Physica B 411 (2013) 140–148

Contents lists available at SciVerse ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Self-organization of copper nanosystems under Volmer–Weber conditions during quasi-equilibrium condensation

V.I. Perekrestov, Yu.O. Kosminska *, A.S. Kornyushchenko, V.M. Latyshev

Sumy State University, R.-Korsakov 2, 40007 Sumy, Ukraine

ARTICLE INFO

Article history:
Received 24 September 2012
Received in revised form
20 November 2012
Accepted 27 November 2012
Available online 2 December 2012

Keywords:
Sputtering
Ostwald ripening
Quasi-equilibrium
Copper nanocrystals
Supersaturation
Porous structures

ABSTRACT

Copper nanosystems were obtained by means of magnetron sputtering and further deposition of extremely weak vapour fluxes onto glass ceramic substrates and KCl cleaved facets. The increased pressure (~10 Pa) of highly purified argon, low discharge powers (~24 W) of the magnetron sputterer, as well as relatively high growth surface temperature (~653 K) have been used during the technological process. The mechanisms of structure formation on different substrates were analysed by SEM, TEM and electron and x-ray diffraction. To explain the self-organization of low-dimensional systems we developed a mathematical model of mass transfer of sputtered substance within the space between the magnetron sputterer and substrate. On the basis of experimental and modelling studies it was found that Ostwald ripening of Cu nanocrystal systems is possible to realize on KCl (0 0 1) cleaved facets under conditions of critically low supersaturations and at increased concentration of nucleation sites.

1. Introduction

Currently the search of advanced formation technologies of monodisperse metallic nanosystems is intensively carried out. Such approach as volume gas condensation followed by subsequent deposition of finished clusters onto a surface [1–6] or synthesis from colloidal solutions [7–10] should be pointed out among the existing techniques of nanoparticles formation by means of "bottom-up" approach. Certain success in synthesis of nanoparticles of approximately identical size, shape and certain spatial arrangement was achieved through deposition onto substrates, containing ordered pores in aluminium oxide [11–13] or through self-organized growth on variously nanopatterned surfaces [14,15]. Self-organized growth is of peculiar interest and it is achieved by restructuring of a surface, e.g. using surface reconstructions, buried dislocation networks, vicinal or nanofaceted surfaces, adsorbed intermediate phases. However, according to the definition of self-organization term by Haken [16], the external action onto a system has to be non-specific, i.e. such that it does not impose a certain structure on the system. Here, if to take into account the effect of symmetrical structure of a substrate surface on the ordered formation of nanoparticles, then such self-organization seems to be partial. From this point of view further search of the technologies, revealing self-organization effects not supported by surface symmetry is still possible.

One of the promising fields is also self-assembly of nanosystems during condensation onto a substrate under proximity to thermodynamical equilibrium [17–20]. The driving force of such self-assembly is free energy minimization, which results in approximately identical forms and sizes of clusters [21–25]. There is a well-known technique of preparing semiconducting nanosystems (quantum dots) by means of molecular beam epitaxy (MBE) and metalorganic chemical vapour deposition (MOCVD), which are ordered spontaneously due to the elastic stress relaxation, occurring in a few monolayers of the deposited material [17,26–33]. In this case the nanosystem formation occurs under Stransky–Krastanov conditions.

In order to form the system of Cu nanocrystals we used low supersaturations and nucleation under Volmer–Weber conditions. At first sight such approach contradicts well-known nucleation mechanisms of metallic condensates. So, it is generally accepted that the nucleation mechanism of metallic condensate films under Volmer–Weber conditions has several stages [34–39]. At the first stage, a layer of overcritical nuclei of different size and shape is formed. The next stage is coalescence of islands which results in formation of channels. And at the final stage one can observe formation of a film with round shaped pores, which are skinned over by means of secondary nucleation. We consider these traditional ideas to be grounded on investigations of nucleation mechanisms during deposition of vapours with rather heightened supersaturations. To confirm this reasoning let us

* Corresponding author. Tel.: +380 542 687767; fax: +380 542 334049.
E-mail addresses: perv@phe.sumdu.edu.ua (V.I. Perekrestov), kosminska@phe.sumdu.edu.ua (Yu.O. Kosminska).

0921-4526/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.physb.2012.11.036

Table 1
The temperatures, corresponding to the equilibrium vapour pressures of 1.3×10^{-6} or 1.3 Pa for some metals, and their melting temperature [40].

Temperatures	Ag	Al	Cu	Cr	Au
Temperature (K) at $P^*=1.3\cdot10^{-6}$ Pa	847	958	955	1110	1080
Temperature (K) at $P^*=1.3$ Pa	1300	1490	1530	1670	1670
Melting point (K)	1233	933	1356	2173	1336

refer to the values of equilibrium vapour pressures (P^*) of the most studied metals. Obviously, equilibrium conditions correspond to the case when pressure of depositing vapour is comparable with its equilibrium pressure above the growth surface. It follows from the table data (see Table 1) that the negligibly low vapour pressures ($\sim10^{-5}$–10^{-6} Pa) are to be used in order to realize quasi-equilibrium condensation of different metals at growth surface temperatures of ~850–1160 K. It should be noted that metals are usually deposited under considerably high vapour pressures (~1.3 Pa). Therefore, in order to get critically low supersaturations, it is necessary to use the growth surface temperature, which exceeds the melting point for some of the metals (see Table 1). Such high condensation temperatures considerably complicate the technological process while using vapour fluxes, obtained by thermal evaporation.

The analysis of extensive experimental material given in [41] shows that the problem of quasi-equilibrium condensation at relatively low temperatures has to be solved through additional influence on the growth surface, e.g. by ions or atoms with heightened energy. The plasma–condensate system [42,43] can be one of the possible solutions. As it is shown below, the additional influence results in decrease in adatom desorption energy to effective value [42,43].

Taking into consideration all stated above, the main task of this paper is to study the self-organization mechanisms of Cu nanosystems at various densities of active nucleation sites on glass ceramics substrates and KCl (0 0 1) cleaved facets. Section 2 describes technological features of condensate formation. In Section 3 the results of structural studies are given, and Section 4 deals with the mathematical model of mass transfer of deposited substance which together with the elements of the Ostwald ripening theory explains self-organization of Cu nanosystems.

2. Experimental technique

The production of Cu nanosystems was carried out in the vacuum chamber equipped with two magnetron sputterers of Ti and one magnetron sputterer of Cu with unbalanced magnetic field. In order to prevent getting of Ti vapours into copper condensation area, the sputterers were partitioned. The necessary purity of argon was obtained by fulfilling the following operations in consecutive order:

i) After rough pumping and heating of the vacuum chamber the pumping system was completely disconnected from the working volume.
ii) The chamber was filled with argon up to the pressure of ~15 Pa.
iii) Two magnetron sputterers of pure titanium were turned on. Ti vapours were condensed onto the inner surface of the vacuum chamber and they absorbed chemically active gases.

The working gas had been purifying for 26–30 h and continued during deposition of copper. At the final stage of purification the total partial pressure of chemically active gases was $\sim8\times10^{-8}$–10^{-7} Pa and argon pressure was 10 Pa. Because of the low content of chemically active gases the probability of impurity phase formation was minimized while deposition of extremely low copper fluxes.

The control of residual gas composition was performed by the mass-spectrometer MX7304A (Selmi, Ukraine), absolute sensitivity of which is $\sim10^{-12}$ Pa. The measurement procedure of composition and partial pressure of residual gases are described in [44]. The investigations showed that oxygen, atomic hydrogen and nitrogen are absorbed sufficiently fast by titanium film; the residual gases consisted of hydrocarbons and their derivatives.

As a criterion of proximity to thermodynamical equilibrium, one can use low values of relative supersaturation

$$\xi=(n_a-n_e)/n_e, \tag{1}$$

where n_a and n_e are current and equilibrium concentrations of atoms above the growth surface correspondingly. The equilibrium concentration in the vapour–condensate system is given by [37,45]

$$n_e=\frac{\Upsilon(T_c)}{k_bT_c}\exp\left(-\frac{E_d}{k_bT_c}\right), \tag{2}$$

where $Y(T_c)$ is coefficient, which depends on growth surface temperature T_c and kind of material, E_d is adatom desorption energy, k_b is Boltzman constant.

The relations (1) and (2) show that low supersaturations can be obtained at decreased values of n_a (i.e. of deposited flux), increase in T_c, and at low values of E_d as well. In this connection it should be noted that the plasma–condensate system is more advantageous in comparison with the vapour–condensate system. The diffusive movement of sputtered atoms in plasma area determines their thermalization and corresponding energy of a few electron volt [46–48]. Thereby, the probability of thermal accommodation on the growth surface is reduced [37]. There is a possibility for plasma particles to transfer their energy to adatoms in plasma–condensate system. These factors in total reduce adatom desorption energy to effective value [42,43]

$$E_d^*=E_d-\overline{E}, \tag{3}$$

where $\overline{E}$ is mean value of energy transferred from plasma particles to adatoms, characterized by dispersion $\sigma_\tau^2\equiv\overline{(E_i-\overline{E})}^2$ (E_i is energy transferred to adatoms in the concrete case). Hence, for plasma–condensate system, the decrease in E_d to the effective value E_d^* brings the condensation conditions closer to equilibrium according to Eqs. (1) and (2). It is also necessary to point out that the energy of sputtered atoms and other plasma particles is averaged [43,46] at increased working gas pressure. This results in lowering of dispersion σ_τ^2 and in its turn defines higher stationarity of condensation process.

To determine the optimal technological conditions for obtaining of copper condensates, at first the series of experiments was carried out to estimate minimum value of magnetron sputterer power of Cu at which the first indications of nucleation took place. It is necessary to note, that extremely weak deposited fluxes were formed not only by low sputtering power ($P_w=24$ W), but also by increased pressure of working gas ($P_{Ar}=10$ Pa) which partially scattered the sputtered flux.

For transmission electron microscopy (TEM) studies, the discrete copper nanocrystals formed on glass ceramics and KCl (0 0 1) cleaved facets were preliminarily strengthened by graphite-like layers. Then a drop of gelatin dissolved in water was put onto condensate strengthened by carbon film. After drying of solution, gelatin with the condensate was separated from substrate, and then gelatin was dissolved in water and condensate was fixed on TEM grid.