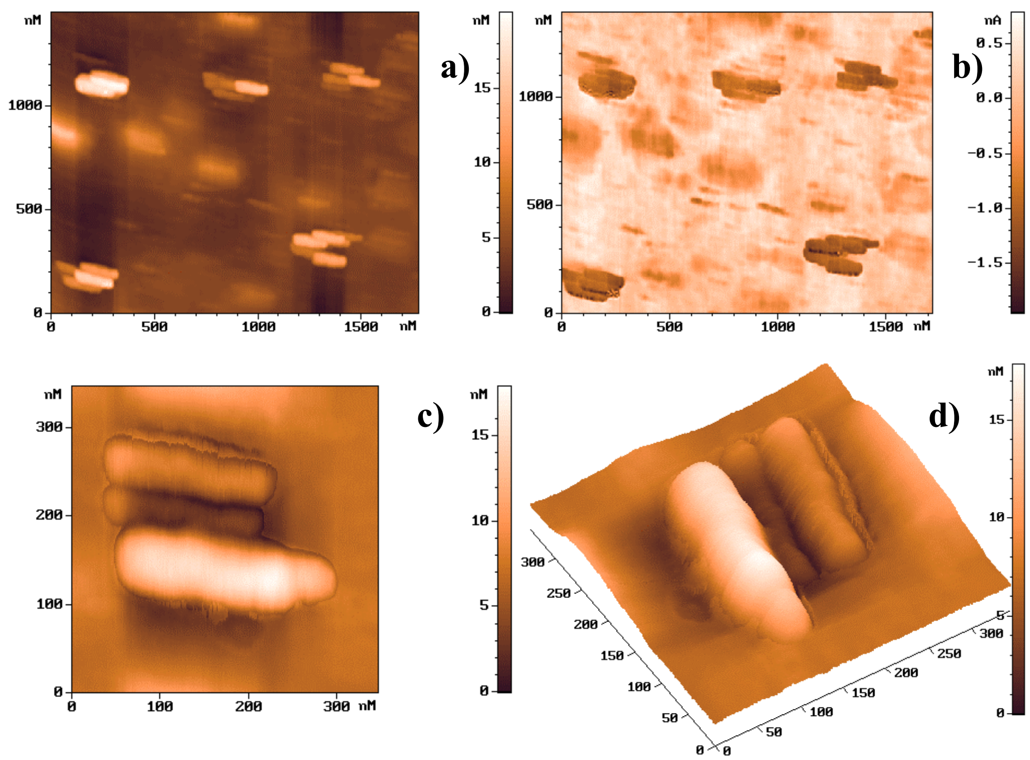

Fig.3. Surface of the film doped with Pt and heated in air: a), c), d) – topography, b) – phase contrast.