



Two step technology for porous ZnO nanosystem formation for potential use in hydrogen gas sensors



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ABSTRACT

The aim of the work was to develop a technology for porous ZnO nanosystems formation and to determine the relationship between their morphology and sensor properties to hydrogen. With this purpose, a two step technology has been used. On the first stage, porous Zn layers with different morphologies have been synthesized under near-equilibrium condensation conditions implemented by means of an accumulating systems plasma-condensate developed by us. On the second stage, the layers have been oxidized in pure oxygen atmosphere. The sensor tests performed at 250 °C have shown that sensitivity of the porous layers was more than 50% at hydrogen concentration 3000 ppm in dry air.

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1. Introduction

Porous metals oxides are of great interest because of their potential application in gas sensors. They have low synthesis cost, high stability, and electrical conductivity responses to different gases [1–3]. Recently, much attention has been devoted to ZnO sensor properties investigation [4–8]. This is due to the fact, that it has high sensitivity, response rate, and recovery rate. Moreover, ZnO has high sensitivity to a number of “invisible gases” such as H₂, CO, alcohol, toluene, and methanol.

Different deposition methods have been used to fabricate ZnO nanostructures. The most often, they are grown by thermal evaporation [9,10], hydrothermal deposition [11,12], sol–gel method [13,14], electrochemical deposition [15,16], magnetron sputtering [17,18], chemical vapor deposition (CVD) [19,20], metal–organic vapor deposition [21,22], and molecular beam epitaxy (MBE) [23,24]. In recent years, many differently shaped ZnO nanostructures have been obtained, such as nanosheets, nanorods, nanoflowers, nanowires, nanotubes, nanobelts, and etc. The above methods, as a rule, require relatively high operating temperatures, high vacuum conditions, and involve complex chemical reactions. Moreover, the conventional techniques involve complicated multistage processes. On the other hand, in order to

obtain reproducible results, steady-state condensation conditions are required. As an alternative approach that can overcome these issues, is synthesis of porous nanosystems under near-equilibrium condensation conditions. In our earlier works [25–29], the possibility of metal porous nanosystems formation under near-equilibrium conditions has been shown.

The main drawback of ZnO based gas sensors, which greatly limits their practical applications, is that they have low selectivity characteristics. One way to increase selective properties, and as a result functionality, is to create multicomponent porous nanosystems, for example, ZnO–CuO [30]. Performance of ZnO based devices can also be improved by synthesis of the nanosystems in the form of three-dimensional networks including synaptic electronics elements [31]. For this reason, nowadays a great importance is attributed to those technologies that allow relatively simple and reproducible forming of three-dimensional nanosystems in the form of “neuron networks” with possibility of synaptic electronics elements.

In this work the two-stage technology of three-dimensional porous ZnO nanostructures formation has been proposed. Because it has potentiality for application in synaptic electronics, particular attention has been devoted to the layers having morphology resembling “neural network”. Thus, the aim of the work consists in solving the following tasks: i) development of technology of Zn porous nanosystems synthesis in different morphological forms with uniform thickness; ii) optimization

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of Zn oxidation processes with purpose to obtain porous ZnO nanostructures without changes in initial morphology; iii) investigation of ZnO sensor properties with respect to hydrogen depending on morphology.

2. Experimental details

The technology proposed by us consists of two stages. At first, Zn porous nanosystems are formed using near-equilibrium steady-state condensation conditions in plasma-condensate system. Further, the layers are oxidized in pure oxygen atmosphere. The near-equilibrium condensation conditions are characterized by extremely small values of supersaturation ξ or chemical potential difference $\Delta\mu$ between a vapor and a condensate state. In the general case, the supersaturation is determined by equation [32]:

$$\xi = (\Delta P/P_0). \quad (1)$$

Here $\Delta P = (P - P_0)$ is the deviation of the depositing vapors pressure P from the equilibrium value P_0 . At this point, the equilibrium pressure is given by:

$$P_0 = A(T) \exp\left(-\frac{E_d}{k_B T_c}\right), \quad (2)$$

where $A(T) = \exp(\alpha + \beta T_c + \gamma/T_c)$ is the temperature dependent coefficient; α , β and γ are constants being characteristic to zinc; E_d is the desorption energy and T_c is the condensation temperature. From analysis of Eqs. (1) and (2) it follows that near-equilibrium condensation conditions can be achieved by an increase in the condensation temperature T_c or a decrease in the depositing vapors pressure P .

To implement quasi-equilibrium steady-state conditions, a custom-built accumulating plasma-condensate system (APCS) has been used. This technology has the following distinctive features: i) condensation occurs at sufficiently low supersaturations to provide proximity to phase equilibrium between the condensate and the depositing substance; ii) this supersaturation remains stable in time to guarantee the steady-state conditions; iii) atoms mainly condense being in ionized state; iv) the growth surface serves also as a cathode surface since being negatively biased. Due to the above conditions, adsorbed atoms can attach to the growth surface only if the strongest chemical bonds are realized to minimize free energy. As a result, adjacent local parts of the condensate grow at different rates. Spatially distributed selectivity of such type is named structural selectivity. The main elements of the system are the direct current magnetron sputtering device 1 combined with the hollow cathode 2 (Fig. 1). It operates effectively at relatively high working gas (argon) pressures 10–12 Pa. Sputtering of zinc target

3 occurs in crossed electric and magnetic fields. The erosion zone is specified by position 4. The magnetic field is created by the system of magnets 5.

Due to the hollow cathode effect [33], atoms of working gas and sputtered substance become completely ionized when get inside the hollow cathode 2. Because of the energy exchange with the working gas atoms at heightened pressures, the sputtered atoms thermalize to average their energy. The thermalization area is denoted by position 8. Then the atoms are accumulated near the substrate 6 by means of diffusion. Further, the majority of atoms re-evaporate by the reason of their excess energy and the plasma action. Furthermore, these atoms ionize again and return repeatedly to the growth surface under the electric field influence. Such a circular mechanism of mass-transfer additionally accumulates depositing atoms in the direct vicinity to the growth surface.

Non-linear interdependence between main technological parameters such as the vapors pressure P , the condensation temperature T_c , and the discharge power P_w determine self-organization of near-equilibrium condensation conditions at APCS operation [34]. An increase in the discharge power P_w causes subsequent increase in the condensation temperature T_c and the vapors pressure P . According to Eqs. (1) and (2) such relation between T_c and P stabilizes supersaturation ξ at a constant level even if the discharge power P_w varies. At the same time, at heightened working gas pressures P_{Ar} used in the experiments, the depositing flux value is also regulated by diffusive motion of sputtered atoms. Due to thermalization, they lose their energy and continue to move diffusively. As a result, the sputtered substance accumulates in the gas discharge area penetrating into the hollow cathode, where the substrate locates. Accumulation of Zn atoms near the growth surface prevents intensification of diffusive flows in the substrate direction. The action of plasma causes secondary evaporation of adatoms and additionally approaches the system to the equilibrium. The mathematical model and phase portraits presented in [34] confirm theoretically self-organization of near-equilibrium conditions in APCS. From the other hand, our experimental results [25] have shown high reproducibility of structural and morphological characteristics of Zn porous layers even if technological parameters change within specific parameters zones. This fact confirms experimentally self-organization of near-equilibrium conditions.

In order to prove originality of the technology proposed, let us compare APCS operation principle with three most commonly used technological systems operating under near-equilibrium conditions. The comparative analysis will be based on interdependence between such technological parameters as the vapors pressure P , the condensation temperature T_c , the relative supersaturation ξ and the presence of an active medium above the growth surface. Besides plasma, chemically active environment can also serve as the active medium. In the latter case, weakly bound to the growth surface adatoms are removed by reverse chemical reactions. For example, when depositing carbon in hydrogen atmosphere, re-evaporation is stimulated not only by the growth surface heating, but also by volatile hydrocarbons formation. That is why, carbon nanotubes can be obtained both by CVD and physical vapors deposition technologies [35–37].

The simplest and the most widespread technology operating under near-equilibrium conditions is given in Fig. 2 variant 1. For this case, low supersaturation values ξ are achieved by adjusting the condensation temperature T_c and the pressure P values. The influence of P and T_c on the relative supersaturation ξ is shown schematically by green arrows (variant 1). At the same time, there is no feedback between supersaturation ξ and the parameters P and T_c . That is why, stationarity of the process and consequently reproducibility of the results are comparatively low. As a rule, this variant relates to thermal evaporation. At this point, the T_c value is controlled by heating the substrate. The pressure above the growth surface P is adjusted by varying the evaporator temperature, in such a way affecting the amount of evaporated substance.

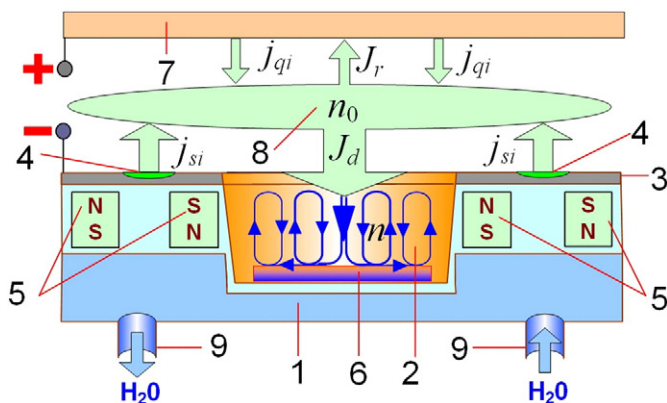


Fig. 1. Schematic cross-section of the APCS: 1 – the magnetron sputtering system; 2 – the hollow cathode; 3 – zinc target; 4 – the erosion zone; 5 – the magnet system; 6 – the substrate; 7 – the anode; 8 – the thermalization area of sputtered atoms; 9 – the running water-based cooler.

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