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Influence of the Substrate Temperature on the Size Distribution and Phase Composition of Ablated HfO_2 Nanoparticles

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The influence of the substrate temperature on the formation of high-temperature phases of hafnium dioxide in the process of pulsed laser ablation is investigated. It is established that the HfO_2 nanoparticles of the high-temperature tetragonal and cubic phases with a quantitative content up to 50 % are formed on the surface of the substrate at room temperature during the laser ablation with intensity of 10^{10} W/m^2. It is shown that with increasing the substrate temperature the average size of the ablated nanoparticles decreases and the quantitative content of the high-temperature phases is increased up to 70 %.

Keywords: Laser ablation, Nanoparticles, Hafnium dioxide, High-temperature phase.

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In the recent decade, the study of hafnium dioxide has become advanced, which is due to the distinctive properties of the given material. Hafnium dioxide features the high melting heat, good strength, heat isolation, optical and dielectric properties that keep within a wide temperature range. This fact ensures its application in a number of areas – from powder metallurgy to space and atomic technology [1].

It is known that pure hafnium dioxide is a polymorphic material, i.e. may exists in a low-temperature (LT) monoclinic phase (< 1700 °C) and high-temperature (HT) tetragonal (1700-2700 °C) and cube (> 2700 °C) phases. At present, widely used stabilization method of high-temperature phases under normal conditions presents doping of pure material with impurities of oxides of Mg, Ca, etc. [2]. However, in some cases the use of stabilizing impurity additives impairs the material properties, namely, reduces the melting temperature, enhances heat conductivity and at high temperatures causes appearance of ionic conductivity. We have shown [3] that one can stabilize, with laser ablation, HT phases of hafnium dioxide under normal conditions without introducing additional impurities. The given method makes it possible to form metastable phases of polymorphic materials owing to the rapid material cooling from melted state in the ablation process [4]. The stabilization of HT phases in this case may be reached at the expense of development of thermo-elastic stresses in surface layers of nanoparticles that are enriched with structural defects [5-7]. In doing so, the temperature of the substance at which ablation particles deposit may heavily influence on both qualitative and quantitative composition of HT phases [8]. The present work is devoted to the examination of such regularities.

Ablation of hafnium dioxide was done on the solid-body pulsed laser YAG : Nd^{3+} laser QUANTUM-15. The laser intensity was 10^{10} W/m^2, pulse duration reached 4 ms, repetition rate from 1 to 25 Hz. As a target for ablation, a fused chemically pure powder HfO_2 was used.

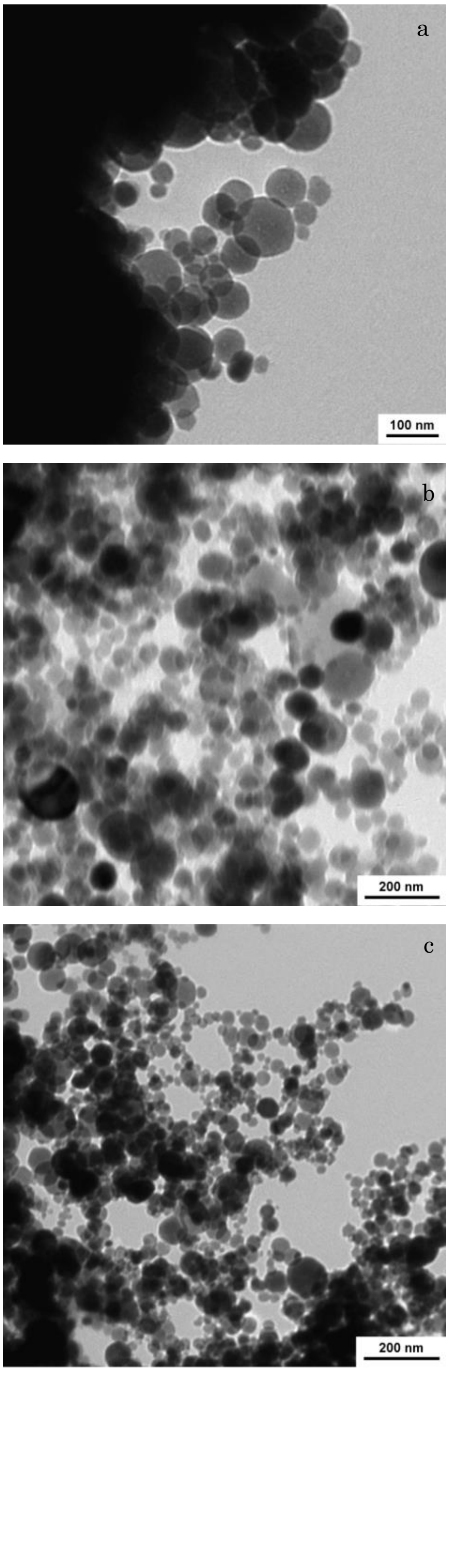
The effect of a pulsed laser radiation caused ablation of hafnium dioxide at which ablated HfO_2 particles deposited onto the substances of the single crystal silicon. The substance heating was implemented with a special instrument that was mounted to the heating element of a soldering device and kept the substance. The temperature control of the substance surface was done with a thermocouple. Depending on the voltage on the soldering device, the substance temperature may be set in the range from 25 to 200 ºC.

Preliminary cooling of substances was done with an instrument that kept the substance and which was fastened to the heat conductor of a tank for the liquid nitrogen. To prevent the formation of water condensate from the atmosphere, a cooled substance was blown on with a continuous flow of inert gas – argon. Within 5 min the substance temperature was set to – 100 ºC and kept stable for the desired period of time. When the desired temperature was set, ablated particles deposited onto the substance.

Morphology and the particle sizes of HfO_2 were studied with atomic-force microscope NTEGRE Prima and AIST-NT Smart. Granulometric investigations were conducted both in a hand mode and with the help of a program packet Gwyddion to atomic-force microscope Aist-NT Smart. The structure and phase composition of HfO_2 nanoparticles were studied in transmission electron microscope ZEISS Libra-120 (accelerating voltage 120 kV) which featured a HAADF detector and an energy Ω- filter. Calibration of electronograms in the microdiffraction mode was done with a test sample for the transmission microscopy on the basis of a polycrystalline Au film. Qualitative and quantitative phase composition were also determined with X-ray diffractometer DRON-7M. The chemical structure was examined by the Raman light scattering with microspectrometer OmegaScope^{tm} (AIST NT, Zelenograd, Russia) that was integrated with scanning probe and confocal microscopes.

Investigations by atomic-force and electron microscopy have revealed that laser ablation of hafnium dioxide occurs as spherical particles the size of 10 to 200 nm. In this case, the substance temperature had a significant effect on the granulometric composition of the deposited particles. Fig. 1 and 2 show transmission electron images and granulometric composition of ablated nanoparticles deposited onto substances at a temperature of: a) – 100 ºC; b) 25 ºC; c) 100 ºC; d) 200 ºC.

Research has revealed that with substance temperature decreasing the average size of deposited particles increases; in this case, the broadening of their granulometric distribution is observed. The most considerable broadening of size distribution is observed at low temperatures of order – 100 ºC. This can be explained by the appearance of a water film at the surface of a cooled



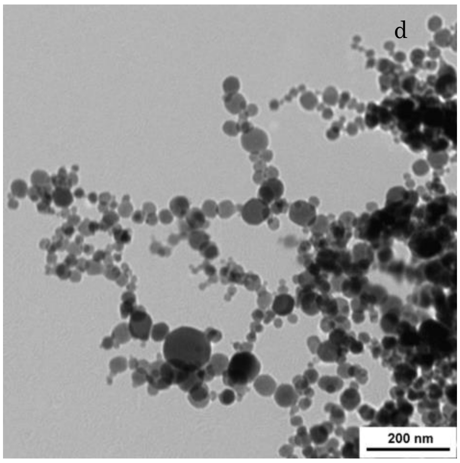
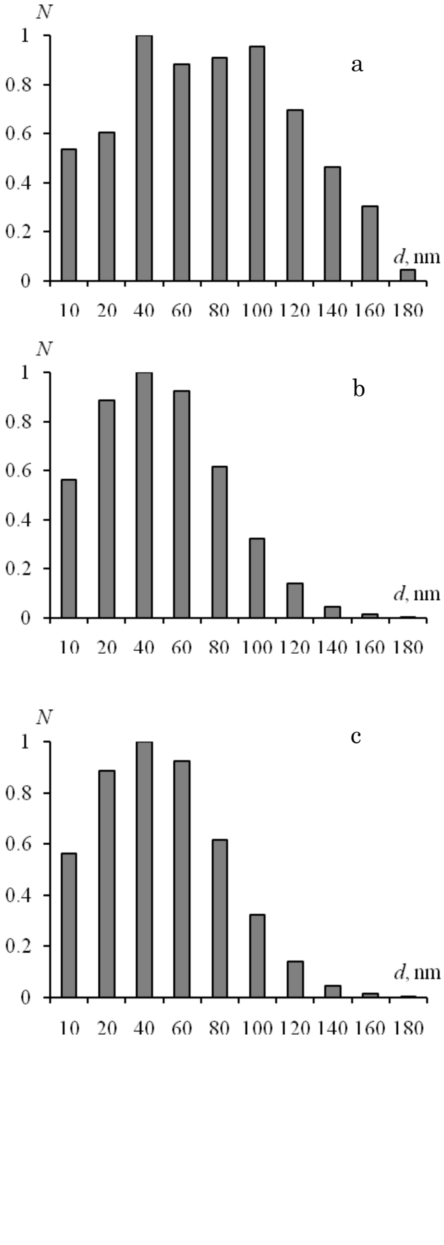


Fig. 1 – Transmission electron images of HfO_2 nanoparticles deposited onto substances at a temperature of: a) – 100 ºC; b) 25 ºC; c) 100 ºC; d) 200 ºC

substance in air, which significantly increases the extent of deposition of both small and big particles.

When the substance is heated, the water film is evaporated and large particles, owing to their high kinetic energies, for the most part elastically repel from the substance surface without being deposited.



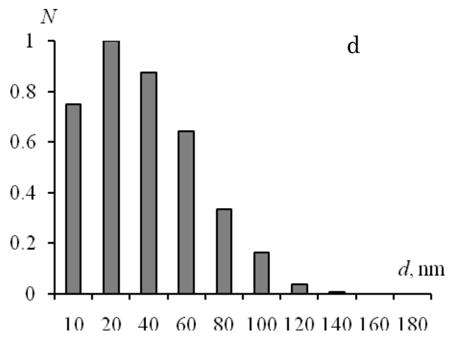


Fig. 2 – Granulometric composition of HfO_2 particles deposited onto substances at a temperature of: a) – 100 ºC; b) 25 ºC; c) 100 ºC; d) 200 ºC.

Research by the XRPA technique has revealed that the phase composition of ablated particles is also dependent on the substance temperature. In Fig. 3 provided are X-ray diffractograms of HfO_2 nanoparticles deposited onto substances at temperatures: a(– 100 ºC; b) 25 ºC; c) 200 ºC. It is seen that the diffractograms of the particles deposited onto cool substance attest to virtually a low-temperature phase of HfO_2.The diagrams at the deposition onto substances at room and high temperature indicate both low-temperature and high- temperature phases. In doing so, if the number of high-temperature phases in nanoparticles deposited onto a substance at 25 ºC reaches 50 %, then for particles deposited at 200 ºC that number amounts to 70 %.

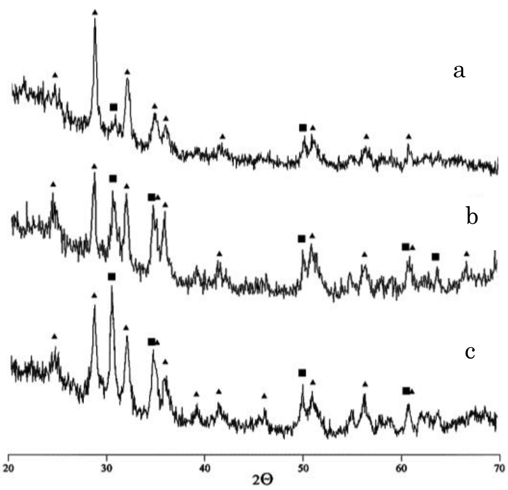


Fig. 3 – X-ray diffractograms of HfO_2 nanoparticles deposited onto substances at temperatures: a) – 100 ºC; b) 25 ºC; c) 200 ºC. ▲ – low-temperature monoclinic phase of HfO_2; ■ – high-temperature tetragonal and cubic phases of HfO_2

The results obtained can be explained by granulometric data as well. At low substance temperatures, particles with an average size of 75 nm are deposited with a wide size range (Fig. 2a). In those particles, low-temperature monoclinic phase is kept. At high temperatures, for the most part small particles are deposited with an average size of 35-45 nm, in which stabilization of high-temperature phases is possible due to surface structural defects.

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