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The paper presents the results of the formation and study of the morphological and structural characteristics of the mesoporous ZnO / Al_2O_3 nanofibers film (ZANF). The deposition of a ZnO layer on Al_2O_3 nanofibers film (ANF) ~ 1 μm thick was carried out by the method of atomic layer deposition. The morphology of the mesoporous composite layer ZnO / Al_2O_3 (ZANF) has been studied by scanning and transmission electron microscopy. It is shown that in the process of atomic layer deposition, the ZnO layer grows according to the Stranski-Krastanov mechanism. A ZnO layer less than 5 nm thick gives an island structure in which Al_2O_3 nanofibers are uniformly coated with ZnO particles, an increase in the ZnO layer thickness to 15 nm demonstrates a continuous coating of Al_2O_3 nanofibers. The system has a core-shell structure. The resulting composite structures are promising for applications in photocatalysis and gas sensing.

1. Introduction

Zinc oxide is a wide-gap semiconducting oxide with a band gap of 3.36 eV, crystallizing in two modifications: the first is a wurtzite structure related to the hexagonal system (symmetry group $P6_3mc$), the second is a sphalerite structure related to the cubic system (symmetry group $F\bar{4}3m$) [1].

Zinc oxide finds more and more applications in various fields of science and technology. Some of the most important applications of zinc oxide are photocatalysis [2] and gas sensors [3]. For effective use of ZnO in photocatalysis and gas sensors, in addition to crystallinity and geometric dimensions of elements less than 50 nm, a highly porous structure of films is required, since chemical transformations occur directly at the interface.

A number of works have proposed a template technique, where ZnO was deposited on various meso and microporous templates, such as porous anodic alumina [4], inverse opal [5], polymer film with gyroid structure [6], and other porous structures. The active ZnO layer is applied by the following methods: ALD [7], CVD, sol-gel method or electrodeposition [5]. This approach makes it possible to obtain highly porous structures with a specific surface area of more than 50 m^2/g [3].

In this work, we propose a simple template based on alumina nanofibers for the preparation of highly porous ZnO films, which can be used in problems of photocatalysis and gas sensors.

2. Experimental details

The formation of porous ANF was carried out according to the following procedure. First, a 0.1% colloidal solution of alumina nanofibers in isopropyl alcohol was prepared. For this, we prepared a weighed portion of 0.01 g of alumina nanofibers. This was followed by the first stage of homogenization, in which the primary blocks of nanofibers are destroyed by intensive stirring of the solution on a magnetic stirrer for 1 hour at a speed of 1000 rpm. The next stage is ultrasonic processing of the previously prepared suspension. The processing was carried out on a tip sonicator of the UZTA-0,15 / 22-O brand (Russia); the processing power was 90% of the nominal, the processing time was 5 min.

The ANF was formed by vacuum filtration. Vacuum filtration was performed using a Sartorius device (Germany). Filtration was carried out through a cellulose acetate filter with an average pore size of 1.2 μm (Vladipor, Russia). The diameter of the working area of the filter was 2 cm. The preparation of ANF with a thickness of 1 μm was carried out as follows: 30 μl of dispersion of alumina nanofibers with a concentration of 1% was diluted in 30 ml of isopropyl alcohol. The resulting solution was filtered through an acetate cellulose filter. Then the ANF on an acetate cellulose filter was printed at 80 °C onto a glass substrate. This was followed by dissolution of the cellulose acetate filter in acetone. Then, ANF on a glass substrate was annealed in a muffle furnace at a temperature of 450 °C for 4 hours to oxidize the residues of cellulose acetate.

The deposition of zinc oxide was carried out by the ALD method on a Picosun R200 setup (Finland). Diethylzinc $Zn(C_2H_5)_2$ (99.999% purity) and vapor of deionized water H_2O were used as precursors. High purity nitrogen N_2 of 99.9999% was used as a carrier gas. The pulse duration of each gas precursor was 0.1 s. The duration of each purging of the chamber with nitrogen after the precursor was 4 s. The temperature of the ZnO deposition process was 200 °C. The ZnO layer thickness was calibrated according to [9]. According to the calibration, the thickness of the layers was chosen 5 nm and 15 nm, which is 27 cycles and 83 cycles, respectively.

The thickness and structural features of the ZANF were studied by high-resolution TEM in the cross section mode. For this purpose, TEM cross-section samples were prepared using a focused ion beam (Ga +) (FIB) with an energy of 40 keV Hitachi FB-2100 (Japan). The protective Ge layer was formed by thermal deposition at room temperature. A Ge layer is required to protect the sample from structural degradation during FIB preparation and to improve contrast in TEM images. TEM images were acquired with a JEOL JEM-2100 brand (Japan) microscope.

Surface morphology ANF and ZANF was studied by scanning electron microscopy (SEM) using a Hitachi S5500 microscope (Japan) at an accelerating voltage of 5 kV.

The powder diffraction data of all samples for Rietveld analysis were collected at room temperature with a Bruker D8 ADVANCE powder diffractometer (Cu-Kα radiation) and linear VANTEC detector. The step size of 2θ was 0.016°, and the counting time was 0.5 s per step. Rietveld refinements of all structures were performed using TOPAS 4.2 [9].

3. Results and discussions

Figure 1 shows SEM images of ANF before and after deposition of a 5 nm ZnO layer (27 cycles, figure 1b) and 15 nm (83 cycles, figure 1c).

SEM images provide complete information on the morphological features of the ANF and ZANF structures. The average diameter of a single alumina nanofiber is 8.7 ± 1.5 nm. Deposition of 27 cycles ZnO, demonstrates non-continuous coating of nanofibers, polydisperse ZnO particles with a size of 3-10 nm are observed. The deposition of 83 ZnO cycles demonstrates a morphology with a “core-shell” structure with a diameter of about 30-40 nm. Thus, the following conclusions can be drawn: a thin ZnO film on the surface of alumina nanofibers grows according to the Stranski-Krastanov mechanism, the thickness of the ZnO layer is a key parameter that determines the morphology of the composite.

According to [10], ANF has the average pore size of ~ 28 nm, although the pore size distribution is quite wide and lays in the range 2–100 nm, no pores larger than 100 nm were found. According to the BET analysis [12], the specific surface area of ANF is ~ 146 m^2/g. The porosity of ANF is ~ 75%. The

deposition of ZnO leads to a decrease in the average pore size and a decrease in the specific surface area.

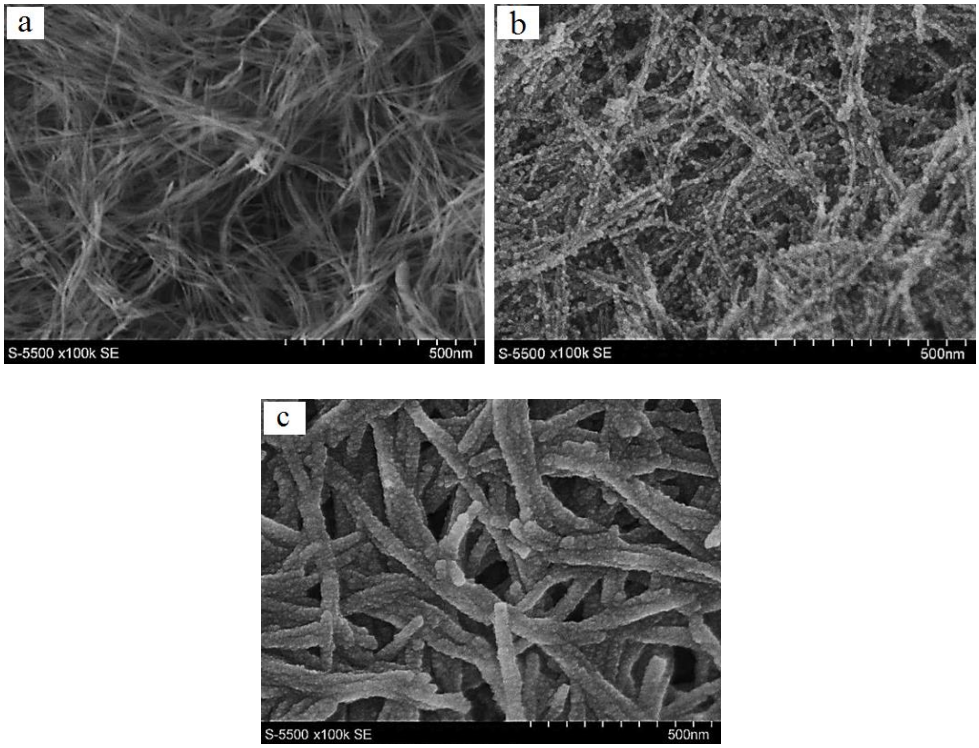

Figure 1. SEM images of composite porous structure ANF (a); ZANF with 27 cycles ZnO (b); ZANF with 83 cycles ZnO (c).

The results of XRD analysis are shown in figure 2. Alumina nanofibers have a cubic lattice, with a spinel structure, belonging to the *Fd*3*m* symmetry group, called the γ-phase of alumina.

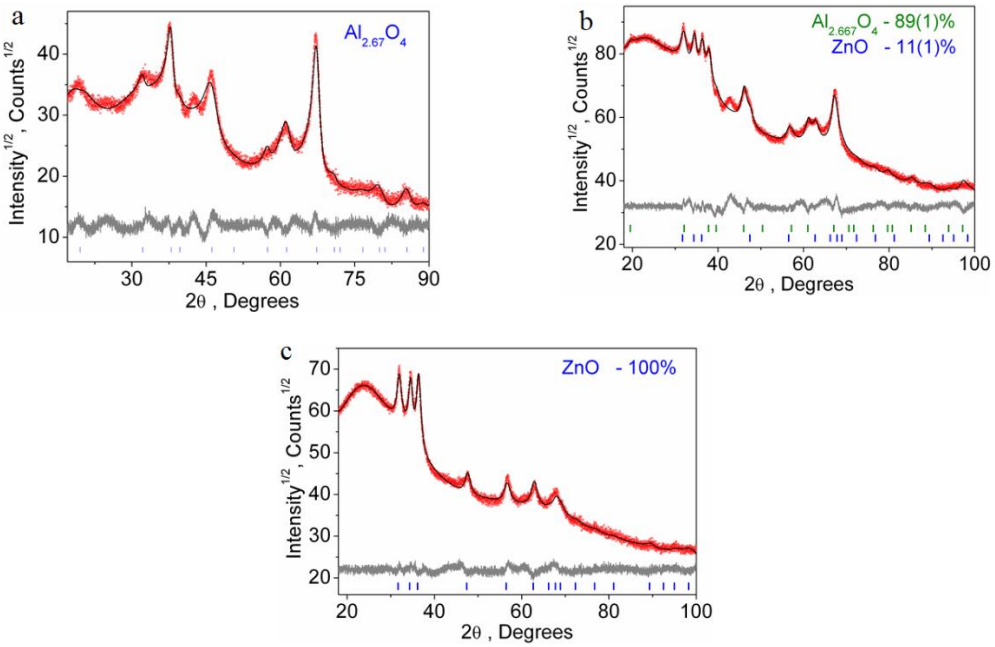

Figure 2. XRD pattern ANF и composite ZANF with 27 (b) and 83 (c) ZnO deposition cycles.

On the ZANF XRD pattern, after 27 cycles of ZnO deposition, two phases are observed, cubic Al_2O_3 and hexagonal ZnO (Wurtzite structure, $P6_3mc$ symmetry group). The percentage of phases is 89% - Al_2O_3 and 11% - ZnO. With 83 cycles of ZnO deposition, only the hexagonal ZnO phase is present on the XRD pattern. This can be caused by two factors, 1 - excess mass of ZnO relative to Al_2O_3; 2- the beginning of a chemical reaction with the formation of a mixed oxide ZnO: Al (AZO), accompanied by amorphization of alumina nanofibers.

The uniformity of the deposition of ZnO on mesoporous ANF is a key parameter that determines the quality of the finished structure and its applicability in problems of photocatalysis and gas sensors. The depth uniformity of ZnO deposition was investigated by the TEM method. Figure 3a shows TEM image ZANF with 83 cycles ZnO deposition in cross-section morphology

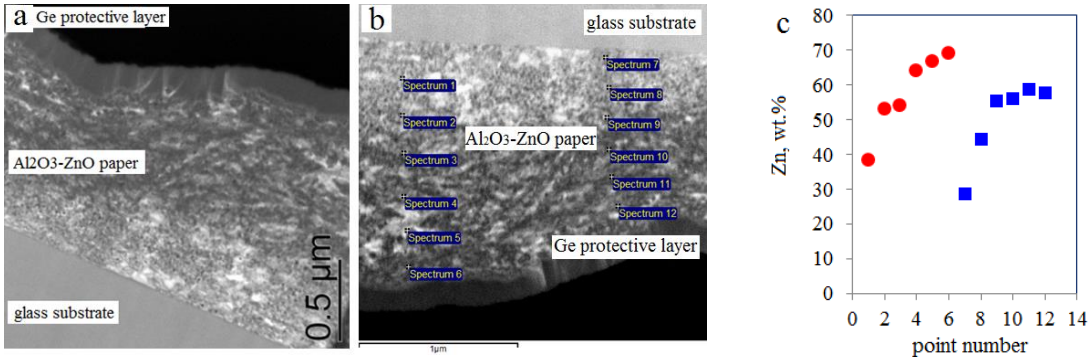

Figure 3. TEM image ZANF with 83 cycles ZnO deposition in cross-section morphology (a) EDX scanning line ZANF with 83 cycles ZnO deposition (b) Zn wt. % ZANF with 83 cycles ZnO deposition EDX dept scanning (c).

EDX analysis was carried out along two straight lines in order to determine the gradient of the mass concentration of Zn over the thickness of the ZANF. The scanning directions are shown along the lines in figure 3b. According to EDX analysis on the ZANF surface with 83 cycles ZnO deposition, the Zn concentration is 69.1 wt. %, at the interface with the glass substrate, the Zn concentration decreases to 38.2 wt. %. It can be seen that in this mode of ZnO deposition there is a significant gradient of Zn distribution over the thickness of the mesoporous film. To increase the uniformity of the Zn thickness distribution, it is necessary to reduce the deposition rate.

4. Conclusion

A method for obtaining composite ZANF with a mesoporous structure by means of the ALD process has been proposed and implemented. The dependence of the morphology of the ZnO layer on an alumina nanofiber film has been studied. The resulting mesoporous composite structures are promising for applications in photocatalysis and gas sensors.

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