Effect of deposition time and potential on the nucleation and growth of nickel nano particles on nitrogen doped diamond-like carbon thin film

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A R T I C L E  I N F O

Available online 8 January 2012

Keywords:
Nickel nano particle
Deposition potential
Deposition time
Nitrogen doped diamond-like carbon

A B S T R A C T

In this report, the effect of electro-deposition parameters (deposition time and deposition potential) on the growth of nickel nano particles (Ni NPs) on nitrogen doped diamond-like carbon (N-DLC) thin film has been investigated. The investigation parameters are 0.1 M Na₂SO₄ aqueous solution containing 4 mM NiSO₄, the deposition period altering from 2 s to 60 s and the deposition potential ranging from −1.1 V to −1.4 V. Voltammetry and potential amperometry have been used to study the electrochemical process. The morphology and chemical composition of the NPs have been examined with atomic force microscopy and X-ray photoelectron spectroscopy. It is found that the growth of Ni NPs is accompanied by the continuous nucleation. The nucleus density and size of the NPs increase with the decrease of deposition potential. Thus the morphology of Ni NPs deposited on N-DLC film can be controlled through the deposition potential and time.

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1. Introduction

Metallic nano particle (NP) modified electrodes have received great attention in electro-analysis due to their high effective surface area, mass transport, catalysis and control over local micro-environment [1,2]. There are two techniques that are commonly used to deposit metallic NPs onto electrodes: vapor deposition and electro-deposition. Electro-deposition is a convenient and attractive technique for electrode modification, because it is applicable to wide-bound substrates and needs no advanced instrument with expensive or complex technology. Furthermore, the process of modification can be easily controlled by deposition parameters such as deposition time and potential, metal ion concentration and deposition stages [3–8].

In the past 30 years, highly boron doped diamond (BDD) thin film electrodes have been investigated widely for electro-analysis because of their low background currents and wide electrochemical windows [9]. They have been used as substrates to deposit metallic NPs such as Cu, Ni, Pt, Ag, Pd, Co [10–15]. However, BDD electrodes can achieve lower detection limits with or without surface modification. The difficulties in the fabrication of BDD film electrodes, i.e. high deposition temperature, pre-treatment for substrates and post-deposition polishing, drawback their applications. Recently, there is research effort to replace BDD electrodes with nitrogen doped diamond-like carbon (N-DLC) thin film electrodes [16,17].

N-DLC thin film electrodes have smoother surfaces because of amorphous structure, and possess many properties similar to those of BDD thin film electrodes [18–20]. N-DLC electrodes possess favorable characteristics, such as excellent chemical inertness, room deposition temperature, non surface pre-treatment required for substrates, easy surface modification, and comparable electrochemical characteristics to those of BDD [20]. Furthermore, N-DLC films can be micro-fabricated with conventional semiconductor technology into micro-electrode arrays to serve as micro-biosensors, which can be easily integrated into micro-fluidic channels to produce lab-on-chip devices.

The authors have reported that the electro-deposited nickel (Ni) NPs on N-DLC film electrodes can be used for glucose sensing [21]. In order to optimize the morphology of Ni NPs for glucose sensing, the NPs with different morphology should be fabricated at first. In this work, the effect of the deposition time and potential on the growth of Ni NPs will be investigated.

2. Experimental

2.1. The N-DLC thin film deposition and the preparation of Ni NPs

The N-DLC films were deposited using the method of radio frequency (RF) plasma enhanced chemical vapor deposition in the company (J&L Tech Co, LTD, Korea). Single-side polished p-silicon wafers <100> (0.001–0.003 Ωcm) were used as substrates. Titanium layers on the rear sides of silicon wafers acted as ohmic contacts. A mixture of nitrogen and methane gases with flow ratio of 1:10 was used for in situ doping and carbon source during the film deposition. The work...
The cyclic voltammogram (Fig. 1) of the N-DLC thin film electrodes in 0.1 M Na₂SO₄ aqueous solution containing 4 mM NiSO₄ has been used to determine the deposition potential. An increasing cathodic current observed at about −0.6 V represents the reduction of aqueous Ni²⁺ to metallic Ni at the N-DLC electrode surface (the inset in Fig. 1). Therefore Ni NPs can be deposited at a potential more negative than −0.6 V Ag/AgCl. An oxidation peak appearing at the potential of −0.5 V on the positive scan corresponds to the dissolution of metallic Ni back into the solution.

### 3. Results and discussion

#### 3.1. Cyclic voltammogram of Ni²⁺ at the N-DLC film electrode

The cyclic voltammogram (Fig. 1) of the N-DLC thin film electrodes in 0.1 M Na₂SO₄ aqueous solution containing 4 mM NiSO₄ has been used to determine the deposition potential. An increasing cathodic current observed at about −0.6 V represents the reduction of aqueous Ni²⁺ to metallic Ni at the N-DLC electrode surface (the inset in Fig. 1). Therefore Ni NPs can be deposited at a potential more negative than −0.6 V Ag/AgCl. An oxidation peak appearing at the potential of −0.5 V on the positive scan corresponds to the dissolution of metallic Ni back into the solution.

#### 3.2. The effect of deposition time on growth of Ni NPs

Fig. 2 illustrates the curve of current–time at the potential of −1.2 V for the electro-deposition of Ni NPs. The deposition process can be divided into five time intervals (the time zones of I, II, III, IV and V in Fig. 2). At the very beginning, the process corresponds to the step of the double-layer charging (zone I). A sharply increased current can be found, i.e. from 0 to 2.7×10⁻⁵ A, followed by a decay of the current. The sharp increase of current is caused by the double layer capacitance charging. Because of the very small value for the double layer capacitance at the N-DLC electrode, the charging period is so short (≪0.1 s) that the electrochemical facility cannot respond to it. The current increases during the period from 2 s to 8 s (zone II), and the increase of current is due to the growth of independent nuclei and simultaneously developed nuclei without overlapping effect. Theoretically, at this step, the current increases with t², and the nucleation is progressive [9]. Therefore, the size and nucleic density of Ni NPs increase. In the period from 9 s to 22 s (zone III), the diffusion overlap to several particles happens. There are two opposite effects occurring in this interval: the development and growth of independent nuclei and the diffusion overlap. Due to the overlap, the rate of current-increase decreases till the current reaches a maximum at 22 s. In the period from 22 to 39 s (zone IV), the domination of the diffusion overlap causes the current to decrease slightly. Since...
39 s (zone V), the rapid development of nuclei makes the current increase again.

Fig. 3 presents the 2-D AFM images of the growth of Ni NPs at different deposition times at $-1.2 \, \text{V} \, \text{Ag/AgCl}$ with the analyzed volume histogram. For the as-deposited N-DLC substrate, the 2-D AFM image and its volume histogram indicate that the surface is very smooth and homogeneous. For the deposition time altering from 2 s to 60 s, the 2-D AFM images and volume histograms show the increase of Ni NP size.

Fig. 3. The 2-D AFM images and volume histograms of the nickel nuclei grown on N-DLC electrodes depending on the deposition time, and comparing with those of an as-deposited N-DLC electrode (the deposition condition: 4 mM NiSO$_4$ + 0.1 M Na$_2$SO$_4$ solution and potential at $-1.2 \, \text{V} \, \text{Ag/AgCl}$).
accompanied with the development of new nuclei. This phenomenon is consistent with the shape of current–time curve in the intervals from II to V in Fig. 2. Fig. 4 presents the dependence of the mean particle volume and particle number on the deposition time at $-1.2\ \text{V} \ \text{Vs Ag/AgCl}$. It is found that the particle number increases with the deposition time. However, there are new nuclei developed continuously, the mean volume of the Ni NPs still increases with deposition time.

3.3. The effect of deposition potential on the growth of Ni NPs

Fig. 5 presents the 2-D AFM images and line profiles of the Ni NPs grown at different deposition potentials. All the particles have a cone-like shape (the line profile in Fig. 5), and the statistic data is presented in Table 1. However the total volume of the Ni NPs increases with the decreased potential, the number of the Ni NPs decreases with the decreased potential. Therefore the mean volume of each particle increases with the decrease of potential (see Table 1). Comparing the respective images of Ni NPs deposited at $-1.1\ \text{V}$ and $-1.4\ \text{V}$, it is found that the particle density decreases while the size of the particles increases with the decrease of deposition potential. The decrease of

<table>
<thead>
<tr>
<th>Potential (V)</th>
<th>Particle Number</th>
<th>Total Volume ($\mu m^3$)</th>
<th>Mean Volume ($\mu m^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-1.1\ \text{V}$</td>
<td>87</td>
<td>$2.47 \times 10^{-2}$</td>
<td>$2.84 \times 10^{-3}$</td>
</tr>
<tr>
<td>$-1.2\ \text{V}$</td>
<td>66</td>
<td>$8.51 \times 10^{-2}$</td>
<td>$1.29 \times 10^{-3}$</td>
</tr>
<tr>
<td>$-1.3\ \text{V}$</td>
<td>49</td>
<td>$8.63 \times 10^{-2}$</td>
<td>$1.72 \times 10^{-3}$</td>
</tr>
<tr>
<td>$-1.4\ \text{V}$</td>
<td>38</td>
<td>$1.63 \times 10^{-1}$</td>
<td>$4.28 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Fig. 5. The statistic results of the nano particles deposited at different time (deposition potential was $-1.2\ \text{V} \ \text{Ag/AgCl}$).

Table 1
The statistic data of the Ni NPs deposited at different potentials (the deposition time was 40 s).

Fig. 5. The 2-D AFM images and line profiles of nickel nano particles deposited on the N-DLC surface in 4 mM NiSO$_4 + 0.1$ M Na$_2$SO$_4$ solution at deposition potentials of (a) $-1.1\ \text{V}$, (b) $-1.2\ \text{V}$, (c) $-1.3\ \text{V}$, and (d) $-1.4\ \text{V}$ (the deposition time was 40 s).
nucleic density would be due to the effect of hydrogen evolution that makes the sites for Ni nucleation more selective.

Fig. 6 presents the XPS spectrum of the Ni NPs modified N-DLC surface. The film surface mainly consists of C, N, and the O elements. The O element comes from the oxides produced with the residual oxygen in the vacuum chamber during deposition and with the oxygen when the film is exposed to air. The zoomed-up curve (the inset in Fig. 6) shows a clear peak at the binding energy of 855 eV corresponding to Ni 2p3/2, and it provides the evidence that the NPs are made of Ni.

4. Conclusion

Ni NPs have been deposited on N-DLC film surface by using electro-deposition technology. The effect of deposition time and potential on the nucleation and growth of Ni NPs have been investigated. The Ni NPs grow with the deposition time and are accompanied by continuous nucleation. The nucleic density decreases with the decrease of deposition potential while the mean particle size increases. Thus the particle size and density can be controlled through the two deposition parameters.

Acknowledgments

Y. Jin is grateful for the scholarship of Brain Korea 21. The authors acknowledge the J&L Tech Co, LTD, Korea for the deposition of N-DLC film. This project was financially supported by the Plasma Bioscience Research Centre (SRC) of the Kwangwoon University through the National Research Foundation of Korea (Grant No: 20100029417).

References