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Formation of Pores in Thin Germanium Films under Implantation by Ge^+ Ions

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Abstract—Results are presented of a study of the morphology of germanium films nanostructured by ion implantation. Film samples were grown by magnetron sputtering in an ultrahigh-vacuum installation and then irradiated with 40 keV Ge^+ ions at fluences in the range of $(1.8–8) \times 10^{16}$ ions/cm^2. Scanning electron microscopy demonstrated that vacancy complexes with diameters of ~50–150 nm are gradually formed in the bulk of implanted germanium with increasing implantation fluence. After a certain implantation fluence is reached, the complexes emerge on the surface, thereby forming a developed surface profile of the irradiated films.

Keywords: nanostructured germanium, ion implantation, lithium-ion batteries.

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Recently, the possibility of using various highly dispersed systems (porous silicon, germanium) as anode materials for lithium-ion batteries (LIBs) has been extensively studied worldwide [1, 2]. Although germanium is more expensive than silicon, it has a substantially higher intrinsic electronic conductivity, as well as a high diffusion coefficient of lithium ions (at room temperature, the diffusion coefficient of a lithium ion in germanium is approximately two orders of magnitude higher than that in silicon). Fast transport of both electrons and Li ions will provide a higher charging/discharge rate of LIBs [3]. Several studies have already been reported in the literature aimed at developing germanium nanostructured electrodes [4–6]. For example, nanoporous germanium (*np*-Ge) was first obtained in [5] by the chemical method, which enabled mass production of electrodes for LIBs. The nanoporous structure was stable against volume changes in the course of lithiation/delithiation and enabled fast charge/discharge processes. At the same time, ion implantation, as a productive and comparatively inexpensive method for modification of the surface properties of various materials [7–9], is widely used in microelectronics and serves to improve the surface-strength properties of various metallic articles. A porous layer appears in the near-surface layer of germanium in implantation of a wide variety of heavy ions with energy in the range from several to hundreds of keV at a threshold implantation fluence of 10^{16} ions/cm^2 [7]. In the present Letter, it is suggested to study a new material for LIB anodes, porous nanostructured films of amorphous germanium (α-Ge) produced by implantation of 40-keV Ge^+ ions into amorphous germanium, and examine how the morphology of the near-surface layer of the resulting films depends on the implantation fluence in the range of $(1.8–8) \times 10^{16}$ ions/cm^2.

Starting α-Ge films with the thicknesses of ~600 nm were produced by magnetron sputtering of a germanium target (purity 99.95%, GIRMET LLC, Russia) in an ultra-high-vacuum setup (SPECS/BESTEC, Germany) at room temperature in an argon atmosphere. Single-crystal (012) Al_2O_3 sapphire plates served as substrates. The substrates were cleaned in several stages: first, ultrasonically with chemical solvents, and, in the final stage, in a vacuum chamber (immediately before the sputtering) by the ion milling method. The base pressure in the magnetron chamber did not exceed 5×10^{-9} mbar, and the working argon pressure was 6×10^{-3} mbar. The magnetron sputtering power was 50 W. The germanium deposition rate was 8.33 nm/min, as indicated by a quartz thickness gauge. The film thickness was measured with a BRUKER Dektak XT stylus nanoprofilometer.