

The Termodynamic Model of Open-Circuit Potential for Electroless Deposition of Ni on Silicon

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This investigation first proposed that open-circuit potential vs time (OCP-*t*) is a novel nonlinear potential step controlled by redox reaction and nucleation. A novel thermodynamic model of OCP-*t* is obtained for electroless deposition of Ni on Pd-activated p-type silicon(100). Thermodynamic transient properties such as capacity of double layer *C*, surface charge density *q*, interfacial tension  $\gamma$ , and resistance of chemical reaction *Rr* are calculated. Results show that the variation of OCP is dependent on the interfacial double layer. The breakdown and rearrangement of the double layer causes surface charge density step, which triggers momentary nucleation of Ni on the substrate. Results also show that reductant pulses would be an effective way to speed nuclei growth.

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Open-circuit potential vs time (OCP-*t*) has been proved a sensitive and effective technique for sensing transient mixed potential at the interface of solid/solution. It has been applied in monitoring the corrosion behavior of metal,<sup>1-3</sup> hydrogen absorption in Pd electrodes,<sup>4</sup> oxygen,<sup>5</sup> carbon monoxide,<sup>6</sup> adsorption in Pt/Pd electrode, and characterization of acrylic hydrogels.<sup>7</sup> Our group also reports its application in electroless deposition of Ag.<sup>8</sup> However, the methodology of OCP-*t* is still undeveloped. Few papers on the mathematic model of OCP-*t* is used to propose for electroless deposition. We believe that it would be helpful to understand the process of electroless deposition and develop further applications of OCP-*t*.

Electroless deposition of metal films on silicon such as aluminum,<sup>9</sup> copper,<sup>9-11</sup> silver,<sup>12,13</sup> gold,<sup>14</sup> nickel,<sup>15,16</sup> NiP alloy,<sup>17</sup> NiB alloy,<sup>18</sup> and CuNi alloy<sup>19</sup> have been investigated. The nucleation and reaction mechanisms<sup>16-20</sup> have also been studied. However, the transient information of electroless deposition is still blurry and needs to find a sensitive technique to describe it. OCP-*t* is an ideal option for this purpose because it can record transient potential of electroless deposition effectively.<sup>8</sup> Other transient techniques controlled by outer circuits such as conventional potential step and current step make it difficult to acquire actual information of electroless deposition.

During the electroless deposition process, there are six processes occurring on the surface of samples, which include: (*i*) mass transport of ions, (*ii*) migration of ions, (*iii*) charge or discharge of double layer, (*iv*) adsorption or desorption of ions, (*v*) chemical reaction, and (*vi*) nucleation on the substrate.<sup>21</sup> In this experiment, the mass transport and migration of ions can be ignored because of agitating strongly. NiSO<sub>4</sub> solution and NH<sub>2</sub>NH<sub>2</sub> reductant are selected because their reactions are clear. Amperometric *i*-*t* is used to acquire transient current of electroless deposition. Ni film and Pd seed layer are characterized by atomic force microscope (AFM) and differential pulse voltammetry (DPV).

#### Experimental

Instruments and software.— AFM (Explorer, Veeco Co., USA) in contact mode, electrochemical workstation (CHI660A, Shanghai, China), and pH meter (PHS-3B, Shanghai, China) were used. A homemade electrochemical cell of Teflon with three-electrode configuration (shown as Fig. 1) was used. A p-Si(100) wafer sample served as the work electrode with a disk area of 12.56 mm<sup>2</sup>. A saturated calomel reference electrode (SCE) and a platinum auxiliary electrode were used. Data of OCP-*t* and *i*-*t* were fitted with Origin 7.0 (OriginLab Co.). The drawing of the cell was done by Autocad2006 (Autodesk Co.).

Chemicals and materials.— Analytical reagent grade NiSO<sub>4</sub>.  $\cdot$ 6H<sub>2</sub>O, NH<sub>4</sub>OH (61%), HCl (36%), H<sub>2</sub>O<sub>2</sub> (31%), HF (40%), NH<sub>4</sub>F, and hydrazine hydrate N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (50%) were used. A solution of 0.05 mol L<sup>-1</sup> NiSO<sub>4</sub> was prepared by dissolving 1.3143 g NiSO<sub>4</sub>·H<sub>2</sub>O in 100 mL redistilled water in a flask. Redistilled water was used throughout. Nitrogen was purged for solution deaeration. A p-type crystalline silicon(100) wafer with a resistivity of 10–20  $\Omega$  cm and a thickness of 525 ± 25  $\mu$ m (Beijing Youyan silicon villa semiconductor) was used.

*Wafer treatment and preparation of Pd seeds.*— The treatment of silicon wafer was the same as in Ref. 8. The etched silicon wafer is immersed in the solution of  $0.005 \text{ mol } \text{L}^{-1} \text{ PdCl}_2 + 0.06 \text{ mol } \text{L}^{-1}$  hydrofluoric acid (HF) for 20 s to obtain the Pd seeds.

*Electrochemical measuring.*— The silicon wafer with Pd seed layer was fixed on the conductor of the cell (see Fig. 1). The measurement of OCP-*t* was done as follows: (*i*) stirred with 753.6 rad/s, (*ii*) 0.05 mol  $L^{-1}$  20 mL NiSO<sub>4</sub> solution was added into the cell at



**Figure 1.** Configuration of electrochemical cell: (1) SCE, (2) stirrer, (3) platinum auxiliary electrode, (4) cell cover, (5) cell bulk, (6) screws, (7) bottom plate, (8) sample (silicon wafer as work electrode), (9) O-ring, (10) conductor, (11) pedestal, and (12) conduct pole.

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Figure 2. AFM images of samples (scan range was 1000 nm, scan rate was 16.3  $\mu$ m/s, resolution was 300): (a) blank p-Si (100), etched in a solution of 10 mL HF (40%) + 100 mL NH<sub>4</sub>F for 2 min at room temperature, (b) Pd seeds deposited on p-Si (100), in 0.005 mol L<sup>-1</sup> PdCl + 0.06mol L<sup>-1</sup> HF for 20 s, and (c) Ni film deposited on Pd seed layer, in 0.05 mol L<sup>-1</sup> 20 mL NiSO<sub>4</sub> and 500  $\mu$ L N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (50%) for 800 s, stirred with 753.6 rad/s.

0 s, (*iii*) 500  $\mu$ L N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (50%) was injected into the cell at 1000 s, and (*iv*) measurement was stopped at 1800 s. The sample was taken out and rinsed with redistilled water and dried by nitrogen gas to acquire AFM images or do DPV. The inner wall of the cell and O-ring are immersed into 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> for 30 min, then rinsed by redistilled water. The procedure of *i*-*t* is the same as that of OCP-*t*. Initial *E* was set as the value of OCP at 0 s. All measurements were performed at room temperature.

In the measurement of DPV, the supporting electrolyte was 0.1 mol  $L^{-1}$  HNO<sub>3</sub> and applied potential was from -1 to 1.3 V.

## **Results and Discussion**

*Characterizations of Ni film and Pd seed layer.*— The Ni film and Pd seed layer deposited on p-Si(100) are characterized by AFM and DPV.

Figure 2a shows the AFM images of blank p-Si(100). It can be seen that the silicon wafer is flat; the tested average roughness degree (Ra) was 0.99 nm. The images represent the surfaces of a hydrogen-terminated silicon substrate.<sup>22</sup>

Figure 2b shows the AFM images of Pd seed layer on the silicon wafer. Pd islands form on the active sites of hydrogen-terminated silicon, and the surface of silicon is not completely covered, which suggests that the nucleation was an island model or a Volmer–Weber (VW) model,<sup>8,23</sup> and the growth of Pd nuclei was a gradual nucleation.<sup>8</sup> The Pd particles have an average size of about 85 nm and the tested average roughness *Ra* is 13.22 nm.

Figure 2c shows the AFM images of Ni films on a Pd-activated silicon wafer. The Pd seed layer is covered completely by Ni film, and the tested average roughness Ra is 11.28 nm. It can be seen that the nucleation of Ni is also VW model.

q

φ,



Figure 3. The curve of DPV in 0.1 mol  $L^{-1}$  HNO<sub>3</sub> solution: (1) Pd seed layer, (2) Ni film on blank silicon (right axis), and (3) Ni film on Pd seed layer.

Curve 1 of Fig. 3 shows the differential pulse stripping peak of Pd. The stripping peak of Pd appeared at -0.3 V. After 0.5 V, the stripping current approaches 0 A because of the oxidation of Si substrate.

Curve 2 of Fig. 3 shows the differential pulse stripping peak of Ni film on blank p-Si(100). The peak at -0.03 V is the first electron transfer, Ni<sup>0</sup>  $\rightarrow$  Ni<sup>+</sup> + *e*, and the peak at 0.6 V is the second electron transfer, Ni<sup>+</sup>  $\rightarrow$  Ni<sup>2+</sup> + *e*.

Curve 3 of Fig. 3 shows the differential pulse stripping peak of Ni film on the Pd seed layer. The peak at 0.04 V is the first electron transfer,  $Ni^0 \rightarrow Ni^+ + e$ , and the peak at 0.4 V is the second electron transfer,  $Ni^+ \rightarrow Ni^{2+} + e$ . The peak of Pd does not appear, indicating that the Pd seed layer is completely covered.

Thermodynamic model of electroless deposition of Ni on Pdactived silicon.— Mathematic description of OCP-t and i-t.— Curve a of Fig. 4 shows OCP-t. The curve is made up of three segments. Before 1000 s, the potential changes gently because of adsorption and desorption of ions, i.e., initial potential  $\varphi_i$  (seg. 1); from 1000 s to 1000.4 s, a potential step  $\varphi_s$  appears due to breakdown of the double layer (seg. 2); after 1000.4 s, potential exponentially shifts to negative because of redox reaction and nucleation, i.e., end potential  $\varphi_e$  (seg. 3).

Curve *b* of Fig. 4 shows the response curve of *i*-*t* under OCP, which is also made up of three segments: initial current  $i_i$  (seg. 1'), current step  $i_s$  (seg. 2'), and end current  $i_e$  (seg. 3').

OCP-t and i-t are fitted accurately with Origin 7.0.



**Figure 4.** The curves of OCP-*t* and *i*-*t* of electroless deposition of Ni on Pd seed layer: (a) the curve of OCP-*t*, and (b) the curve of *i*-*t*; (1) initial potential  $\varphi_i$ ; (2) potential step  $\varphi_s$ , and (3) end potential  $\varphi_e$ ; (1') initial current  $i_i$ , (2') current step  $i_s$ , and (3') end current  $i_e$ .

$$p_i = -0.11e^{-t/110.83} + 9.0 \times 10^{-5}t - 0.63 \ (0 < t \le 1000)$$
$$R^2 = 0.9919$$
[1]

$$= -0.10 + 0.92/(1 + e^{(t-999.81) \times 100/5.60}) (1000 < t \le 1000.4)$$

$$R^2 = 0.9972$$
 [2]

$$\varphi_e = -0.43 + 132.26e^{-t/149.83} (1000.4 < t \le 1800) R^2 = 0.9906$$
[3]

$$i_{i1} = (29.28e^{-t/8.43} + 3.32) \times 10^{-6} (0 < t \le 13) R^2 = 0.9962$$
[4]

$$i_{i2} = (12.72 - 11.41/(1 + e^{t - 102.46/183.17}))$$
$$\times 10^{-6} (13 < t \le 1000) R^2 = 0.8818$$
[5]

$$i_s = 1.78 \times 10^{-4} (t - 1000) \ (1000 < t \le 1000.4) \ R = 0.98509$$
[6]

 $i_e = 0.16e^{-t/120.72} + 5.95 \times 10^{-5} (1000.4 < t \le 1800) R^2 = 0.9962$ [7]

The explanation of OCP-t and i-t.—  $Ni^{2+}$  is easy to form  $Ni(H_2O)_6^{2+}$  in  $NiSO_4$  solution. Because some of  $Ni(H_2O)_6^{2+}$  is hydrolyzed, the solution presents as acidic<sup>24</sup>

$$Ni(H_2O)_6^{2+} \rightarrow Ni(H_2O)_5^+OH_{ad} + H^+ \rightarrow Ni(H_2O)_4(OH_{ad})_2 + 2H^+$$
[8]

A weak bond exists for 2  $OH^-$  to  $Ni(H_2O)_4^{2+}$ . H<sup>+</sup> is dissociative and pH is 3.0. When aqueous  $NiSO_4$  solution is added into the cell, H<sup>+</sup> is adsorbed to the Pd seed layer immediately. The specific adsorption layer of H<sup>+</sup> forms first, and the potential rises gradually but current decays quickly to a limit due to saturation of specific adsorption within 13 s. As the diffusion layer of H<sup>+</sup> and  $Ni(H_2O)_6^{2+}$  form, potential remains raised because of concentration polarization, and current also rises slowly because of ions diffusion. After 300 s, the potential decays linearly because of the formation of an anion layer at the interface of diffuse layer; current also decays but lags to potential due to a charge of double layer.

 $N_2H_4{\cdot}H_2O$  is easy to hydrolyze. The pH of 0.5282 mol  $L^{-1}$   $N_2H_4{\cdot}H_2O$  is 10.81

$$N_2H_4 \cdot H_2O \rightarrow N_2H_5^+ + OH^-$$
 [9]

According to Ref. 24, when  $N_2H_4$ · $H_2O$  is used as a reductant, the electroless deposition of Ni is divided into four steps in acidic solution. Hydrolyzation first takes place on the surface of the active sample, and then other reactions follow

$$2H_2O \rightarrow 2H^+ + 2 OH^-$$
 [10]

$$Ni^{2+} + 2 OH^{-} \rightarrow Ni(OH)_{2}$$
[11]

$$Ni(OH)_2 + N_2H_4 \rightarrow Ni + N_2H_2(OH)_2 + 2H$$
 [12]

$$N_2H_2(OH)_2 + 2H \rightarrow N_2 + 2H_2O + H_2$$
 [13]

Overall: 
$$Ni^{2+} + N_2H_4 \rightarrow Ni + N_2 + H_2 + 2H^+$$
 [14]

In fact, when  $N_2H_4$ · $H_2O$  is added into aqueous NiSO<sub>4</sub> solution, OH<sup>-</sup> rushes to the H<sup>+</sup> layer and neutralization of H<sup>+</sup> and OH<sup>-</sup> first takes place, then the double layer of H<sup>+</sup> collapses immediately. Consequently, a remarkable potential step and current step appear (seg. 2 of OCP-*t* and seg. 2' of *i*-*t*). Then the double layer rearranges and a new layer of Ni(H<sub>2</sub>O)<sup>2+</sup><sub>6</sub> forms. When Reactions 11–13 occur on the surface of the Pd seed layer, the potential exponentially shifts to negative and the current exponentially decays (seg. 3 of OCP-*t* and seg. 3' of *i*-*t*). DPV and AFM affirm the formation of Ni film.

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**Figure 5.** Scheme of equivalent circuit of electroless deposition:  $(R_1)$ , resistance of solution,  $(R_r)$ , resistance of redox reaction, and (C) capacity of double layer.

*The model of equivalent circuit.*— Electroless deposition of Ni on the Pd seed layer can be modeled as a novel nonlinear potential step controlled by redox reaction and nucleation, which is more complicated than traditional transient techniques. However, it obeys the basic principles of potential steps and can be described with the method of equivalent circuit.<sup>21</sup>

The model of equivalent circuit for electroless deposition is shown in Fig. 5. The capacity of double-layer C connects in parallel with the resistance of chemical reaction  $R_r$ , and the resistance of solution  $R_1$  connects to the circuit in series.

In electroless deposition, the redox reaction and nucleation are dominant factors, so  $R_1$  is far less than  $R_r$  generally. Moreover,  $R_r$  can be treated as a constant when redox reaction carries out at a steady rate, i.e.,  $R_1/R_r \approx 0$ ,  $R_r = \text{constant}$ . The capacity of the double layer is a key step to calculate other thermodynamic parameters.

*Model of capacity.*— Capacity can be derived from potential and current with the above equivalent circuit. The equation of current i can be derived from Ohm's law without polarization of concentration

$$\frac{\varphi - iR_1}{R_r} + C\frac{d}{dt}(\varphi - iR_1) = i$$
[15]

$$C\frac{d\varphi}{dt} + \frac{\varphi}{R_r} = R_1 C\frac{di}{dt} + \left(1 + \frac{R_1}{R_r}\right)i$$
[16]

When  $R_1/R_r \approx 0$ , Eq. 11 can be simplified as

$$C\frac{d\varphi}{dt} + \frac{\varphi}{R_r} = i$$
 [17]

$$C = \frac{i - \varphi/R_r}{d\varphi/dt}$$
[18]

When no redox reactions take place,  $R_r = \infty$ , Eq. 18 can be simplified as

$$C = \frac{i}{d\varphi/dt}$$
[19]

Equation 19 can also be derived from the definition of capacity

$$C = \frac{dq}{d\varphi} = \frac{idt}{d\varphi} = \frac{i}{d\varphi/dt}$$
[20]

At the stage of the initial potential and potential step, no redox reaction occurrs, so Eq. 14 is adopted. For end potential, Eq. 13 must be adopted because redox reaction occurrs and a new Ni layer forms. Differential capacity is calculated out and plotted on a graph. The curve of C-t (shown in Fig. 6) is also made up of three segments, i.e., initial capacity  $C_i$ , capacity step  $C_s$ , and end capacity  $C_e$ 

$$C_i = -2.48 \times 10^{-10} + 1.25 \times 10^{-10} e^{t/110.08} \ (0 < t \le 1000)$$
[21]

$$C_s = -5.65 \times 10^{-3} (t - 1000) (1000 < t \le 1010)$$
 [22]



**Figure 6.** The curve of C-*t* for electroless deposition of Ni on Pd seed layer: (1) initial capacity  $C_i$ , (2) capacity step  $C_s$  (3) end capacity  $C_e$ .

$$R_r = \lim_{t \to \infty} \frac{\varphi_e}{i_e} = \frac{-0.43}{5.95 \times 10^{-5}} = -7.22 \times 10^3$$
[23]

$$C_e = -0.18e^{-0.0016t} - 0.02 \ (1010 < t \le 1800)$$
[24]

To confirm the presumption of  $R_1/R_r \approx 0$ , a traditional potential step<sup>21</sup> is used to estimate the scale of  $R_1$  and  $R_r$  approximatively because electroless deposition would not rigorously satisfy the condition of a traditional potential step.

Using Laplace transform and reverse transform for Eq. 16, we obtain

$$i = \frac{\varphi_k}{R_1 + R_r} \left[ 1 + \frac{R_r}{R_1} e^{-t/RC} \right]$$
[25]

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_r}$$
[26]

$$\varphi_k = \lim_{t \to \infty} \varphi_e = -0.43$$
 [27]

Comparing Eq. 25 with Eq. 7, we obtain

$$R_r = -7.22 \times 10^3$$
$$R_1 = -2.75$$
$$R_1/R_r \approx 0$$

Results show that the presumption is appropriate.

It can be seen from the figure that the magnitude of the initial capacity is from  $10^{-11}$  to  $10^{-7}$ ; capacity step reach  $-5.58 \times 10^{-2}$ , end capacity is exponentially decayed from -5.58 to  $-3.07 \times 10^{-2}$ . A noticeable focus is the time interval of the capacity step, which is not synchronous with potential or current step. The potential or current step finishes within 0.4 s, but the capacity step remains 10 s; the cause may be the rearrangement of the double layer after the breakdown of the H<sup>+</sup> layer.

*Model of surface charge density.*— Surface charge density can be derived from the definition of capacity (Eq. 20), but cannot be calculated with current directly because the current is made up of faradaic current and nonfaradaic current. Faradaic current is caused by redox reaction; however, nonfaradaic current is caused by charge of the double layer. Only nonfaradaic current contributes to surface charge density

$$q = \int_{\varphi_i}^{\varphi_e} C d\varphi / A$$
 [28]

Submitting  $\varphi_i$ ,  $\varphi_s$ ,  $\varphi_e$ ,  $C_i$ ,  $C_s$ ,  $C_e$ , and  $A = 12.56 \text{ mm}^2$  into Eq. 28, acquire



Figure 7. Curve of q-t for electroless deposition of Ni on Pd seed layer: (1) initial surface charge density  $q_i$ , (2) step of surface charge density  $q_s$ , (3) end surface charge density  $q_e$ , and (3') amplification of end surface charge density  $10^{-4}q_{e}$ .

$$q_i = 1.11 \times 10^{-13} e^{t/111.54} + 4.37 \times 10^{-13} \ (0 < t \le 1000)$$
[29]

$$q_s = 9.70 \times 10^{-2} (t - 1178) \ (1000 < t \le 1010)$$
 [30]

$$q_e = -1.53e^{-t/120.48} - 0.21e^{-t/149.83} + 5.98 \times 10^{-4} (1010 < t \le 1800)$$
[31]

The curve of q-t is shown in Fig. 7. The initial surface charge density  $q_i$  is from  $10^{-15}$  to  $10^{-10}$ , the step of surface charge density  $q_s$  reaches -17.15 within 10 s, and the end surface charge density  $q_e$ rebounds to  $10^{-4}$ . Compared with the initial surface charge density, the step is so high that nucleation is very easy to trigger. A Ni monolayer or submonolayer may be deposited on a Pd seed layer instantaneously because the surface charge density decreases from -17.15 to  $3.39 \times 10^{-6}$  within 1 s. The end surface charge density increases from 3.40  $\times$  10<sup>-6</sup> to 5.95  $\times$  10<sup>-4</sup> and remains steady after 1600 s, which shows that, after 1600 s, the diffusion of ions in the boundary layer still plays an important role although agitated strongly, so the growth of Ni nuclei may be gradual.

Based on the above discussion, we can make the conclusion that the nucleation rate may depend on surface charge density. Reductant pulse may be an effective way to speed nuclei growth because pulse can increase surface charge density. A special deposition layer may be obtained by special reductant pulse.

Model of interfacial tension.- The interfacial tension of electrode/ solution plays an important role for adsorption and diffusion of ions. It interacts with surface charge density and can be calculated with the Lippmann equation<sup>2</sup>

$$\gamma = -\int_{\varphi_i}^{\varphi_e} q d\varphi \qquad [32]$$

Submitting  $\varphi_i$ ,  $\varphi_s$ ,  $\varphi_e$ ,  $q_i$ ,  $q_s$ , and  $q_e$  into Eq. 32, we acquire

$$u_i = 10.79 - 3.90 \times 10^{-2}t + 8 \times 10^{-5}t^2 - 6.25 \times 10^{-8}t^3 (0 < t \le 1000)$$
[33]

$$\gamma_{s1} = -5 \times 10^{-3} \ln(t - 999.7) - 0.89/(t - 999.7)$$

$$+ 2.97 (1000 < t \le 1000.4)$$
 [34]

$$\gamma_{s2} = -25.13 + 2.34 \times 10^{-2} t \ (1000.4 < t \le 1010)$$
 [35]

$$\gamma_e = 764.18 - 7.72 \times 10^4 e^{-t/222.19} (1010 < t < 1800)$$
 [36]

The curve of  $\gamma$ -*t* is shown in Fig. 8. The initial interfacial tension is from  $10^{-11}$  to  $10^{-13}$ ; the step of interfacial tension increases from  $-7.37 \times 10^{-12}$  to 1.70 within 0.4 s, then decreases to -1.65 and



Figure 8. Curve of  $\gamma$ -t for electroless deposition of Ni on Pd seed layer: (1) initial interfacial tension  $\gamma_i$ , (2) step of interfacial tension  $\gamma_s$ , (3) end interfacial tension  $\gamma_e$ , and (3') amplification of end interfacial tension  $10^{-6}\gamma_e$ .

remains about 10 s; the end interfacial tension increases from  $-10^{-7}$ to  $-10^{-4}$ . The step of interfacial tension first increases and then decreases; the signal direction changes from positive to negative, proving that the double layer collapses first and then rearranges.

# Conclusions

OCP-t is a novel nonlinear potential step controlled by redox reaction and nucleation. The thermodynamic model of OCP-t for electroless deposition can be set up by modeling of the double layer and equivalent circuit. Thermodynamic parameters such as capacity of double layer, resistances of chemical reaction, surface charge density, and interfacial tension can be derived from OCP-t and i-t. Thermodynamic curves all include three segments but have different characters. The potential and current step are synchronous, indicating they have the same mechanism, but the capacity step lags to them because of the charge of double layer.

Results show that surface charge density is an important factor because nuclei growth may be dependant on surface charge density. Reductant pulse can cause very high surface charge density and triggers momentary nucleation, but the step time is only 10 s. Repetitious reductant pulses may be an effective way to speed nuclei growth and form different configures.

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# List of symbols

- area of electrode (mm<sup>2</sup>)
- $C_i$ initial capacity (F)
- $C_s$ capacity step (F) end capacity (F)
- $C_{e}$ Ċ capacity (F)
- F
- Faraday constant (C)
- specific adsorption current (A)  $i_{i1}$
- diffuse current (A) i<sub>i2</sub>
- current step (A)
- end current (A) i<sub>e</sub> response current (A)
- initial surface charge density (C/mm<sup>2</sup>)  $q_i$ step of surface charge density (C/mm<sup>2</sup>)
- $q_s$ end surface charge density (C/mm<sup>2</sup>)  $q_e$
- resistance of solution  $(\Omega)$  $R_1$
- $R_r$ resistance of chemical reaction  $(\Omega)$
- Ŕ parallel resistance of  $R_1$  and  $R_r$  ( $\Omega$ )
- time (s) t
- open-circuit potential (V) φ
- initial potential (V)

- $\varphi_s$  potential step (V) end potential (V)
- $\varphi_{\rho}$
- initial interfacial tension (N/mm)  $\gamma_I$
- $\gamma_s$  interfacial tension step (N/mm)  $\gamma_e$  end interfacial tension (N/mm)

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