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Synthesis and Study of KH_2PO_4 Nanotubes (Nanorods) Embedded in Al_2O_3 Porous Matrix

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In this report, the problem of obtaining and using nanocomposite materials for radio networks of the optical and terahertz frequency bands is addressed. Nanoporous structures of anodized aluminum oxide Al_2O_3 with 40 and 85 nm pore diameters were prepared. We were succeeded in synthesis of a nanocomposite material composed of nanowires and nanotubes of the crystalline material KH_2PO_4, embedded into the pores of Al_2O_3 matrix. As a result, the created nanocomposite material Al_2O_3:KH_2PO_4 can be potentially used as an active medium in the optical range, as well as a decelerating material and element of antenna-feeder devices of radio networks.

topics: crystalline nanocomposite, KH_2PO_4 (KDP) nanocrystal, Al_2O_3 (AAO) matrix

1. Introduction

The creation of new functional materials with adjustable optical properties used in membrane technology, optics, quantum electronics, and analytical instrumentation is still of high technological importance. The so-called porous glasses are promising matrices for such materials due to their unique set of adsorption, diffusion, optical and other characteristics combined with controlled structural parameters in the nanoscale range.

When substances with designed physical properties are introduced in porous matrices, the functional capabilities of the embedded components are expanded and the practical significance of such structures increases significantly [1, 2]. Therefore, composite nanostructured materials based on porous oxides are currently the subject of comprehensive study [3], among which aluminum oxide Al_2O_3 (AAO) plays a significant role due to the relative simplicity of production in sulfuric, oxalic and phosphoric acid electrolytes [4, 5].

The development of modern technology opens up new opportunities for combining advances in various technology directions. Multimedia data transmission has led to the emergence of 100G and 40G Ethernet networks. Today's wireless radio networks use almost all the licensed and unlicensed bandwidths. The use of multi-position modulation was not enough to provide high-speed data transmission over the radio channel. Developers of transceiver equipment are increasingly focusing on the subterahertz and terahertz bands (60–3000 GHz), which do not require a license. Until now, there was no technological base for the production of such devices. The specific features of radio wave propagation in this band entail several limitations related to the flow rates and weather conditions. Significant attenuation of radio waves in the air reduces the receiving range. The high demands on the antennas also increase due to the stabilization of the main part position. The advantages include the reduction of the interference and diffraction levels, as due to the reduction of the receiving range, it is possible to increase the number of stations in the cell, reducing the size of the antennas. The presented problems indicate the need for the development of new materials for antennas, modulators and transducers using nanotechnology [6].

2. Current state of research

The great interest in nanostructures is a result of their numerous potential applications in various fields of technological activity, such as biomedicine, electronics, optics, magnetism, energy storage, and electrochemistry. It is established that ultra-small nanostructured blocks have a wide range of improved mechanical, optical, magnetic, and electrical properties compared to a bulk matter of the same chemical composition. It has recently been proven that the ordered sequence of $PbHPO_4$ nanowires demonstrates significant evolution of their optical properties compared to the bulk $PbHPO_4$ crystal [7]. A similar conclusion is applicable to the optical properties of porous silicon in comparison to a bulk Si single crystal [8].

Many papers devoted to anodized aluminum oxide AAO suggest various ways of its implementation [6, 9–15]. These implementations account for various features of AAO, i.e., ordered structure, optical and physical properties, biocompatibility. A great practical interest of AAO-based structures is in biomedicine, sensors and filter technology, optics, micro- and nanoelectronics.

Matrix synthesis is a popular approach for obtaining nanomaterials because of its simplicity and low cost [10–16]. As a matrix, AAO has several advantages, namely the ability to control the geometric parameters of the porous structure, periodicity, high porosity, cylindrical pore shape, and high aspect ratio. AAO can be easily dissolved without damaging nanostructures within pores [16]. Depending on desired conditions, partial or complete filling of pores can be achieved, so that quantum dots and nanotubes/nanorods of various shapes and sizes can be obtained [17, 18]. The process of implanting particles of metals, metal oxides, semiconductors, polymers, or biological compounds into the pores and further dissolving the aluminum oxide substrate is one of the simplest methods of creating arrays of the desired nanomaterials [5, 16].

3. Problem

New requirements, which set modern standards in the field of communication, impose the development of new materials and devices for the sub- and terahertz range [19, 20]. This became possible due to a technological breakthrough in the production of nanocomposite materials, and concerns the creation and testing of elements and technology of new generation electronic, photonic, and hybrid devices. Methods of creating nanostructures with designed shape, dimensions, chemical composition and alloying of structures are well-known. However, there are still problems related to the uneven nanomatrix formation, the nanocrystal growth, internal impurities and additives that can lead to various defects of matrix. It is difficult to determine in advance the initial characteristics and features of nanocomposites due to the use of new methods of their production. Therefore, it is necessary to study the mechanical, electrical, magnetic, frequency, optical and acoustic properties of nanocomposites, which is an urgent problem determining the areas of their further use. For example, the development of new materials and methods for generating and detecting sub- and terahertz emissions in new wireless standards is particularly interesting. Existing radiation sources cannot fully solve the problem [21].

Linear effects in semiconductors, as well as the effect of nonlinear optical rectification, are used for pulsed, coherent generation of terahertz electromagnetic waves. The nonlinear optical effect was initially discovered in the KH_2PO_4 (KDP — potassium dihydrogen phosphate) crystal [22] and later in other nonlinear optical crystals SiO_2 [23], $LiNbO_3$ [24], $LiTaO_3$ [25], GaP [26] and $CaWO_4$ [27]. Significant results have been achieved with nanowires, quasi-one-dimensional nanostructures whose length is much larger than their diameter for photonic and optoelectronic devices such as LEDs [28], lasers [29–31], electronic emitters [32], and photodetectors [33].

As noted above, porous AAO is often used as a nanomatrix for nanowires embedded into the pores of matrix. This is a high-quality material that could be used in the submillimeter and millimeter ranges. The KDP crystals in the pores of the nanomatrix modify the already known properties of each component of the composite.

The development of efficient sub- and terahertz receivers and sources based on the ability to drive electromagnetic fields using nanocomposites is often limited by technological problems [5]. The nanomatrix formation depends on the technological process of their production, it provides the periodicity of the structure, openness or closedness of nanopores, and their shape. The nanomatrix material determines not only the range of application, optical or radio, but also the linear or nonlinear properties, suitability for one or another method of filling of the crystal.

To conduct studies of optical properties, some requirements for geometric dimensions and surface finish must be met. As a result, the formed structures can be used as an active environment in the optical range. Nanocomposites deserve attention in the quasi-optical range whereby the implementation of inhomogeneities, such as changes in dielectric permittivity and the formation of retarding structures, is possible. Therefore, the conditions for the construction of antenna and filters are created.

Water-soluble KDP crystal was used in our study as the filling material, and the host matrix was made from thin sheets of aluminum by anodizing procedure [6].

4. Results

There is a relation between the geometry of nanoporous AAO structure and its physical characteristics. By changing the anodizing technological conditions for further structure modification, it is possible to obtain AAO with various characteristics and properties [5, 34–37].

We prepared AAO nanoporous structures from polished aluminum sheets with pore diameters of 40 and 85 nm. To obtain the AAO oxide layers under controlled conditions, anodic oxidation (anodizing) is used [6]. It is an electrochemical process that

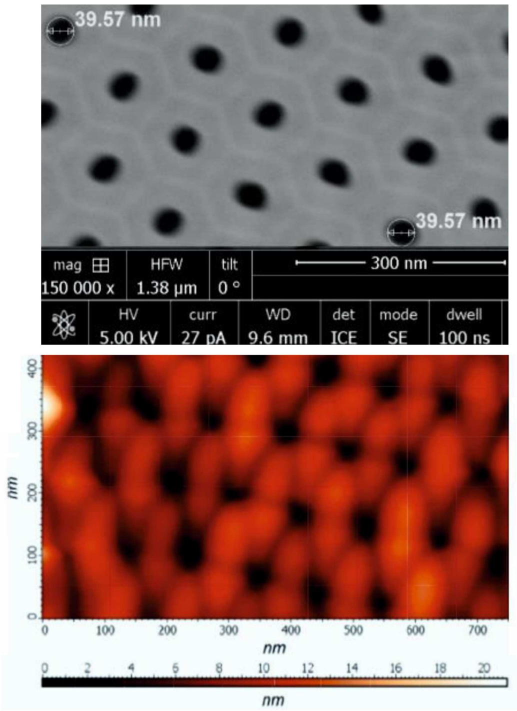

Fig. 1. AAO membrane with a nanopore diameter of 40 nm made of polished aluminum (SEM image).

provides the formation of oxide on metal surfaces due to anodic polarization in an oxygen-containing aqueous environment with ionic conductivity [5]. AAO membranes were made by electrolytic passivation of thin (0.2–1 mm) high purity aluminum sheets (> 99.999%) in an acid solution. The Al sheets are cut according to the shapes and then used in chemical manipulations to obtain a nanoporous structure. The surfaces of the sheets were cleaned. The electrochemical polishing of aluminum was carried out using a solution of $HClO_4$ and C_2H_5OH.

Further, a two-step anodizing process was applied. This technological step was used to obtain highly ordered deep pores without the need to prepaint the surface. Both anodizing steps were performed under the same conditions. The first step ended as the anodizing current approaches steady state. After anodizing, the thickness of the oxide layer was measured with an infrared thickness gauge. If the thickness was insufficient, the anodizing continued. When anodizing was complete, the aluminum layer under the oxide was removed using an aqueous solution of $CuCl_2$ and HCl. Due to the fact that the reaction with aluminum is extremely exothermic, the solution was constantly cooled using a cryogenic unit.

The oxide layer after aluminum extraction looks like a matrix with pores on one side penetrating through most of its thickness, but closed on the side that was in contact with the aluminum. This side of the matrix is etched with 10% H_3PO_4 acid at 30°C. The membranes are thoroughly rinsed in deionized water and dried [34].

Figure 1 presents scanning electron microscope (SEM) images of the prepared AAO porous structure. The preparation process of a saturated aqueous solution for the growth of KDP nanocrystals in porous AAO matrices consists in recrystallization of raw material KH_2PO_4 (KDP) and subsequent obtaining of saturated solution at the growth temperature. The KDP crystals obtained as a result of recrystallization were poured into a glass vessel with deionized water. Then, the vessel with the solution was placed on a magnetic stirrer with controlled heating at $T = 57$°C until the KDP crystals were completely dissolved [6]. After that, the solution was moved to a water thermostat (stabilization temperature ±0.05°C) at 54°C for evaporation at a rate of less than 1 mm/day, until the first crystals precipitated. Two porous AAO matrices with pore diameters of 40 and 85 nm in separate containers were immersed in the received saturated solution. The whole system was stabilized by temperature for 4–5 h. Then the solution temperature was decreased by 4°C to 50°C. The growth of the already nucleated KDP crystals was observed in the solution. Finally, after 3 h of the synthesis procedure the membranes were removed, wiped twice with a cloth dampened with deionized water, and wiped dry. The obtained samples were incubated at 80–100°C for one day [5].

After the growth operations performed with AAO membranes in a saturated aqueous KDP solution, a series of studies were performed to visualize and control the pore filling with KDP crystals on the SEM (FEI type) with a resolution of 0.8 nm. As a result, the structures in the form of KDP nanorods/nanotubes embedded into AAO matrix were confirmed by SEM (see Fig. 2). X-ray diffraction studies (Fig. 3) of the obtained KDP nanocrystals in AAO matrix confirm the presence of the crystal structure of KDP.

In addition, we studied samples obtained with longer growth times of KDP nanocrystallites. The surface morphology and quality of all samples were also investigated by SEM. The AAO surface consists of clusters with a quasi-periodic pore structure. In the AAO:KDP sample (Fig. 4a), which has been kept in a saturated KDP solution for 4.5 h, the pore diameter becomes slightly smaller compared to the pure AAO matrix. When the AAO:KDP sample (Fig. 4b) was in a saturated KDP solution for 24 h, the pore diameter becomes smaller even compared to AAO:KDP.

The full KDP filling of the AAO pores was possible within a day. At the same time, many microcrystals appear on the surface of the AAO:KDP sample. Based on our crystal growth experience, we can propose the following way for the formation of the KDP nanocrystals. In the initial stage, after immersing the AAO membrane in a saturated solution of KH_2PO_4, some nucleated KDP crystals appear near the pore walls, thus forming KDP nanotubes with cavities in the center. As can be seen in Fig. 2a,

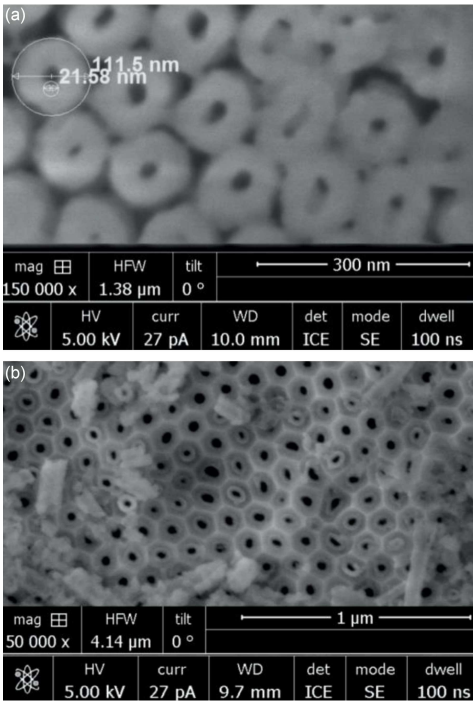

Fig. 2. SEM images of the AAO:KDP nanocomposite grown for 3 h on the AAO matrix of a pore diameter of 40 nm.

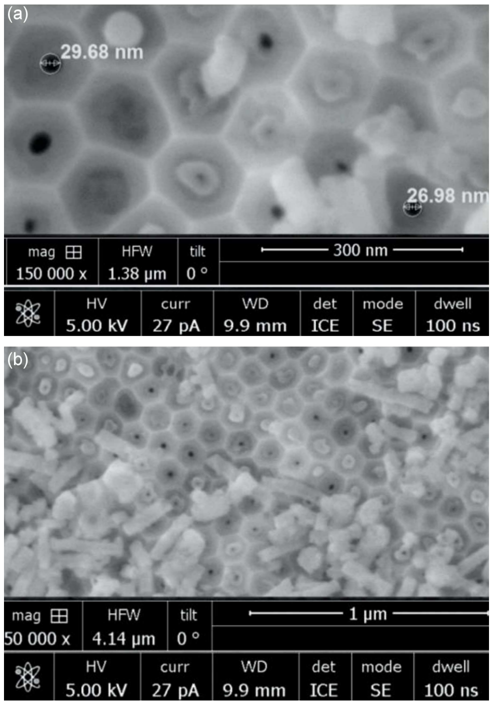

Fig. 4. SEM images of the AAO:KDP nanostructure pores (85 nm) grown for (a) 4.5 and (b) 24 h of the growth.

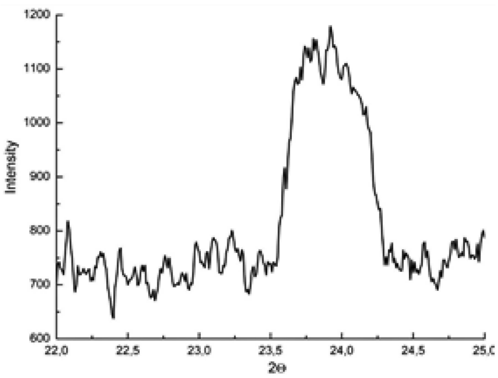

Fig. 3. X-ray diffraction patterns of the obtained KDP nanocrystals in the AAO matrix.

the cylindrical-shaped nanotubes grow perpendicular to the AAO plate. At this stage, nanotubes are isolated from each other and do not aggregate in general. This process changes significantly with increasing exposure time. After about 20 h of soaking of the AAO membrane in a saturated KH_2PO_4 solution, the formed crystals (KDP) fill the entire space in the pores, thereby creating almost uniform aggregation. At the same time, the inner diameter of the empty nanotubes becomes smaller. In some of them it is almost zero, thus turning nanotubes into nanorods/nanowires (Fig. 4b) [5].

Not only the surface of the AAO:KDP nanocomposite but also its spatial internal morphology is explored using the focused ion beam (FIB) technique [5]. Instead of electrons in the SEM technique, the FIB technique uses a focused beam of ions — in our case high-energy gallium atoms — to visualize the internal morphology of the studied material. The high-energy gallium atom beam hits the sample and destroys/grinds the surface. The destruction of the material surface depends on the ion beam energy and the exposure time. By performing ion beam scanning at selected locations on the surface, unique information about the morphology of a material's internal structure can be obtained. The importance of this method is especially significant in the case of probing composite materials consisting of different chemical and aggregate state substances (in our case of amorphous anodized aluminum and crystalline KH_2PO_4) [5].

Figure 5 clearly shows the presence of KDP nanotubes formed in the process of soaking the AAO matrix in a saturated aqueous solution of KDP for 24 h. The fact that in the process of creating the AAO:KDP nanocomposite, the KDP nanotubes or nanorods are formed (depending on the soaking time of the AAO sample in a saturated KDP solution) is clearly demonstrated in Fig. 5a. As can be seen from the chipped sample (Fig. 5b), it consists of a conglomerate of nanotubes/nanorodes, the diameter and spatial arrangement of which are set by the pore structure of the AAO host matrix. At the same time, prolonged incubation ($>$ 20 h) of the AAO matrix in a saturated KDP solution leads to the destruction of the AAO matrix itself.

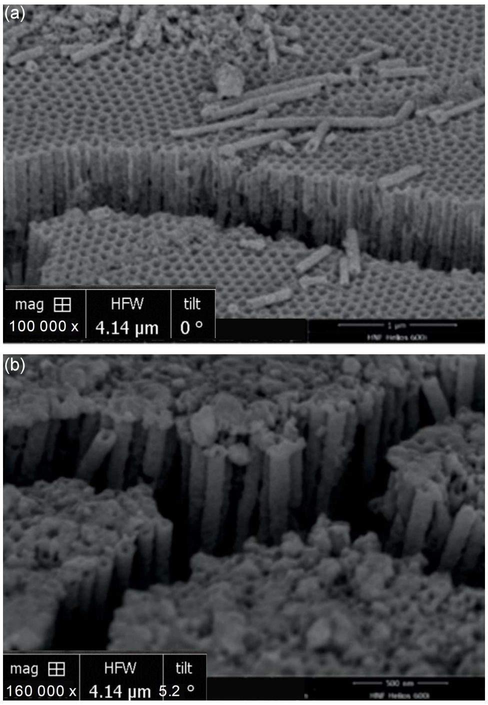

Fig. 5. SEM images of AAO:KDP nanocomposite after 24 h exposure of anodized aluminum AAO matrix in a saturated KDP solution.

The preliminary spectroscopic experiments performed by us on the AAO:KDP nanocomposite [35] indicate that the main lattice dynamics features of nanosized KDP crystals embedded in the AAO matrix correlate well with those inherent for hydrogen-bonded crystals of KDP type [37–40].

5. Conclusions

Good quality anodized aluminum oxide nanostructures with a pore diameter of 40 and 85 nm were obtained. By adjusting the exposure time of the AAO nanoporous matrices in a saturated aqueous solution of KDP, it is possible to obtain crystalline compounds in the form of nanorods or nanotubes. It is confirmed by the SEM images and by the FIB technique. Depending on chosen conditions, it is possible to achieve a partial or complete pore filling and different shapes and sizes of nanotubes/nanorods. The increase of crystallization time results mainly in the synthesis of nanorods without an internal cavity. Consequently, the formed structures may found technological application as an active nanosized medium. Exactly the AAO:KDP nanocomposites deserve attention in the optical and quasi-optical range as prospective materials for designing, e.g. retarding devices by including inhomogeneities such as variation of dielectric permittivity. Another potential application of the AAO:KDP nanocomposites could be radio-network antenna-feeder devices.

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