Nanocomposites and nanomaterials

Nano-porous thin film VN_x hydrogen absorbents: method of production, structure formation mechanism and properties

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The present work is devoted to the study of structural and absorptive characteristics of nanocrystalline porous VN_x films produced with the help of ion-stimulated deposition technology, when vanadium film formation takes place at the simultaneous bombardment by nitrogen ions with the energy of 30 keV. Such ion bombardment exerts an influence on the structure and component composition of the film both at the stage of its nucleation and at the stage of its growth (50-60 nm). By adjusting the process parameters (the ion beam density, the gas pressure, and the substrate temperature) it is possible to generate not only the nanocrystalline structure, but also to ensure that the bulk of the film can accumulate more nitrogen than it is necessary for the nitride phase formation. In such a case, the excess gas molecules will condense at the grain boundaries forming a system of gas-filled intergranular pores preventing the grain boundaries thickening. Such pores combined by grain boundaries form an open porous structure that can be used for the storage of large amounts of hydrogen after its thermal activation.

In order to investigate the influence of the implanted nitrogen concentration on the structure of pores, the films of the thickness from 5 to 25 nm was obtained. Their structure was studied by means of transmission electron microscope JEM 100CX. Also the films of thickness of 1.5 µm were deposited on sapphire substrates. The structure of these films was investigated with the help of the scanning electron microscope JSM 7001F. Additionally, electrophysical properties, absorption and desorption of hydrogen were studied on these samples.

Electron microscopy investigation of the initial stage showed that VNx films have three types of the hydrogen traps, namely, the relatively large interparticle pores, the grain boundaries and intergrain nano-pores, and, finally, the vacant sites in nano-grains. The configuration of intermediate intergrain pores in our film structures is not just a system of pores that directly traverse each other (it is a feature of metal-organic and carbon film structures). The pores in the present case are interconnected by relatively long (~ 10 nm) intermediate intergrain boundaries, whose width does not exceed 1 nm. The availability of such branched pore system connected by narrow and long channels provides the fast delivery of molecular hydrogen to the film volume and its retention at the room temperature.

During hydrogen desorption at the temperature interval 30-130°C the hydrogen releases from large interparticle pores. Therefore, the amount of released hydrogen in this temperature range does not exceed 2 wt.%. The freed volume is filled with hydrogen from grains and intergrain pores. Then at 130-180ºC, a complete hydrogen release from the grain boundaries and pores takes place. So, finally, at 180-275°C, the hydrogen is released from these vacant positions associated into molecules and is desorbed from the interparticle pores. It is the removal of hydrogen from intergrain and interparticle pores that leads to a catastrophic increase of the resistance. And it is in this temperature range a major amount of hydrogen (5 wt.%) is released.