

## Growth-inhibited nucleation of Ni nanoparticles on TiN substrates

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The electrochemical nucleation and growth of nanoparticles and thin films has been the focus of research over the past decades. For example in interconnect technology, high nucleation densities are needed for thin conformal seed layers to fill narrow features [1]. Nanoparticles are also of interest as electrocatalysts for fuel cells and electrolyzers [2], as well as for chemical catalysts for growth of one-dimensional nanostructures. For example, nickel nanoparticles are well suited for catalytic CVD of carbon nanotubes (CNT) [3]. In order to obtain high density CNT, high density of small Ni nanoparticles are needed. Therefore, we have studied the electrochemical deposition of Ni nanoparticles on TiN and found that the presence of  $H_3BO_3$  has a significant influence on the appearance of the deposit.

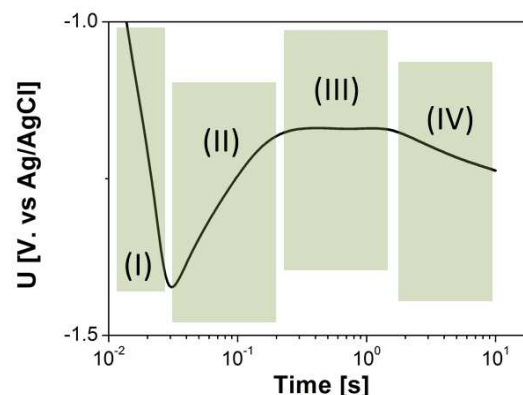
Figure 1 shows the potential transients during galvanostatic deposition of Ni. Typically, four different regimes are visible. After capacitive charging (I), Ni nanoparticles nucleate on the substrate causing the potential to shift to less negative potentials (II). The third regime (III) relates to the growth of the particles. The drop in potential in regime IV is associated with the termination of Ni deposition. It was observed that  $H_3BO_3$  has a significant influence on both the nucleation as the growth phase of the particles. Indeed, when lowering the  $H_3BO_3$  concentration, the particle density (nucleation stage) increases, however it also reduces the active time of Ni particle growth (i.e. faster growth termination). Hence, boric acid controls the balance between particle size and particle density.

To explain these observations, we propose a growth-inhibited nucleation model linked to the surface pH close to the particle (Figure 2). During Ni deposition, part of the current is consumed by hydrogen evolution resulting in a rise in the surface pH. This typically leads to the formation of undesired  $Ni(OH)_2$ . To counteract this, boric acid is commonly added to the solution to buffer the surface pH [4]. However, our observations indicate that the formation and adsorption of  $Ni(OH)_2$  on the Ni particles during the nucleation stage inhibits further particle growth. When the growth of existing nuclei is blocked by an inhibitor, the system is forced to form new nuclei on the substrate. Therefore, a higher particle density is observed at low  $H_3BO_3$  concentrations.

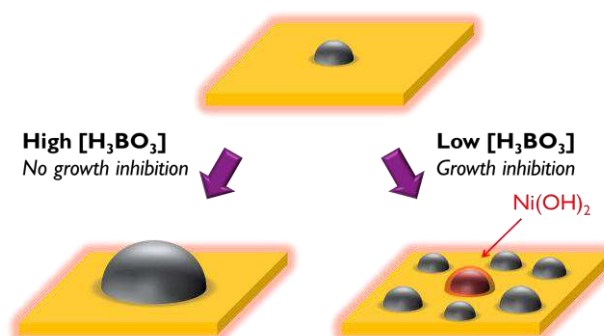
The drawback of low  $H_3BO_3$  concentrations is that also the Ni deposition itself gets terminated quickly after  $Ni^{2+}$  reduction becomes diffusion limited. Indeed, when also the proton reduction becomes diffusion limited, the strong increase in surface pH as a result of water reduction, causes the termination of the Ni deposition reaction. Boric acid prolongs the stage of proton reduction by its buffering reaction, thereby postponing the onset of

water reduction. This phenomenon determines the attainable particle size but, importantly, also affects the particle density in case termination already happens during nucleation stage. Hence, a trade-off boric acid concentration is found for certain maximum particle density and size.

From the learning above, we adjusted the bath composition to achieve a high degree of growth-inhibition without termination in the nucleation stage. In this way, continuous thin films down to 1nm were fabricated. In this paper, we will describe the mechanism behind this growth-inhibited nucleation and how to electrochemically deposit thin Ni films.



**Figure 1:** Potential transient during galvanostatic deposition of Ni on TiN using 5 mM  $NiCl_2$  + 100 mM KCl + 50 mM  $H_3BO_3$  (pH=3) at  $-10 \text{ mA/cm}^2$ . Four different regimes are present in the deposition of Ni.



**Figure 2:** Model of deposition modes of Ni deposition on TiN as function of  $H_3BO_3$  concentration. Left: No growth inhibition at high  $H_3BO_3$  concentration. Right: Growth inhibition at low  $H_3BO_3$  concentration.

### References:

- [1] M. Nagar, A. Radisic, K. Strubbe, P. M. Vereecken, *Electrochim. Acta* **92**, pp. 474-483 (2013)
- [2] M. Shao, K. Sasaki, R. R. Adzic, *J. Am. Chem. Soc.* **128**(11), pp. 3526-3527 (2006)
- [3] A. Romo-Negreira, D. J. Cott, S. De Gendt, K. Maex, M. M. Heyns, P. M. Vereecken, *J. Electrochem. Soc.*, **157** (3), K47-K51 (2010)
- [4] R. Orinakova, A. Turonova, D. Kladekova, M. Galova, R. M. Smith, *J. Appl. Electrochem.* **36**, pp. 957-972 (2006)