



Formation of porous nickel nanosystems using alumina membranes as templates for deposition



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ARTICLE INFO

Article history:

Received 5 March 2015

Accepted 29 March 2015

Available online 6 April 2015

Keywords:

Nanosystem

Nickel

Alumina membrane

Magnetron sputtering

Near-equilibrium condensation

ABSTRACT

A new technological approach has been proposed to obtain ordered porous nickel nanoclusters consisting of weakly connected uniform nanocrystals less than 10 nm in diameter. The near-equilibrium condensation conditions are used in combination with ultra-thin alumina membranes (UTAM) as templates. The low density nickel vapor flow obtained by magnetron sputtering at low discharge power was directed into the nm sized pores of the alumina membrane by means of perpendicular tubes positioned in the target-substrate area. The selective formation of porous structures inside the alumina membrane pores is caused by a low supersaturation of the nickel vapor and by a high temperature gradient along the pore length.

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1. Introduction

Nowadays, the catalysts based on porous nickel structures are widely used in chemical, food, pharmaceutical and other industrial applications [1–4]. It is known that catalysts performance is greatly enhanced by increasing porosity and decreasing the structural feature sizes to nanoscale. Porous metal systems are typically synthesized using de-alloying processes [5–11] or nano-patterning technologies [12–17]. It is necessary to point out that these methods do not allow the combination of high layer porosity and critically small sizes of the structural elements.

In contrast to the conventional methods mentioned above, we have proposed a technological approach that allows the formation of porous metal structures by condensation of the steady-state low-supersaturated vapor fluxes [18–26]. Here, the nucleation appears only on specifically active sites with an increased chemical binding potential. Further intergrowth of these structural fragments leads to pore formation. At this point, the crystals interface areas serve as new active sites for subsequent secondary nucleation. The cyclicity of these processes provides formation of rather thick porous layers.

As it have been shown in our previous experiments, nickel layers can be synthesized in the form of weakly bonded, roundish shaped crystals with diameter in the range of 3 to 10 nm using

near-equilibrium condensation conditions [26]. The present work is aimed to combine the near-equilibrium condensation concept with the use of ultra-thin alumina membranes as a template for deposition. It is supposed that such a combination allows the formation of ordered nanostructure systems on substrate surfaces with tuneable shapes, sizes and distances between the structural elements which themselves consist of nanosized structural elements.

2. Experimental

The porous nickel structures were obtained under near-equilibrium conditions in an ultrapure argon atmosphere additionally purified from chemically active residual gases using titanium sputtering method [27]. After this procedure, the partial pressure of all residual gases was $8 \cdot 10^{-8}$ Pa. The conditions close to thermodynamic equilibrium are characterized by extremely small value of the chemical potential difference $\Delta\mu$ for particles in vapor and condensed state. In general, the value of the chemical potential difference is determined by the following relation [22]:

$$\Delta\mu \cong k_B T ((P - P_0)/P_0) = k_B T \xi. \quad (1)$$

here T is the growth surface temperature; $\xi \cong (P - P_0)/P_0$ is the relative supersaturation; $\Delta P = (P - P_0)$ is the deviation of depositing vapor pressure P from the equilibrium value P_0 , which is

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determined by

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

where E_d is the adatoms desorption energy; $A(T) = \exp(\alpha + \beta T + \gamma/T)$ is a temperature dependent coefficient with constants α , β and γ characteristic for a particular material.

Relations (1) and (2) hold true only for low energy condensing atoms, in other words, when the vapor and the growth surface temperatures are close. The conditions are fulfilled when vapor flux is formed by a thermal evaporation method. On the other hand, ion sputtered atoms have energies in the range of 4–10 eV, which is almost one order of magnitude higher than that of thermally evaporated atoms [28]. This is the reason why the condensation process for ion-sputtered atoms proceeds in two stages. During the first stage, atoms interact with the growth surface partially losing their excess energy and adsorbing to the surface. Due to the energy exchange the temperature of the growth surface increases. As a result, according to relationships (1) and (2), the $\Delta\mu$ value decreases and the system approaches the equilibrium condition. At the same time, the probability of an incomplete thermal accommodation is rather high and atoms return back to the vapor state very frequently. In summary, it can be concluded that the probability for adatoms re-evaporation is much higher for ion-sputtered atoms than for thermally evaporated atoms. As a result, near-equilibrium conditions are more easily achieved. In our previous work [20] it was shown that for ion sputtered fluxes with elevated energy, the desorption energy value in Eq. (2) decreases to its effective value, which is given by

$$E_{dr} = E_d - \langle \Delta E \rangle. \quad (3)$$

here $\langle \Delta E \rangle$ is the mean decrease in the desorption energy due to the energy transfer from ion-sputtered atoms to the growth surface. This value was calculated in our previous article [22] to be proportional to the temperature of the ion-sputtered atoms. Substituting the effective desorption energy value E_{dr} , which is lower than the desorption energy E_d , into Eq. (2) leads to a decrease of the supersaturation value. This fact also confirms that near-equilibrium conditions are easier to be realized for ion sputtering techniques than for thermal evaporation. The calculations made in our previous works [18,20] have shown that porous layers are formed when $\xi < 0.1$.

Near-equilibrium condensation conditions have been realized using direct current magnetron sputtering. It is known that in the case of ion sputtering, the sputtered fluxes move in different directions with equal probability. For magnetron sputtering the atom velocity distribution is of cosine character [29]. Because the substrate area is considerably large, the direction distribution of the atoms near the growth surface is rather broad. This can lead to the deposition of atoms on the alumina membrane pore walls causing fast pore closure and, therefore, preventing ordered nanostructure formation.

In order to overcome this obstacle we have developed a new technological approach that allows the formation of narrow deposition fluxes that are strictly directed along the pores in the alumina membrane. The main element of the developed setup is a densely packed array of thin-walled copper tubes which have an inner diameter of 2 mm. This array is placed in the pathway of sputtered flux from the target to the substrate. The schematic cross-section of the setup is illustrated in Fig. 1.

It is necessary to point out that only the sputtered atoms moving parallel to the tubes array 6 can reach the membrane, the rest of them will be deposited on the tubes walls. The effectiveness of the narrow directed fluxes formation depends on the distance between the target 2 and the substrate 9. The flux is of the highest

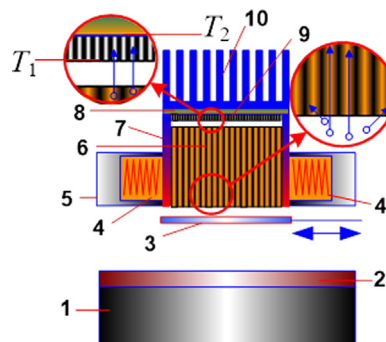


Fig. 1. The sputtering device with (1—magnetron sputter facility, 2—nickel target, 3—shield, 4—heating element, 5—heating element, 6—tubes array, 7—copper cylinder, 8—substrate, 9—membrane and 10—cooler).

value when the distance is comparable to the mean free path length of the sputtered atoms.

Besides formation of strictly directed fluxes of ion sputtered atoms, one additional problem needs to be addressed. Using the setup presented in Fig. 1, the condensation on the alumina pore walls has been prevented. But on the other side, the condensation on the membrane top surface must also be excluded, because it can impede atoms penetration inside the pores of the membrane. In order to minimize undesired condensation, the top surface of the alumina membrane was heated up to a temperature T_1 and critically low nickel vapor fluxes were used. Under the above described conditions, the chemical potential difference value above the membrane surface approaches $\Delta\mu \approx 0$. At the same time, the area of contact between the substrate and the ultra-thin-membrane should have a lower temperature T_2 (Fig. 1).

The temperature gradient $T_1 > T_2$ is realized by cooling the substrate 8 with the cooler 10 and simultaneous heating of the membrane surface by the heating element 4. Thereby, predominant condensation of nickel inside the pores of the ultra-thin alumina membrane is possible if the condition $\Delta\mu(T_2) > \Delta\mu(T_1) \approx 0$ holds true. According to Eqs. (1) and (2), these conditions can be realized by formation of critically small depositing fluxes at low vapor pressure values P and elevated temperatures T_1 .

For ordered nickel nanostructure formation ultra-thin alumina membranes with different pore diameters of 55, 70 and 95 nm have been used. The membrane itself was attached to the surface of a silicon substrate. The temperatures T_1 and T_2 are difficult to determine directly. Therefore we measured and controlled the temperature inside the copper cylinder 7 and the cooler 10 (Fig. 1). These values were varied in the range from 480 to 520 °C and from 130 to 170 °C, correspondingly. The working gas pressure was about 1.2 Pa.

3. Results and discussion

A set of experiments under a reduced discharge power has been performed in order to determine experimentally the technological conditions corresponding to porous nickel clusters formation. The discharge power P_w was gradually increased from 0.53 to 1.1 W. SEM (FEI NanoSEM 230 equipped with energy dispersive X-ray elemental analysis) and AFM (BRUKER Dimension Icon) investigations have shown that the cluster growth rate is negligibly slow at low discharge powers $P_w < 0.9$ W. In this case, the clusters height is less than 10–15 nm after 2.5 h of growth at $P_w \approx 0.8$ W. At the same time, no pore closure was observed at the top surface of the membrane.

In Fig. 2 SEM and AFM images of the structures obtained at $P_w \approx 1.1$ W are shown, (a) before and (b, c and d) after membrane

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