

ELECTROCHEMICAL DEPOSITION OF FLOWER-LIKE NICKEL NANOSTRUCTURES ON WELL-DEFINED n-Si(111):H

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Abstract In this paper the electrodeposition of nickel on n-Si(111):H substrate, in the presence of sulphuric acid, was studied. Cyclic voltammetry has been used to characterize the electrochemical behavior of the system. The nickel deposits had a flower-like morphology with the spherical nanostructure nucleus, distributed uniformly on the surfaces of the prepared n-Si(111) substrate.

Keywords Deposition, Metals, Alloys, Microstructure, Nanomaterials

چکیده: رسوب الکتروشیمیایی نیکل روی تک کریستال سیلیکون (۱۱۱) در حضور اسید سولفوریک مطالعه گردید. از ولتامتری چرخه ای برای فهم رفتار الکتروشیمیایی سیستم استفاده شد. رسوبات نیکل دارای شکل گل مانندی بودند که از جوانه های نانویی شکل گرفته بودند. این رسوبات روی سطح کاملاً یکنواخت توزیع شده اند.

1. INTRODUCTION

Electrodeposition of nickel nanostructures has been investigated intensively during the past decades in relation to its particular mechanical properties and numerous applications in industry [1-3]. Nano-sized nickel catalysts have received increasing attention since these materials exhibit many fascinating chemical and physical characteristics and show great potential for many technological applications [4]. It is reported that nano-sized nickel catalysts show better catalytic properties in the catalytic hydrogenation or dehydrogenation reactions [5-8]. In addition, Electrodeposited nickel has been subjected to extensive scientific investigations, in the areas of mechanical properties [9,10] and creep behavior

[11]. Nickel has been deposited from several electrolytes such as Watts, sulphatic, chloride, nickel sulphamate and nickel flouoroborate.

Thin metallic films electrodeposited onto silicon surfaces are of great interest in the metal/semiconductor Schottky junctions. Many researchers have reported their electrochemical conditions for deposition of metal films on silicon substrates [12,13]. Among semiconductors, silicon is one of the most interesting and important materials due to its vast range of applications, e.g. microelectronics, solar cells and etc. Thus, deposition on a silicon surface is a rapidly growing area of research [14]. Reitzle, et al [15] used an acidic electrolyte containing H₂SO₄, for electrodeposition of copper nanostructures. In the present study, a similar acidic solution was used

for electrodeposition of nickel nanostructures on well-defined n-Si(111):H.

Scanning electron microscope (SEM) was utilized to study the deposition process and morphology of the electrodeposited nickel novel nanostructure. A new novel morphology was observed during the electrodeposition processes.

2. EXPERIMENTAL

One-sided polished n-Si(111) samples and phosphorus-doped, with a miscut angle of about 0.1° were used. They were cleaned by following the RCA cleaning procedure [16], which meant degreasing in 2-propanol under reflux for 2h and then boiling them alternatively in basic and acidic H_2O_2 solutions ($NH_3:H_2O_2:H_2O = 1:1:5$ and $HCl:H_2O_2:H_2O = 1:1:5$) for 15 min each. Prior to each experiment the samples were etched for 1 min in 50 % HF to remove the oxide layer and for 3 min in 40 % NH_4F . This last step is known to result in well-defined, monohydrid-terminated Si(111) [Si(111):H] surfaces with large, atomically flat terraces [16].

All electrochemical measurements were carried out in a typical three-electrode cell. A platinum rod was used as counter electrode. All potentials are reported with respect to the Ag/AgCl electrode. Nickel was deposited from 0.1 M H_2SO_4 + 0.1mM $NiSO_4$ solution was prepared from $NiSO_4$ (Merck, Germany), H_2SO_4 (Merck, Germany). The preparation of the solution was completed by dissolving the above in triply distilled water. All electrochemical experiments were carried out using an Autolab potentiostat/galvanostat model PGSTAT30. Cyclic voltammetry sweeps were recorded and the scan rate were from 50 to 500 mV/s. The voltammetric scans were performed in the potential range from -0.5 to -1.7 V vs. Ag/AgCl electrode. The potentiostatic transients were recorded at time intervals of 10 s. The potential was stepped from 0 V to -0.7 V and also every 50 mV up to -1.3 V for the nickel.

The transition times were also measured as a function of current density. The morphology of the electrodeposits was characterized with a scanning electron microscope (SEM, Philips XL30), equipped with energy dispersive X-ray (EDX)

analysis which was used for compositional analysis of the electrodeposited nanostructures.

3. RESULTS AND DISCUSSION

Cyclic voltammetry was used to define the reduction potential regions, and characterize the nickel deposition process. Cyclic voltammograms for the deposition of nickel on n-Si(111):H, at different scan rates, are shown in Figure 1. These curves show no reduction peak. Generally, in the cyclic voltammetry curves, the presence of a peak in the forward sweep indicates the behavior of the electrolyte follows the ion transfer mechanism. In this case, no reduction peak was observed which shows, the deposition from this electrolyte follows the charge transfer mechanism. This result can be attributed to the absence of the agents in the solution [17].

The voltammograms showed that in more negative potentials the slope of the curves decreased intensely. It can be more obviously seen, at the potentials more negative than -0.65 V, the curves were mostly smooth and the slopes of the curves decreased. These variations in the slopes of the curves can be attributed to the hydrogen released from the cathode. Note that the sufficient pH for deposition of nickel is in 5-6 range, and in this study the pH was about 1, in which high concentration of hydrogen caused its release on the cathode. In the first stages of this electrochemical process, the current density increased with respect to the potential. It means that the proton reduction occurred rapidly, with the increase in absolute potential. Increasing in scan rates, causes more vertical curves and the vertical part is called hydrogen walls. As more negative potential, the proton transfer to cathode is the limiting factor which caused the flat portion of the CV. It is noticeable that the cation reduction probably occurred in parallel. It can be observed in the following, the reduction of the nickel ions also occurred, but the amount is negligible and not observable in the electrochemical results.

Chronoamperometric analysis was used to study the mechanism of electrodeposition of nickel. A typical Potentiostatic current density-transient curves are shown in a wide range of the cathodic

potentials from -0.7 to -1.3 V in Figure 2. Each transient has one well defined recognizable current maximum as a clear peak, followed by a sharp fall. The I-t transients have a normal dependence to overpotential, whereas the current density increases with the increasing of overpotential.

At such acidic pH and also a diluted Ni concentration, the partial current related to Ni^{2+} reduction is about 0.01 to 0.001 of the total parallel current which is mainly arising from the reduction

of protons. Hence, we can not deduce anything reliable about the nucleation and growth modes from the current transients. Consistent with this fact, transients only show a current decay, which is probably related to depletion of protons as the reaction proceeds.

Morphological analyses were performed by scanning electron microscope (SEM). The images of the deposits are shown in Figure 3. Figure 3a shows that the deposition process has not occurred

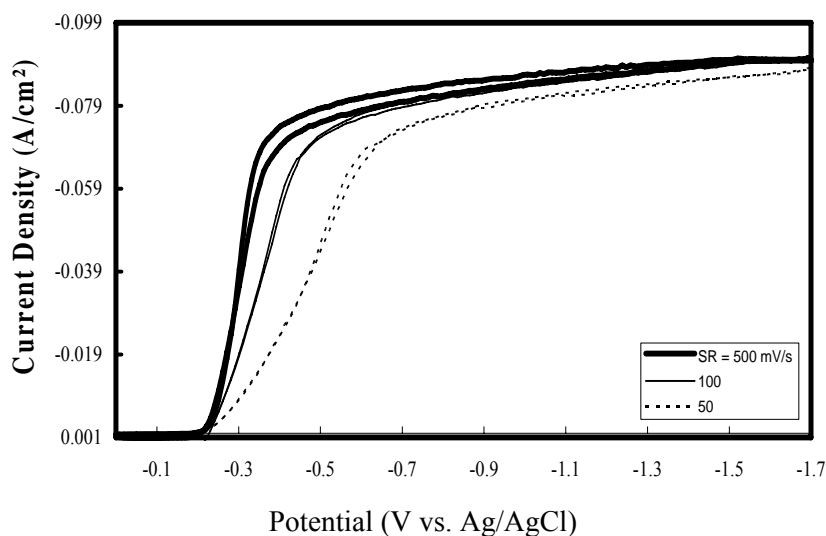


Figure 1. Cyclic voltammograms for deposition of nickel in 0.1 M H_2SO_4 + 0.1 mM NiSO_4 (scan rate = 50-500 mV/s).

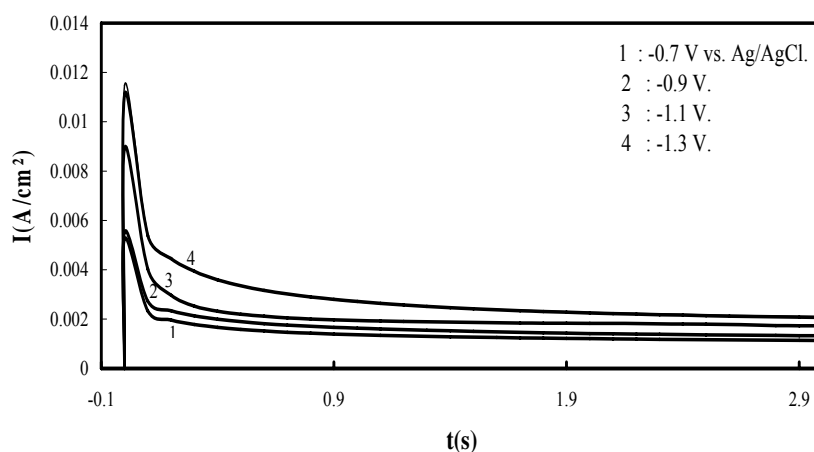


Figure 2. Potentiostatic I-t transients for deposition of nickel in 0.1 M H_2SO_4 + 0.1 mM NiSO_4 , potential range of -0.7 to -1.3 V vs. Ag/AgCl electrode.

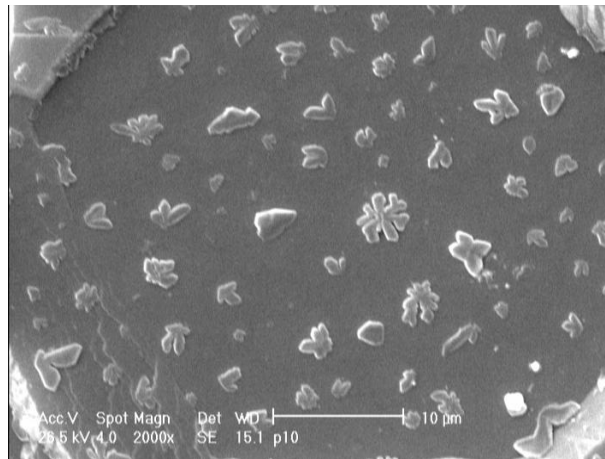
preferentially and distribution of the deposits on n-Si(111) is perfectly uniform. When high growth rates are observed, it can be seen that, growth does not take place in preferential directions hence spherical nucleus are obtained [19]. In this study the nuclei were spherical (Figure 3b), but the final deposits which were grown from these nanoscale nuclei had a flower-like structure (Figure 3c). Although it is reported that nickel deposits mostly grew three dimensional and have a spherical shape, here the deposits have a flower-like structure with convex angles which showed the growth direction of the nickel grains (Figure 3c). It is important to note that the grains which have convex angles will grow and form the final nanostructures. The electrocrystallization includes several steps in which the final step is the appearance of the deposited morphology. Generally, the deposits growth follows the nucleation of very thin molecular layers. These growth centers will develop to reach each other and form initial monolayer deposits. Then, more growth is needed to nucleate some new centers on these initial layers. Such a growth mechanism of the monolayer deposits is known as two-dimensional electrocrystallisation. EDX compositional analyses performed on the deposits, confirmed the formation of, pure nickel nanostructures in the electrochemical conditions applied to the system. Also regarding the electrochemical conditions applied to the system and pH of the initial solution, formation of pure nickel is thoroughly expected. Formation of such a flowerlike nanostructure has not been reported for nickel. This novel structure of nickel has a very attractive application, as a very effective nanocatalyst for synthesis of carbon nanotubes using chemical vapor deposition (CVD) method which will be reported by the same authors in the near future.

4. CONCLUSION

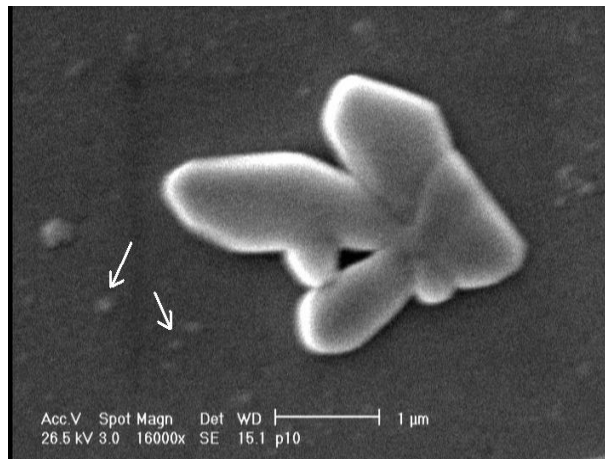
The electrodeposition of nickel nanostructures on n-Si(111):H substrate, in the presence of sulphuric acid, was investigated. The final morphology of the nickel deposits was a flower-like formation while the initial nucleus had a nano scale size and a spherical shape. “”

5. REFERENCES

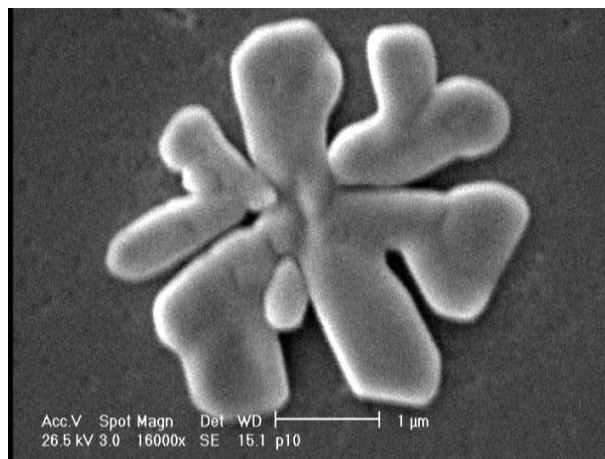
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(a)



(b)



(c)

Figure 3. SEM images of nickel nanostructures.

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