Investigation of the deposition of calcium fluoride nanoparticles on the chips of CaF$_2$ single crystals

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Abstract

The deposition of calcium fluoride nanoparticles on single crystal chips of calcium fluoride was studied. CaF$_2$ nanoparticles were synthesized by co-precipitation from aqueous nitrate solutions using hydrofluoric acid as a fluorinating agent at a batch system. The prepared samples were examined by atomic force microscopy, scanning electron microscopy, transmission electron microscopy and optical transmission. There is an inhomogeneous coating of the substrate surface with submicron particles of about 100–150 nm in size, which are clusters of nanoparticles of 15-20 nm in size. The initial nanoparticles coherently grow on the surface of the crystal substrate. Heat treatment of the substrate-deposited layer composite at 600 °C leads to the coalescence of submicron particles and the formation of a porous layer of a complex structure.

Keywords: Fluorite, Single crystals, Nanoparticles, Co-precipitation, Mechanism of oriented attachment growth

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1. Introduction

In recent years, a paradigm change (correction) has taken place in the science of crystal growth: the totality of experimental data reliably indicates that in many cases the growth of crystals in laboratories, in industry, in nature, including in living organisms, is not carried out by attaching of atoms or ions from the environmental medium to the surface of a growing crystal, it proceeds by the oriented attachment of nano-, micro-, or volumetric particles [1–3]. Research on nonclassical crystal growth by the oriented attachment of particles is a “hot topic” of modern materials science [4–14].

One of the main scenarios for nonclassical growth consists of the oriented attachment of small crystalline particles to the surface of a large crystal [15]. The consideration of the possibility of creating surface crystalline layers on a single-crystal substrate in this way is promising.

The aim of this study was the investigation of the deposition of calcium fluoride nanoparticles on chips of calcium fluoride single crystals. The design of experiments was similar to the classic experiment of Shaskolskaya and Shubnikov in 1933 [2, 16] (deposition of small alum crystals on the face of a large alum crystal) with a change in the crystallized substance (calcium fluoride is practically insoluble in water, unlike alum) and particle scale.

2. Experimental

High-purity fluorite single crystals (Hellma, Germany) were split by cleavage by a specially designed manual guillotine [17]. The chip orientation [111] corresponded to the exit of the third-order symmetry axis. The thickness of the plates was about 2 mm. Atomic force microscopy showed that the surface is atomically smooth and contains steps (Fig. 1).

CaF$_2$ nanoparticles were synthesized by coprecipitation from aqueous solutions [18] in the batch system. The main parts of the synthesis system were: a polypropylene reactor, a magnetic stirrer, and feed dispensers for initial substances. Hydrofluoric acid was used as a fluorinating agent. Calcium nitrate Ca(NO$_3$)$_2$·4H$_2$O (LANHIT, Russia, 99.99 wt. %), neodymium nitrate Nd(NO$_3$)$_3$·6H$_2$O (LANHIT, Russia, 99.99 wt. %), hydrofluoric acid (extra pure grade 27-5) were used as initial substances. Precipitation at room temperature was carried out by the dropwise addition of a calcium nitrate solution ($C_{Ca} = 0.5$ M) into a solution of hydrofluoric acid ($C_f = 5$ M) with vigorous stirring with a magnetic stirrer. The colloidal solution was formed as a result of a chemical reaction. The precipitate formed from colloidal solution and then was washed with bidistilled water.

The high specific electrical conductivity of colloidal solutions, which is $\sim 3$ mS/cm, makes it impossible to experimentally determine their zeta potentials.

A single crystal plate of calcium fluoride was placed horizontally and completely immersed in a colloidal solution (mother solution or wash water with a precipitated reaction product). The plates were placed in the solution one by one: for 1 hour directly during the synthesis process, for a day after the end of precipitation, for 14 days after twice washing the precipitate from the mother solution with bidistilled water. Washes were carried out until the diphenylamine reaction to nitrate ions was negative.

Fig. 1. AFM images of sample No. 1 (a) – precipitation, 1 hour, No. 4 (b, c) – precipitation from the mother solution, exposure for 1 day. A step in the chip is visible on the substrate surface.
The obtained samples were investigated by atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and optical transmission.

Surface relief of CaF$_2$ single crystal with deposited nanoparticles was studied using AFM. Measurements were carried out using a scanning probe microscope Ntegra Prima (NT-MDT Spectrum Instruments, Russia) in tapping mode. The silicon cantilevers used (Tipsnano, Estonia) are characterised by the following parameters: resonant frequency $f \sim 37$ kHz, tip radius $R \sim 10$ nm and stiffness constant $k \sim 0.65$ N/m. All experiments on the study of the surface of the samples were carried out under the controlled conditions of the TRACKPORE ROOM-05 measuring complex (class 5 ISO (100), humidity 40 rel. % ± 1% and temperature 24 ± 0.05 °C).

For scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), a Carl Zeiss NVision 40 electron microscope (Zeiss, Germany) was used in a high vacuum mode at an accelerating voltage of 20 kV ($\text{LaB}_6$ cathode). Images were formed with a backscattered electron detector (BSE) and a secondary electron detector (SE).

For structural studies, a high-resolution JEM 2100 transmission electron microscope (JEOL, Japan) was used. The JEM 2100 microscope has a spatial resolution of 2.3 Å (point-to-point) and 1.4 Å (lines), a maximum accelerating voltage of 200 kV. The $\text{LaB}_6$ cathode was used as a source of electrons. When obtaining a high-resolution image, an objective lens diaphragm with the diameter of 40 μm was used, which allowed passing a sufficient number of diffracted beams through the optical system of the microscope. For spatial coherence, a condenser lens diaphragm with a diameter of 50 μm was used. The average beam diameter for obtaining images was approximately 100 nm (3 Spot size). Survey images were obtained at low magnifications (5,000–20,000). For a more detailed study of the structure and observation of traces of atomic planes, a direct magnification of 400,000–600,000 was used.

For the investigation of particles on a substrate, samples were prepared in cross section. In order to cut the workpiece from the starting material, ultrasonic cutting was used; the cutting tool was an empty tube with an inner diameter of 3 mm. Cutting was carried out by excitation of the lead zirconate titanate (PZT) crystals at 26 kHz. The cutting medium was a boron carbide abrasive suspension. Ion etching was performed using a PIPS II system (Precision Ion Polishing System, Gatan) at an accelerating voltage of 3 keV.

The optical transmission of fluorite single crystals, both pure and deposited by layers, was investigated in the IR and terahertz ranges. Measurements were performed using a Bruker IFS113v (IR FT) Fourier spectrometer and a time-domain spectrometer (TDS) described in [19]. Transmission spectra were obtained in the transparency regions of the material in the THz and mid-IR ranges. In the region of high absorption, the reflectance spectra were measured. Reflection spectra were normalized versus a silver mirror reference with a radiation incidence angle of not higher than 6°. All measurements were performed at a temperature of 20 °C. The resolution in IR range was 2 cm$^{-1}$, in the THz range – 0.2 cm$^{-1}$.

### 3. Results and discussion

Typical AFM data are shown in Figs. 1–3. They slightly varied from experiment to experiment. In general, an inhomogeneous coating of the substrate surface with submicron particles with a size of about 100–150 nm was observed. Particle faceting was not revealed by AFM. The observed pattern is similar to the agglomeration of particles in samples of natural silicites, specifically samples of flints and chalcedony [20].

For a sample prepared by deposition with exposure time of 1 h (sample No. 1, Fig. 1a), formations with a size of 40–150 nm were characteristic. When the time of exposure in mother solution was increased up to 24 h (sample No. 4), a significant increase in the size of the formations (70–150 nm) was not observed, however, the general compaction of agglomerates and clearer boundaries between individual formations were noted.

In clusters of particles, agglomerated triangular formations corresponding to the symmetry of the substrate of micron sizes were visible (Fig. 2). SEM data were more informative (Fig. 3). These data allowed visualization of initial small (about 15–20 nm) faceted nanoparticles.
located on the substrate and mutually oriented. Submicron formations had clusters of these nanoparticles.

Transmission electron microscopy data (Fig. 4) indicated a coherent growth of fluorite nanoparticles precipitated on a single-crystal substrate. The crystallographic planes of the particles, precipitated on fluorite single crystal had a continuation into the substrate. In addition, the particles of the second deposition layer also retained their orientation relative to the particles of the first layer.

These results confirm the data of the classical experiment of Shubnikov and Shaskolskaya [2, 16] on the oriented growth of small particles during their deposition on the surface of a large crystal.

The optical transmission spectrum of a fluorite plate with deposited fluorite particles contains absorption lines in the regions of 1450–1730 and 2850–2930 cm⁻¹ corresponding to vibrations of water molecules and hydroxyl species (Fig. 5). This is natural, since adsorbed water forms tightly bound layers on the surface of fluorite nanoparticles prepared by precipitation from an aqueous solution.

The heat treatment of a fluorite single crystal substrate with a precipitated layer of CaF₂ at 600 °C was performed. Atomic force microscopy images of the formed layers are shown in Fig. 6. As expected, the attachment growth of the initial particles deposited on the substrate surface with

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Fig. 2. AFM image of sample No. 7, precipitation from the washing solution, exposure for 2 weeks

Fig. 3. Atomic force (left shot) and scanning electron microscopes (right shot) images. Sample No. 6, mother solution, exposure for 1 day

Fig. 4. TEM micrograph, sample No. 1, series “a”
the formation of a single continuous agglomerate of complex topology was observed. The formation of the layer did not finish. The profile of the layer is complex, with strong height differences at the level of 10–30 nm (Fig. 6c).

4. Conclusions

Thus, the deposition of fluorite nanoparticles on the surface of a CaF₂ single crystal is oriented with a coherent attachment growth to the surface of the single crystal (Fig. 4). However, the formation of associates of nanoparticles in the initial colloidal solution promotes the chaotic deposition of submicron particles on the substrate surface (Figs. 1–3). The structure formed during the deposition process after heat treatment creates a nanoarchitecture of complex topology. This circumstance prevents the formation of a homogeneous monolithic film suitable for use in photonics on the surface of a single-crystalline substrate. However, this structure of the deposited film can be attractive, for example, for the creation of catalysts.
Authors contributions


Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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