The Process Chain of Electrodeposition

W. Plieth

Technische Universität Dresden, Institute of Physical Chemistry and Electrochemistry, 01062 Dresden, Germany

Received December 21, 2009

Abstract—The electrochemical processes on a growing metal layer can be described as a chain of processes consisting of nucleation and formation of a stable grain, growth of the active grain, and death of the active grain. Considering the statistical nature of the process chain, mean growth rate, mean lifetime, mean death rate, mean density and mean size of the active grains can be defined. Equations for the rate of nucleation are given in the literature. Stationary growth of the metal film is achieved if the rate of nucleation is equal to the death rate of active grains. From the condition of stationary growth an equation for the dependence of the average grain size on the experimental parameters can be derived. Several situations of metal deposition with different process parameters are discussed and compared with experimental results.

DOI: 10.1134/S1023193510100071

1. INTRODUCTION

Nucleation as the initiating process of formation of a new phase is well investigated and a variety of models have been developed. In electrodeposition two-dimensional nucleation on a silver surface has obtained special attention especially with the development of a process of preparation of mono crystalline silver surfaces free of any defects [1]. On the other hand, nucleation was studied by chronoamperometry on a variety of substrates and equations were derived describing the phenomena of instantaneous nucleation and progressive nucleation in a quantitative manner [2, 3]. But nucleation is only one step in electrocrystallization, followed by the sequence of steps a metal ion undergoes on its way to be built into the growing grains. Steps are bulk diffusion, charge transfer, surface diffusion and crystallization, each step connected with an individual part of the overpotential [4]. Recently the model of a process chain consisting of nucleation and formation of a stable grain, growth of the active grain, and death of the active grain was suggested. In this model nucleation is an essential step determining the properties of the newly formed film [5]. This model will be described in this paper in more detail.

2. THE FIRST STEPS OF FILM FORMATION

The initial step of film formation in electrodeposition is nucleation on the own or a foreign substrate. In case of a foreign substrate nucleation differs considerably from the traditional description of statistical nucleation, e.g. by the Volmer–Weber model. For high bond energies between the surface atoms of the substrate and the metal ions in the electrolyte underpotential deposition is expected and some epitaxial layers might be deposited before three-dimensional nuclei will be formed at surface and film defects. If the bond energies between the surface atoms of the substrate and the metal ions in the electrolyte are weak, the discharge of metal ions at surface structures and surface defects will start nucleation. The number of nucleation centers under such conditions is either constant (instantaneous nucleation) or might be increasing with increasing time (progressive nucleation). The number of nucleation centers will also depend on the overpotential, because with increasing overpotential less energetic sites will be available as nucleation centers [6]. Under such conditions different structures will develop, reproduction of the substrate structure, the development of field oriented structures or even completely non-oriented structures. Only at larger overpotentials nucleation according to the statistical probability of cluster formation (e.g. according to the Volmer-Weber model) will contribute.

The situation differs, if suitable additives are added to the electrolyte. If the additives are adsorbed on the substrate surface and are blocking the intrinsic nucleation centers, nucleation is only possible on the basis of statistical cluster formation, stationary aggregation with a critical size and a critical energy, before continuous growth of the cluster gets possible. These nuclei are formed on statistical positions on the surface of the substrate and, later on, on the surface of the growing layer. This is the principal basis for forming deposits with a microcrystalline structure, no longer reproducing surface topography.

The different conditions are also manifested in experimental current–potential curves. Anodic scans of zinc electrodeposition on a zinc surface are shown in Fig. 1 [7]. Curve (I) shows a scan in an industrial
alkaline electrolyte without additives. The cathodic current is increasing immediately after passing the equilibrium potential, is approaching a diffusion controlled limiting current before at higher overpotentials, caused by additional electrode processes, the current is increasing again. Curve (2) shows a scan in the same alkaline electrolyte after adding additives. Typically two types of additives, one for inhibition and a second one as grain refiner are used. The current is strongly inhibited because nucleation is inhibited. The current starts to flow, if the rate of nucleation gets large enough. The rate of nucleation is controlled by the statistical probability for nucleation. The current increases, probably proportional to the increasing rate of nucleation. It finally approaches a limiting current, which in this case is not diffusion controlled.

3. THE PARTIAL STEPS OF THE GROWING LAYER

To develop a picture of the growing metal layer it is necessary to understand that continuous growth is a special process chain with the chain elements continuously repeating on the surface. The chain elements are:

**Nucleation**

Nucleation can occur on grain boundaries, defects, steps or other structures of the surface. Inhibitors can block nucleation on such intrinsic nucleation centers. Then, following the laws of statistical nucleation, on the surface of the growing metal layer in a continuous manner new nuclei are formed. The process can be described by a nucleation rate, $r_{\text{nuc}}$, the number of nuclei formed per surface area and per second.

Equations for the nucleation rate depend on the model describing the nucleation process (chapter 4).

**Formation of a stable grain, growth of the grain**

The nucleus forms a stable grain, the grain is growing, it is called an active grain. In this process the volume of the active grain, $V_n$, is increasing with time and the growth rate can be defined by the equation:

$$ r_{\text{gr}} = \frac{dV_n}{dt}. $$

The volume on the surface of a growing metal layer has two independent coordinates, the area the active grain occupies on the surface, $F_n$, and the height, $h_n$: $V_n = F_n h_n$. The growth rate follows this separation:

$$ r_{\text{gr}} = h_n \frac{dF_n}{dt} + F_n \frac{dh_n}{dt}. $$

The average number of active grains on the surface, $N_n$, the density of active grains, is limited. A statistical image of the number of active grains on the surface in their different growth states is shown in Fig. 2. Only a limited area for each active grain is available on the surface. The statistical maximum area is $F_{n,\text{max}}$, which

---

**Fig. 1.** Cathodic potential scans of zinc electrodeposition on a zinc electrode (rotating disc electrode, 1000 rpm) [7]; (1) typical industrial zinc electrolyte without additives; (2) zinc electrolyte with additives; 10 mV/s.