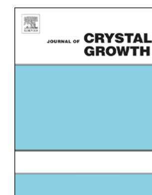
Journal of Crystal Growth 442 (2016) 68–74

Contents lists available at ScienceDirect

Journal of Crystal Growth

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



Formation of copper porous structures under near-equilibrium chemical vapor deposition

A.S. Kornyushchenko*, V.V. Natalich, V.I. Perekrestov

Sumy State University, Laboratory of Vacuum Nanotechnologies, 2, Rimsky-Korsakov Str., 40007 Sumy, Ukraine

ARTICLE INFO

Article history:
Received 31 August 2015
Received in revised form
25 February 2016
Accepted 26 February 2016
Communicated by: D.W. Shaw
Available online 4 March 2016

Keywords:
A1. Crystal morphology
A1. Nanostructures
A1. Nucleation
A3. Chemical vapor deposition processes
B1. Metals
B1. Nanomaterials

ABSTRACT

The mechanism of copper structure formation under near-equilibrium conditions in a chemically-active medium-condensate system has been investigated. The desired conditions have been implemented using CVD system. Copper chloride $CuCl_2$ was used as a source material, and mixture of hydrogen with nitrogen served as a working gas. The influence of the evaporation temperature, condensation temperature and state of the growth surface on the porous structures formation has been investigated. It has been established, that the structure formation mechanism is determined by layer-by-layer or normal crystal growth, nucleation and growth of whiskers, and also by partial intergrowth of structural elements.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Depending on structural and morphological characteristics porous structures and nanoparticles systems have great potential for application as catalysts [1–5], sensors [6–10], electrodes in electrochemical batteries [11–14], solar cells [15], fuel cells [16] and other active elements. Different methods are used with the purpose to form nanoparticles systems with uniform size and shape. Among them homogeneous nucleation from supersaturated vapors [17–22] and colloidal self-assembly [23,24]. Alumina membranes are widely used in order to form ordered nanoparticles arrays on the substrate [25–28].

One of the most widespread method of nanoporous metal structures formation is dealloying process, which consist in selective chemical or electrochemical etching of a desired component from its alloy [29–34]. Also porous metal nanosystems can be synthesized using a template with desired pore structure. After the cavities in the template are filled with a metal, the template material is removed [35,36].

Thus, the conventional methods of metal nanosystems synthesis in the form of ordered nanoparticles or nanoporous structures utilize rather complicated multistage processes. Our previous works [37–40] have shown that, self-assembling of ordered nanoparticles system or nanoporous structures can be implemented under near-equilibrium condensation conditions in the plasma-condensate system. It has been established, that the nucleation occurs only on the limited amount of active centers. In this case, the free energy minimization together with Ostwald ripening determine the monodispersity of the nanoparticles shape and size on the nucleation stage [41–44]. The more prolonged condensation results in the porous structures growth which is caused by an incomplete intergrowth of newly formed nanoparticles [45,37–39].

The analysis of literature reviews has shown that the technology of nanoporous metal structures self-assembling is at the early stage of its development. It is not mentioned even in quite recent reviews [46]. In order to provide an effective performance of the technologies operating near-equilibrium, tree problems have to be solved implementation of technological conditions for metals condensation at critically small supersaturations; realization of steady-state condensation conditions which allow to obtain reproducible structural and morphological characteristics; investigation of the interdependence between the process technological parameters and the structure formation mechanisms.

It is known that metals are bad-volatile substances having a low value of the equilibrium pressure. This fact complicates near-equilibrium conditions implementation. Obviously, under such conditions, the depositing vapor pressure should be of the same order as the equilibrium pressure. For the majority of metals (except Mg, Zn, Cd and Hg [47]) the equilibrium pressure does not exceed 10^{-5} Pa even for high temperatures. The realization of near-equilibrium conditions also requires deposition of extremely

* Corresponding author.
E-mail address: ganna.korniushchenko@fulbrightmail.org (A.S. Kornyushchenko).

http://dx.doi.org/10.1016/j.jcrysgro.2016.02.033
0022-0248/© 2016 Elsevier B.V. All rights reserved.

weak vapor fluxes. All these together, make it hard to control such weak fluxes and obtain reproducible results.

The equilibrium pressure can be increased conventionally by an increase in re-evaporation processes intensity. One solution is to influence by plasma onto the growth surface. In this case, the re-evaporation is enhanced not only by plasma heating, but also by direct energy transfer from the plasma particles to adatoms. In our previous works [38,45], this energy exchange was taken into account by the decrease in the desorption energy up to the effective value. It is known that, the equilibrium pressure value P_0 is determined by equation [48]:

$$P_0 = A(T_c)\exp\left(-\frac{E_d}{k_B T_c}\right), \quad (1)$$

here $A(T_c)$ is a coefficient which depends on the condensation temperature T_c, k_B is Boltzmann constant, E_d is the desorption energy.

Eq. (1) follows that a decrease in the desorption energy to the effective value leads to an increase in the equilibrium pressure value. Therefore, the plasma action onto the growth surface allows to deposit more intense and as a result more controlled vapor fluxes even at low supersaturations. In such a way the stationarity of the deposition process can be increased. In this context, a question arises how the chemically active medium influences the system approaching to the equilibrium. In [38] we have suggested that weakly bounded to the growth surface adatoms may react with other chemical elements and return to vapor state. For example, the adsorbed carbon atoms can be bonded with hydrogen and transform into more volatile hydrocarbon fraction which vaporizes at relatively low temperatures.

In order to provide near-equilibrium conditions for low-volatile substances, chemically active media such as chemically active gases should be used. In this case, re-evaporation of adatoms weakly bound to the growth surface is stimulated by reverse chemical reactions. In other words, the usage of the chemically active medium provides removal of adatoms which are weakly bound with the growth surface, providing selective condensation exclusively on active centers. The influence of the active medium leads to a decrease of the desorption energy up to effective value, and stimulates the approach of the system active medium-condensate to thermodynamic equilibrium conditions.

Quite often similar structures are obtained using absolutely different technologies utilizing plasma-condensate or chemically active medium-condensate systems. An example would be formation of different carbon molecular forms using CVD or PVD technology under near-equilibrium conditions [49–51]. Such similarities in the structures can be explained by identical thermodynamic conditions, which in turn are determined by the same values of the chemical potential difference of atoms in vapor and condensed state.

That is why, the aim of the work, firstly, is to study on the example of copper the nucleation and the growth mechanisms of condensates formation under near-equilibrium conditions implemented in the chemically active medium-condensate system. Secondly, to compare peculiarities of condensate formation mechanisms with our previous results obtained for the plasma-condensate system. We believe that this study will broaden significantly understanding of underlying physical process at condensation under near-equilibrium conditions.

In our previous works [44,52,53] the nucleation and growth of copper layers under near-equilibrium conditions in plasma-condensate system have already been studied. That is why copper has been selected in this work as a material for comparative analysis. It is necessary to point out, that the choice of copper is also caused by wide application of copper-based porous nano-systems as catalytic materials and biosensors [54–59]. Besides that, during the condensation process copper reacts badly with chemically active residual gases as compared to other metals. This fact is very important at low deposition rates. Thus, according to [60,61] pure copper layers can be formed under near-equilibrium conditions even in oxygen medium. The negligible influence of chemically active gases will allow to understand better peculiarities of the condensation process.

2. Methodology of the experiment

2.1. Materials

It is known, that decomposition of metallo-organic compounds is often used in order to synthesize metals by CVD. But these metallo-organic precursors are often unstable and can contaminate the resulting layer with carbon and oxygen. One of widespread methods of metals formation by CVD is usage of hydrogen reduction reaction from chlorides. In the case of copper, deposition can be carried out by the hydrogen reduction of the copper I chloride or copper II chloride. In [62] the following reduction reaction is given for CVD copper formation:

$$\mathbf{CuCl_2(powder) + H_2(gas) \rightarrow Cu(solid) + 2HCl(gas)} \quad (2)$$

In the article [63] the table of known copper precursors for CVD is presented. Among the all precursors both copper I chloride and copper II chloride are listed. Thus, $CuCl_2$ and CuCl both are well-known precursors.

But $CuCl_2$ is one of the most widespread copper compounds after copper sulfite. It's melting temperature is 498 °C and boiling temperature 993 °C. At 1000 °C copper II chloride decomposes into CuCl and Cl_2. For comparison, CuCl has melting point at 426 °C and boiling point at 1490 °C. In our work, the problem was to create extremely week copper deposition rates. That is why, we have chosen $CuCl_2$ as a precursor, because this compound has less amount of copper. As a source $CuCl_2$ 99.999% purity from the company ABCR was used, the mass of the substance used for one experiment was 8–10 g.

Silicon wafers with ⟨111⟩ orientation were used as substrates. It is known, that under near-equilibrium conditions the structure formation mechanism depends greatly on the growth surface state. That is why silicon substrates with both polished and rough (treated with a sandpaper) surface were used.

2.2. Methods

A self-made chemical vapor deposition (CVD) system was used in order to form copper layers. The schematic representation of the system is given in Fig. 1. The main element of the setup is a quartz tube which can sustain high heating temperatures. A tube of smaller diameter having narrowed end was installed inside in order to form a directed flow of a carrier gas. A mixture of hydrogen and nitrogen in ratio 1:3 was used as the carrier gas. The speed of the gas inlet was controlled by means of the flowmeter. The pressure control was installed with purpose to maintain a desired pressure. The vacuum conditions have been created by means of a turbo pump. The CVD setup has three temperature zones identified in Fig. 1 as zone 1, zone 2, zone 3. Different

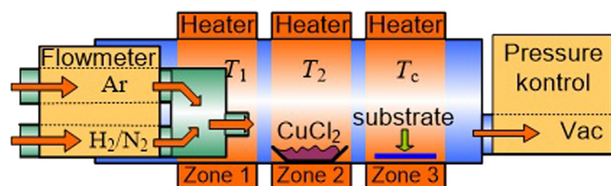


Fig. 1. Schematic representation of CVD device.

Download English Version:

https://daneshyari.com/en/article/1789677

Download Persian Version:

https://daneshyari.com/article/1789677

Daneshyari.com