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Zinc-Nanosystem-Structure Formation Using Anodic-Oxidized Aluminum Membranes

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Abstract—We propose a new method for the formation of zinc nanosystems by condensation of a weakly supersaturated Zn vapor in pores of the anodic-oxidized aluminum membrane (AOA)—silicon substrate system. For this purpose, a weak Zn vapor flow is created by magnetron sputtering of Zn target in a high-purity inert gas atmosphere and maintaining a temperature of the porous AOA membrane outer surface higher than that of the substrate. This drives a directional Zn vapor flow inward membrane parallel to the pore generatrix and favors effective penetration of Zn vapor into the membrane.

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Ordered arrays of metal and semiconductor nanoislands have drawn much research interest due to the good prospects of their use in electronics, optoelectronics, sensors, thin displays, and high-density data-storage media [1, 2]. Various metal nanosystems are usually obtained with the aid of nanotemplates of porous anodic-oxidized aluminum (AOA) membranes [3–5], electron-beam nanolithography [6–8], and self-assembly processes [9, 10]. It should be noted that the template approach employing AOA membranes is usually realized by means of electrolytic deposition [4, 5]. A necessary condition for implementing this method is a sufficiently high electric conductivity of substrates, which imposes certain limitations on the spectrum of acceptable substrate materials.

In contrast to using electrolytic deposition for the formation of ordered Zn nanoisland arrays, we propose a more universal method of substance condensation near thermodynamic equilibrium onto the anodic-oxidized aluminum membrane (AOA)–substrate system. In this case, the conductivity of a substrate is not important and the effective formation of nanosystems in the porous membrane template is favored by creating a directional vapor flow inward into the pores and maintaining vapor supersaturation at the substrate surface higher than that over the outer membrane surface. This approach allows nanosystems to be formed on arbitrary substrates.

Some peculiarities of the self-organization of low-dimensional systems during the condensation of weakly supersaturated vapors have been considered in our previous works [11–14]. Particular interest is related to characteristic features of the formation of Zn nanosystems directly on the outer surface of AOA membranes under conditions of ultimately weak supersaturation of deposited vapors. The choice of zinc is explained by the fact that, in combination with a quite simple oxidation method, this approach can be used for obtaining ZnO nanosystems with a broad spectrum of potential applications.

In this context, the main aim of this work was to study the mechanisms of structure formation in Zn nanosystems on the surface of a Si substrate and the outer surface of AOA membranes during the condensation of weakly supersaturated Zn vapors onto the membrane–substrate (AOA–Si) system under conditions of a lower temperature of the substrate surface as compared to that of the outer membrane surface.

The condensation of a substance under conditions close to thermodynamic equilibrium is possible provided that current pressure P of the deposited vapor slightly exceeds equilibrium pressure P_0. Since the latter value is $P_0 \propto \exp[-E_d/(k_bT_c)]$ [15], nearly equilibrium deposition conditions can be achieved at a relatively high temperature of the growth surface T_c and small values of desorption energy E_d of adatoms. Note that even rather insignificant temperature differences between various regions of the growth surface can lead to significant differences between the corresponding deposition rates, which is a basis of the proposed technological approach.

Evidently, small values of pressure P of a deposited vapor can be achieved by forming ultimately weak stationary flows of this substance. In turn, small deposition rates increase the probability of formation of a condensate containing impurity phases, thus influencing the process of nanosystem-structure forma-

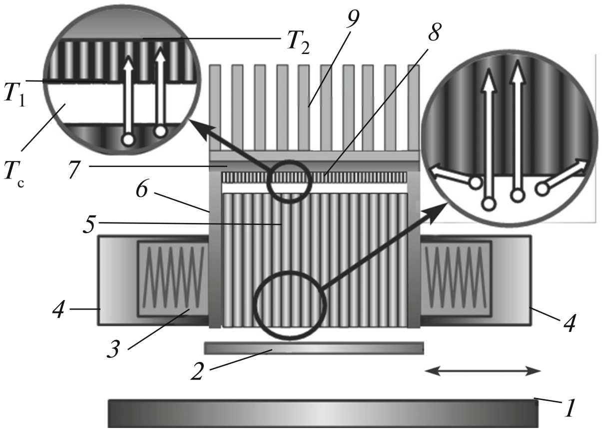

Fig. 1. Schematic diagram of the cross section of a device used for the formation of Zn nanosystems: (*1*) Zn target for magnetron sputtering, (*2*) shutter, (*3*) halogen-lamp radiative heater, (*4*) heater case, (*5*) system of thin copper tubes, (*6*) copper cylinder, (*7*) substrate, (*8*) AOA membrane, and (*9*) cooler radiator.

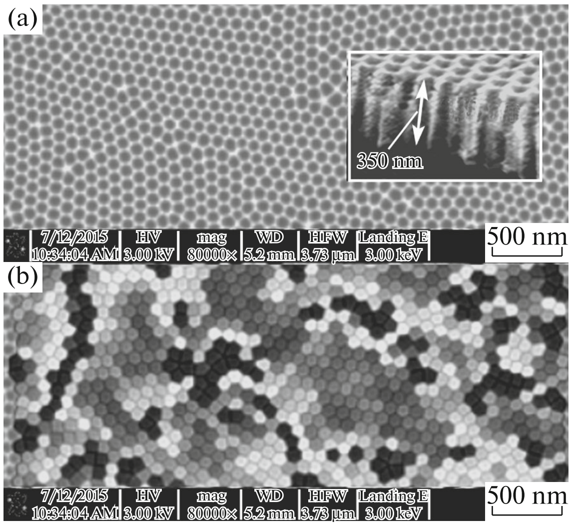

Fig. 2. SEM images of a porous AOA membrane (a) before and (b) after processing with the aid of special software.

tion. For this reason, in order to obtain impurity-free Zn condensates, we have used a vacuum chamber equipped with three unbalanced magnetron-sputtering systems. Two of these were used to purify the working inert gas (Ar) from chemically active admixtures by means of titanium sputtering [16]. This process was carried out in the absence of Ar flow, and the partial pressure of residual reactive gases after purification was as low as 8×10^{-8} Pa [16]. The third magnetron-sputtering system was shielded from the former two by a system of screens and only used for obtaining Zn condensates.

As is known, the directional distribution of velocities of magnetron-sputtered atoms obeys the cosine law [17]. Taking into account the rather large area of the zone of target sputtering, it can be assumed that sputtered atoms approaching AOA membrane pores are characterized by a broad spectrum of motion directions. This circumstance can lead to blocking of the open membrane pores by the deposited substance, which would hinder the formation of ordered nanosystems on substrates by the template method. In order to solve this problem, we have used a device that was developed previously [18], which helps forming a narrow-directional flow of magnetron-sputtered atoms. Figure 1 shows a schematic diagram of the cross section of this device together with the target of a magnetron-sputtering system. An important part of this device is the system of tightly adjacent thin-walled copper tubes with diameters of ~2 mm and the axes oriented parallel to the generatrices of pores in the AOA membrane. The main purpose of system of tubes *5* was to transfer only those sputtered atoms that move along the axes of tubes, i.e., parallel to the generatrices of pores in the AOA membrane. The efficiency of formation of a narrow-directional flow of sputtered atoms in the pores is maximum provided that the mean free path of atoms is comparable with the distance from target *1* to substrate *7*.

The undesired blocking of pore openings on the membrane by the condensate can also be minimized by more intense heating of this surface. For this purpose, the substrate surface that contacted with the membrane was maintained at lower temperature T_2 than that (T_1) of the outer surface of the AOA membrane (see the top inset to Fig. 1). The condition of $T_1 > T_2$ was ensured by cooling the substrate (radiator *9*) and heating the outer membrane surface (radiative heater *3*). For homogeneous heating of system of tubes *5* and outer membrane surface, these tubes were arranged inside copper cylinder *6*.

The morphology of obtained Zn condensates and geometric characteristics of AOA membranes were studied by scanning electron microscopy (SEM) on an FEI NanoSEM 230 instrument.

Figure 2a shows the electron-microscopic image of an ultrathin AOA membrane. As can be seen, the membrane comprises regions with strictly ordered arrangement of pores, the symmetry of which is violated on the boundaries of these regions. In order to increase the informativity of data with respect to the homogeneity of obtained structures, the images were processed using special software. In the resulting images, the regions of identical blackening correspond to pores of the same type, which are oriented in one direction (Fig. 2b). Depending on the technological conditions, the diameter of holes in membranes changed from ~55 to 95 nm and their thicknesses varied within 350–400 nm.

Calculations performed using a method described in [17] showed that, at a working gas pressure of $P_{\mathrm{Ar}} <$

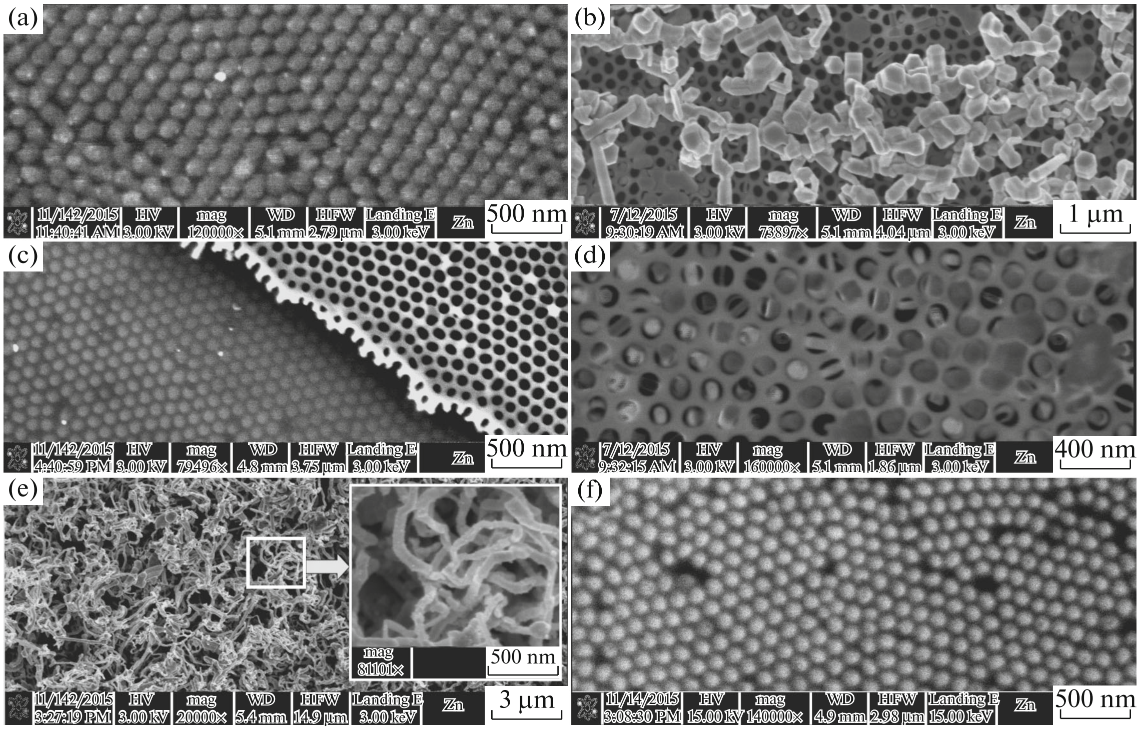

Fig. 3. SEM micrographs showing the structure of Zn nanosystems formed (a, c, d, f) on the surface of Si substrate (or inside pores of the AOA membrane) and (b, e) on the membrane surface: (a) T_c = 35–70°C, t_c ~ 0.4–0.6 h; (b) T_c = 35–70°C, t_c ~ 0.4–0.6 h; (c) T_c = 150°C, t_c = 0.6 h; (d) T_c = 150°C, t_c = 0.9 h; (e) T_c = 150°C, t_c = 1.6 h; and (f) T_c = 35–70°C, t_c = 04–0.6 h.

2.2 Pa, the mean free path of sputtered Zn atoms exceeds the target–substrate distance (~90 mm). Since the stability (steady-state character) of magnetron-sputtering decreases at P_Ar < 0.8 Pa, the effective formation of a narrow-directional flow of magnetron-sputtered Zn atoms inside AOA pores takes place at P_Ar ~ 0.8–2.2 GPa.

Another, no less important, task was to determine the condensation temperature and magnetron discharge power P_w for zinc sputtering at which Zn nanosystems are predominantly formed on the Si substrate rather than on the outer surface of the AOA membrane. It should be noted that strict determination of temperatures T_1 and T_2 (Fig. 1) is a rather difficult task. For this reason, we have first determined temperature T_c in the gap between system of tubes *5* and membrane *8*, which approximately corresponds to T_1 (Fig. 1). It was found that the change of T_c from 35 to 150°C was accompanied by variation in the temperature of cooler *9* within 30–65°C.

Let us consider the laws of structure formation in Zn nanosystems deposited at various T_c, P_Ar ~ 1.5 Pa, and magnetron-sputtering discharge power 12 W. Analysis of the structure and morphology characteristics of obtained Zn nanosystems showed that, at relatively low T_c (35–70°C), an ordered system of Zn nanoislands is formed on the Si substrate (Fig. 3a). At the same time, SEM data showed that a porous Zn structure is also formed on the outer surface of membranes at T_c ~ 35–70°C (Fig. 3b). It should be noted that the first signs of porous-structure formation on the membrane surface are observed for condensation times within t_c ~ 0.4–0.6 h. However, at relatively high temperatures (T_c ~ 150°C) and deposition time of t_c ~ 0.6 h, the growth of porous structures on the membrane surface was not observed (Fig. 3c). It was established that, at T_c ~ 150°C, condensates can be obtained entirely inside pores even for a condensation time of 0.9 h (Fig. 3d). However, in this case, pores are filled with Zn condensate to various degrees, while longer condensation (t_c ~ 1.6 h) leads to the appearance of porous structures in the form of 3D nanowire networks (Fig. 3e).

The obtained data did not reveal any differences in mechanisms of Zn-nanosystem-structure formation for membranes with relatively large (0.9 nm) and small (0.55 nm) diameters of holes under otherwise equal technological conditions (Figs. 3a, 3f).

Thus, we have proposed a new universal technological approach to the formation of ordered arrays of nanoislands and interconnected Zn nanowires using near-equilibrium condensation of metal vapor onto the membrane–substrate (AOA–Si) system.

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