Technical Physics Letters, 2022, Vol. 48, No. 13

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Metal-stimulated decomposition of sapphire surface in flux electrons with an energy of 70 keV

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Received May 4, 2021
revised July 6, 2021
accepted July 6, 2021

Abstract: Metal-stimulated decomposition of sapphire surface at room temperature in a flux of electrons with energy of 70 keV. The stimulant used is an ensemble of crystalline islands of gold. It was first established that the presence of an ensemble of gold islands on the surface of sapphire significantly reduces substrate temperature and electron energy at which decomposition occurs surfaces. Etching pits form near gold islands and have an elongated shape with the following dimensions: length up to 1.2 μm, width up to 0.8 μm and average depth 20 nm. Maximum area the base of the islands increases from 0.6 to 1.8 μm^2.

Keywords: sapphire, gold, metal-stimulated decomposition, electron flux.

DOI: 10.21883/TPL.2022.13.53365.18858

The radiation decomposition of sapphire surface has been attracting much attention of researchers for a long time due to the use of sapphire in various structural elements in reactors, accelerators, spaceships, etc. [1]. In particular, high-purity sapphire surfaces are used in the elements of X-ray optics, as substrates for multilayer mirrors, in windows and monochromators operating in X-ray conditions, as well as in outer space [2]. In this regard, the most important factor is radiation resistance of sapphire. It is known [3–7], that as a result of radiation exposure not only structural defects, but also aluminum precipitates are formed on the sapphire surface. Thus, the practical application requires selection of conditions to minimize the probability of precipitates formation. In all cases [3–6] the sample was in vacuum $10^{-5}-10^{-8}$ Pa, however, the parameters of its exposure to radiation varied: the accelerating voltage of the electronic beam varied within a range of $100-200$ kV, the exposure varied within a range of $10^{23}-10^{27}\,e\cdot\mathrm{cm}^{-2}$, the exposure time varied within a range of $120-3600$ s, the sample temperature varied from room temperature to 1130 K. According to these data, with an increase in the temperature of the electron-bombed sapphire sample the probability of aluminum precipitates formation increases [3,6]. At the same time, it is difficult to establish a correlation between the radiation resistance of the irradiated sapphire surface and the electron energy based on this data.

Sapphire is also used in nanotechnology, including for substrates of microelectronic components, which can be operated in the conditions of radiation exposure [7]. Thus, the effect of radiation on the sapphire surface with some components on it needs to be studied. It is known that gold is widely used in the manufacturing of integrated circuits [8]. Previously we have studied the processes of gold deposition on the (0001) sapphire surface [9].

This work was focused on studying the effect of gold island coating on the processes of sapphire surface decomposition under the exposure to electron irradiation, in particular, in the conditions of vacuum. In general, the decomposition of high-purity dielectric surface in vacuum ($\sim 10^{-2}-10^{-4}$ Pa) under the exposure to electron flux can be slowed down significantly by the electric field, associated with its charging [10]. On the contrary, the presence of gold islands should accelerate the decomposition process of the sapphire surface because the islands can serve as effective centers of charge drain.

The samples were (0001)-oriented sapphire substrates with chemical-mechanical polishing on one side. Then Au layers with a thickness of about 100 nm were formed on a cold sapphire substrates using vacuum-evaporation technique (VN-2000 apparatus). After that, the substrates with metallized surface were annealed in the air (Naber tube furnace) for 2 h at 700°C to achieve guaranteed formation of discrete Au islands on the sapphire surface. No vacuum annealing was used because partial desorption of gold is possible at these temperatures. Such a discrete structure of islands on the substrate surface is optimal for studying and analyzing the possible processes of islands evolution and sapphire surface decomposition under exposure to electron irradiation based on microscopic (topographic) data. Microscopic studying of the sample surfaces were carried out using Ntegra Aura atomic force microscope (NT-MDT). To identify the effects of sapphire surface decomposition, accelerated electrons were applied (with an electron flux density of $10^{21}\,\mathrm{cm}^{-2}\cdot\mathrm{s}^{-1}$, an accelerating voltage of 70 kV). The experiments were carried out using EMR-100 electronograph with a pressure of $\sim 10^{-4}$ Pa. The incident angle of the electron beam was 45°. A focused beam with a spot diameter of 0.5 mm was used.

The gold deposition obtained by vapor deposition in vacuum on the surface of (0001) sapphire at a room temperature of the substrate, did not show any preferred orientation. Subsequent annealing in the atmospheric conditions at 800°C led to the formation of the island structure of gold film on the sapphire (Fig. 1).

In case of exposure of the sapphire surface with crystalline Au islands to a focused electron beam with an accelerating voltage of 70 kV at a room temperature, an interesting result was found: etch pits appear on the sapphire surface in the neighboring area of the gold islands (Fig. 2). Fig. 2, *b* shows a typical profile of the etch pit. The etch pits have an elongated shape with the following dimensions: length up to 1.2 μm, width up to 0.8 μm and average depth 20 nm. At the same time, in the area neighboring the islands with a height of less than 30 nm (Fig. 2, *a*, island *1*), no etch pits were found. For an island with a height of 67 nm an etch pit is visible (Fig. 2, *a*, island *2*). The fact of the sapphire surface etching in the process of treatment by electrons is also confirmed by the investigation in the mode of mismatch signal of the atomic force microscopy (Fig. 3, *a*). A contrast image of the area covered by the electron flux can be observed. In general, a crater is formed in the process of the sapphire surface irradiation (insert in Fig. 3, *a*).

As to micromorphology, the etch pits are generally of elongated geometry. Only near individual particles the pits have a widened shape: width $\sim 1\,\mu$m, length ~ 600 nm. It follows from Fig. 2, *a* and the topographic section of the surface near the crater (insert in Fig. 3, *a*) that the wide pits are formed near flat islands, while the elongated pits are formed near domed islands of gold. The etch pits are formed on the side of the incident electron beam. However, the central axis of the pits does not lie in the plane of incidence, but forms an acute angle with it (insert in Fig. 2, *a*). Probably the highest intensity of the etching process takes place along one of main directions, such as $[1\bar{1}00]$ or $[11\bar{2}0]$, in the basal plane of the sapphire.

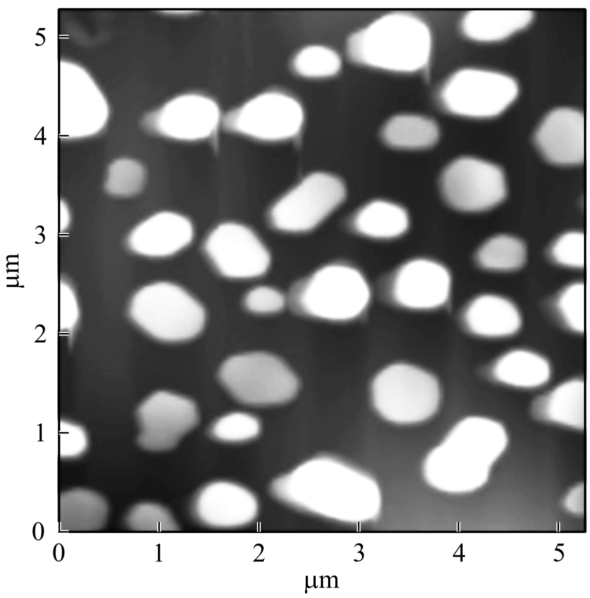

Figure 1. Topography of the sapphire surface with crystalline gold islands.

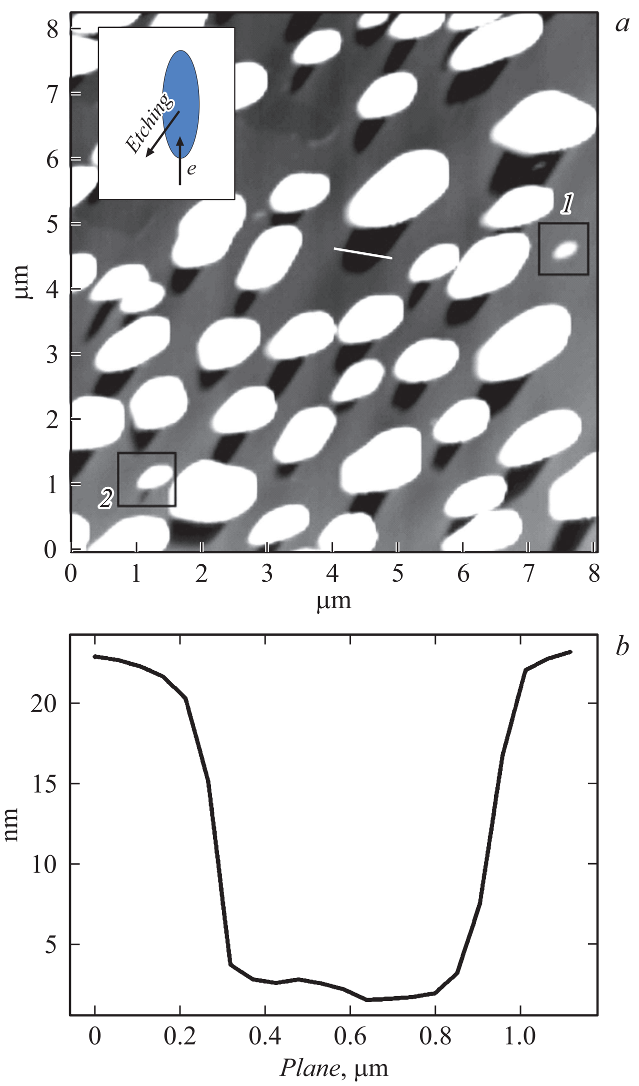

Figure 2. *a* — topography of the sapphire surface with crystalline gold islands after treatment in electron flux *1* — island with a height of 30 nm, *2* — island with a height of 67 nm. In the insert — scheme of etching, *e* — direction of the electron flux. *b* — profile of the etch pit along the direction shown with a light line in *a*.

The formation of etch pits in the sapphire is accompanied by an increase in size of the gold islands. It is confirmed by bar graphs of gold islands distribution by their base area before and after the exposure to electron flux (Fig. 3, *b, c*). Maximum base area of the islands increases in this case from 0.6 to 1.8 μm^2.

The observed decomposition of the sapphire surface under the exposure to electron irradiation occurs as a result of the following reaction:

$$2Al_2O_3(solid) \rightarrow 4Al(solid) + 3O_2(gas).$$

The electron irradiation results in intense charging of the sapphire surface with islands of gold on it. The islands serve as effective centers of charge drain and accumulation and create electric fields that weaken the interatomic bonds in the near-surface layers of the sapphire. Most likely, a forced displacement of atoms is observed, which just continue to increase when bombed with electrons and, naturally, leads to a nonequilibrium state when oxygen atoms (or ions) are desorbed, and atoms of aluminum in Al_2O_3 change to the metal state of aluminum. The growth of islands is accounted for by the diffusion of positively charged aluminum atoms to negatively charged gold islands.

However, this is not the only possible approach, explaining the experimentally observed decomposition of the sapphire. It can also be assumed that a thermally activated motion of atoms takes place in the near-surface sapphire layer as a result of local heating under the exposure to the electron beam. Calculations according to [11] show that the local heating of the sapphire surface in the conditions of our experiment can hardly lead to thermal desorption of oxygen and further decomposition of the sapphire. Also, one can consider the factor of direct electron-stimulated desorption of atoms as a result of collision with an incident electron and transfer of kinetic energy ΔE from it. The estimate based on the collision theory shows that when bombing the sapphire surface with electrons having an energy of 70 keV and incidenting at an angle of 45°, the kinetic energies ΔE transferred to oxygen and aluminum atoms are ~ 5 and 3 eV, respectively. In this case the energies required to displace atoms of aluminum and oxygen from the crystal lattice are ~ 18 and 75 eV [12], which, of course, are significantly higher. It seems to us that under the conditions of experiment the most likely is the process of radiolytic decomposition of sapphire [13], which is based on the effect of Auger decay [14]. More specifically, the radiolysis process can be represented as follows: as a result of external electron impact a hole is formed in the internal electron shell of the Al($2p$) aluminum ion. Then one valence electron in the O($2p$) of O^{2-} anion jumps into this hole with emission of additional anionic valence electrons of oxygen. As a result, the O^{2-} anion changes its charge state and is displaced from the Al_2O_3 lattice.

Thus, in this work a metal-stimulated decomposition of the sapphire surface at a room temperature under the exposure to electron beam with an energy of 70 keV was studied. An ensemble of crystalline gold islands was used as the stimulant. It was established that the presence of an ensemble of gold islands on the sapphire surface greatly reduces temperature and energy of electrons at which the surface decomposition occurs. The obtained results seem to be very important in the study of radiation and chemical resistance of sapphire crystals.

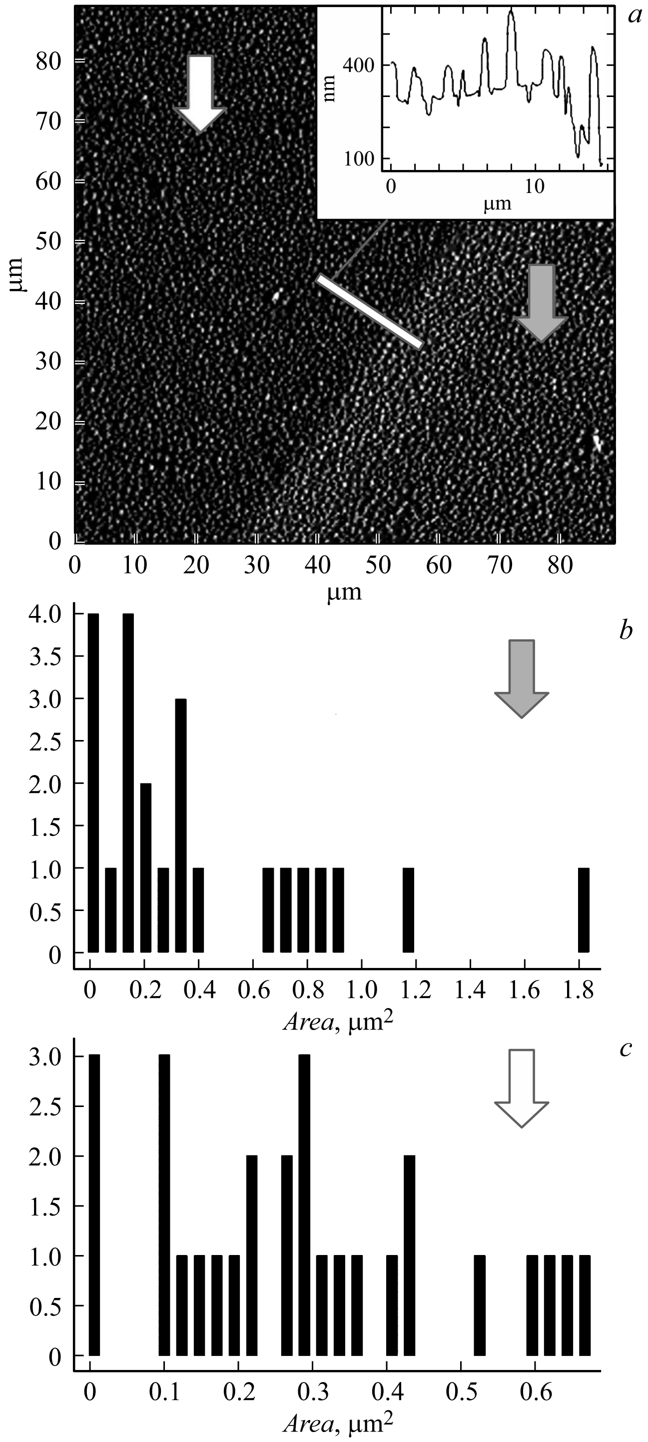

Figure 3. *a* — topography of the sapphire surface with crystalline gold islands after treatment in electron flux (the investigation in the mode of mismatch signal of the atomic force microscopy). In insert — topographic section of the relief. *b, c* — bar graphs of gold islands distribution by base areas of gold island. Light arrow — area not irradiated by electrons; dark arrow — area irradiated by electrons.

Funding

The research was carried out within the scope of works under the state assignment of FSRC „Crystallography and Photonics“ of RAS, as well as with support from the Federal Research Center "Crystallography and Photonics", Russian Academy of Sciences (grant project No. 20-21-00068 Rosatom).

Conflict of interest

The authors declare that they have no conflict of interest.

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