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Nucleation and growth in electrodeposition of metals on n-Si(111)

R. Krumm^a, B. Guel^b, C. Schmitz^a, G. Staikov^{a,*}

^a Institut für Physikalische Chemie und Elektrochemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstraße 1, Geb. 26.32, 40225 Düsseldorf, Germany

^b Faculté des Sciences et Techniques, Universié de Ouagadougou, Ouagadougou, Burkina Faso

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Abstract

Initial stages of electrodeposition of Tl, Cd and Cu on n-Si(111) from sulfate electrolyte solutions are studied using cyclic voltammetry and chronoamperometry. Capacitance measurements in metal ion free solutions were used to determine the flat band potential of n-Si. Results show that the relative position of the metal equilibrium potential with respect to the substrate flat band potential influences significantly nucleation and growth kinetics. Within appropriate potential ranges the initial deposition kinetics corresponds to a model including progressive nucleation and diffusion controlled cluster growth. Nucleation rate and the number of atoms in the critical nucleus are determined from the analysis of current transients at different overpotentials. Results are compared with data obtained previously for electrochemical nucleation of these metals on other semiconductors and foreign metal substrates. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Electrodeposition; Nucleation; Crystal growth; Semiconductors; Flat band potential

1. Introduction

Electrochemical deposition and dissolution of metals can be generally expressed by

$$Me_{solv}^{z+}(El) \Leftrightarrow Me^{z+}(Me)$$
 (1)

where $Me_{solv}^{z+}(El)$ represents the metal ions in the electrolyte phase (El) and $Me^{z+}(Me)$ denotes the metal ions in the metal bulk phase (Me), which are coupled to the electrons $e^{-}(Me)$ in the Me-crystal lattice (Me^{z+} ($Me) + ze^{-}(Me) = Me$). At the so-called Nernst potential $E_{Me/Me^{z+}}$, $Me_{solv}^{z+}(El)$ and $Me^{z+}(Me)$ are in equilibrium, which is defined by the equality of the

corresponding electrochemical potentials ($\tilde{\mu}_{Me^{z}+}^{(El)} = \tilde{\mu}_{Me^{z}+}^{(Me)}$). The deviation from equilibrium $\Delta \tilde{\mu} = \tilde{\mu}_{Me^{z}+}^{(El)} - \tilde{\mu}_{Me^{z}+}^{(Me)}$ is given by:

$$\Delta \tilde{\mu} = -zF(E - E_{\mathrm{Me/Me}^{z+}}) = -zF\eta$$
⁽²⁾

where *E* and η are the actual electrode potential and the overpotential, respectively. If the kinetics of metal deposition and dissolution are not controlled by charge transfer, ion transport or additional chemical reaction steps, η represents the so-called crystallization overpotential [1]. In this case Eq. (2) defines the thermodynamic driving forces of the phase formation and dissolution processes, i.e. supersaturation ($\Delta \tilde{\mu} > 0$ for $\eta < 0$) and undersaturation ($\Delta \tilde{\mu} > 0$ for $\eta < 0$).

Mechanism of metal electrodeposition on foreign substrates (S) depends strongly on the Me-S interaction [1]. In systems with weak Me-S interaction (weak adhesion) metal deposition starts at supersaturation in

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^{*} Corresponding author. Tel.: + 49-211-8113686; fax: + 49-211-8112803.

E-mail address: georgi.staikov@uni-duesseldorf.de (G. Staikov)

the so-called overpotential deposition (OPD) range $E < E_{Me/Me^{z+}}$ with nucleation and growth of the 3D Me bulk phase. In the case of a strong Me–S interaction (strong adhesion), however, the deposition process can start even at undersaturation in the so-called underpotential deposition (UPD) range $E > E_{Me/Me^{z+}}$ with formation of low-dimensional metal phases, which act as precursors for the nucleation and growth of the 3D Me bulk phase in the OPD range.

Kinetics and mechanism of metal electrodeposition and the involved phase formation phenomena can also be influenced significantly by electronic properties of the foreign substrate. In the case of deposition on foreign metal substrates the substrate surface is a continuum of electronic states and thus, sufficient supersaturations for nucleation of the Me bulk phase are usually reached by application of relatively low cathodic overpotentials. The situation, however, becomes more complicated in the case of electrodeposition of metals on semiconductor substrates. The influence of the space charge layer in the semiconductor has to be taken into account in this case [2-6]. For a not very high doped n-type semiconductor, the surface concentration of electrons and the band bending at the actual electrode potential play an important role in the electrodeposition process. Neglecting the influence of surface states, the mechanism of metal deposition in this case depends strongly on the relative position of the equilibrium potential $E_{Me/Mez+}$ with respect to the flat band potential $E_{\rm fb}$ of the semiconductor substrate (Fig. 1). If $E_{Me/Me^{z+}} \ll E_{fb}$ accumulation layer is formed at $E = E_{Me/Me^{z+1}}$ and the deposition of the Me bulk phase usually occurs at relatively small cathodic overpotentials, such as on metal substrates (Fig. 1a). However, if the equilibrium potential $E_{Me/Mez+}$, is located in the



Fig. 1. Schematic band diagrams for electrodeposition of different metals (Me₁ and Me₂) on a n-semiconductor with a flatband potential $E_{\rm fb}$. Relative positions of corresponding metal equilibrium potentials with respect to $E_{\rm fb}$ are also indicated. (a) $E_{\rm Me_1/Me_{\bar{1}}+} \ll E_{\rm fb}$; deposition potential E_1 , (b) $E_{\rm Me_2/Me_{\bar{2}}+} \gg E_{\rm fb}$; deposition potential E_2 .

band gap, and is more positive than the flat band potential $E_{\rm fb}$ ($E_{\rm Me/Me^{z+}} \gg E_{\rm fb}$) a depletion layer is formed in the n-type semiconductor at $E = E_{\rm Me/Me^{z+}}$. Thus, electrode potentials more negative than the flat band potential ($E < E_{\rm fb}$) are needed in this case to reach a sufficient surface electron density (accumulation conditions) and electrodeposition of metals in such systems occurs at high cathodic overpotentials (Fig. 1b).

Mechanism of metal deposition and structures of electrodeposits on foreign metal substrates have been extensively studied using various electrochemical methods and in situ SPM (scanning probe microscopy) techniques [1]. Despite its technological importance, electrodeposition of metals on semiconductor substrates has been the object of relatively few studies to date [2-12]. Recent investigations of metal electrodeposition on n-GaAs(100) [7,8], n-Si(111) [9–11] and n-Si(100) [12] provided new important information about the nucleation and growth kinetics, and the role of substrate surface inhomogeneities in the deposition process. More studies are needed, however, to understand the complex nature and mechanism of electrochemical metal phase formation on semiconductor substrates.

In this paper we present new results on the mechanism and kinetics of the initial stages of metal electrodeposition, on H-terminated n-Si(111) substrates from acidic sulfate electrolyte solutions. The systems n-Si(111)/Tl⁺ and n-Si(111)/Cd²⁺ are selected as typical examples for systems characterized by $E_{\rm Me/Me^{z}+} \ll E_{\rm fb}$, whereas n-Si(111)/Cu²⁺ is chosen as an example for a system with $E_{\rm Me/Me^{z}+} \gg E_{\rm fb}$. The experimental results are compared with data obtained by electrodeposition of the same metals on other substrates.

2. Experimental

The experiments were carried out in the following systems:

- 1. n-Si(111)/5 mM Tl₂SO₄, 0.5 M Na₂SO₄, 5 mM H_2SO_4 (pH 2),
- 2. n-Si(111)/5 mM CdSO₄, 0.5 M Na₂SO₄, 5 mM H₂SO₄ (pH 2),
- 3. n-Si(111)/10 mM CuSO₄, 0.5 M H₂SO₄ (pH 0.3).

Electrolyte solutions were prepared from Suprapure chemicals and Millopore[®] water. Prior to each measurement, the solutions were deaerated in the electrochemical cell with pure nitrogen (99.999%). The electrochemical cell consisted of a Pt counter electrode, a reference Hg/HgSO₄/Na₂SO₄(sat.) electrode (MSE) and a n-Si(111) working electrode. All electrode potentials are referred to the SHE potential and/or to the corresponding Nernst equilibrium potential $E_{Me/Me^{z+1}}$.

Silicon working electrodes were made from n-doped Si(111) wafers (Siltronix, France) of $1-5 \Omega$ cm resistivity and 0° misorientation. Samples were subsequently



Fig. 2. Cyclic voltammograms (a) (cathodic sweep) and Mott– Schottky plots (b) in the system: n-Si(111)/ SO₄²⁻, H⁺ (pH 0.3 and 2). Scan rate $|dE/dt| = 5 \text{ mV s}^{-1}$; T = 298 K; capacitance measurements at f = 1014 Hz.

cleaned in trichloroethylene, acetone and ethanol and etched for 1 min in 2% HF solution and 6 min in deaerated 40% NH₄F solution. Si(111) surfaces prepared in such a manner are H-terminated and exhibit atomically flat terraces. The substrates were mounted into a Teflon holder and have an active surface area of 0.3 cm². An ohmic contact at the back of the substrate face was established by Ga–In alloy. All experiments were performed at T = 298 K in dark using standard electrochemical measurement equipment.



Fig. 3. Flat band potentials E_{fb} of n-Si in NH₄F and H₂SO₄ electrolyte solutions at different pH values.

3. Results and discussion

3.1. Electrochemical behavior of n-Si(111) in metal ion free electrolytes

Fig. 2a shows cyclic voltammograms of n-Si(111) in metal ion free electrolytes at pH 0.3 and 2. The sharp current increase at -0.6 and -0.8 V versus SHE is related to the H₂ evolution reaction. Potential dependencies of space charge capacitance measured under depletion conditions are shown in Fig. 2b. From the corresponding Mott–Schottky $(C^{-2}-E)$ plots flatband potentials of $E_{\rm fb} = -0.24$ and -0.14 V versus SHE could be estimated for the solutions at pH 2 and 0.3, respectively. In Fig. 3 these values are compared with results obtained previously by Allongue et al. [13], in NH₄F solutions at various pH values and by Itaya et al. [14] in H₂SO₄ solution at pH 1. All data seem to correlate well to a linear $E_{\rm fb}$ -pH dependence with a slope of -45 mV/pH deviating from the Nernstian slope of -60 mV/pH observed in many other systems. The results indicate that anions do not affect significantly the flat band potential of H-terminated n-Si(111) substrates.

3.2. Deposition of metals with $E_{Me/Mez+} \ll E_{fb}$

Equilibrium potentials of Tl and Cd in systems (i) and (ii) are about 270 mV more negative than the flatband potential of n-Si(111) in the corresponding electrolyte solutions ($E_{\rm fb} = -0.24$ V). Fig. 4 shows typical cyclic voltammograms of deposition and dissolution of Tl and Cd on n-Si(111) in systems (i) and (ii), respectively. Reversible deposition/dissolution reactions observed in both systems indicate a formation of n-Si(111)/Me contacts with ohmic behavior. Equal charge densities are estimated for metal deposition and dissolu-



Fig. 4. Cyclic voltammograms for Tl and Cd deposition and dissolution in the systems: $n-Si(111)/Me^{z+}$, SO_4^{2-} , $H^+(Me^{z+} = Tl^+$ and Cd^{2+} , pH 2). $|dE/dt| = 1 \text{ mV s}^{-1}$; T = 298 K.



Fig. 5. System n-Si(111)/Tl⁺, SO₄²⁻, H⁺ (pH 2). T = 298 K. (a) Current transients for Tl deposition at different overpotentials η ; (b) $t_{\text{free}}^{2/3}$ vs. t plot of the initial parts of the transients shown in (a).



Fig. 6. System n-Si(111)/Cd²⁺, SO₄²⁻, H⁺ (pH 2). T = 298 K. (a) Current transients for Cd deposition at different overpotentials η ; (b) $i_{\text{free}}^{2/3}$ vs. t plot of the initial parts of the transients shown in (a).

tion processes in both cases, which excludes the occurrence of a parallel H_2 evolution reaction. No UPD of Tl and Cd could be observed in any of the two systems indicating a weak interaction (weak adhesion) of these metals with n-Si(111). A comparison of cyclic voltammograms in Fig. 4 shows that initial deposition kinetics of Tl is faster. This is reflected in the higher onset overpotential for deposition.

Nucleation and growth kinetics in the initial stages of TI and Cd deposition on n-Si(111) were studied using the current transient technique. Figs. 5a and 6a show typical current transients for deposition of TI and Cd at relatively low cathodic overpotentials. The initial parts of the current transients are represented in Figs. 5b and 6b as $i_{\rm free}^{2/3}$ versus *t* plots. The obtained linear relationships show that the kinetics of the initial stages of metal deposition in these systems can be explained by a model including progressive nucleation and cluster growth controlled by hemispherical diffusion [1,15]. According to this model the current density $i_{\rm free}(t)$ at relatively short times, i.e. for deposition without overlapping of diffusion zones, can be generally described by the equation

$$i_{\rm free} = -zF \frac{2}{3} \pi J (V_{\rm m})^{1/2} (2Dc_{{\rm Me}^z+})^{3/2} \left[1 - \exp\left(\frac{zF\eta}{RT}\right) \right]^{3/2}$$
$$(t - t_{\rm o})^{3/2}$$
(3)

where J represents the nucleation rate, t_o the induction period of nucleation, V_m the molar volume of Me, D the diffusion coefficient and c_{Mez+} the concentration of Me^{z+} in the electrolyte. At relatively high cathodic overpotentials the nucleation sites are virtually converted to nuclei instantaneously and the initial current density i_{free} is proportional to $t^{1/2}$. With increasing t hemispherical diffusion zones of the growing clusters start to overlap leading to the appearance of a maximum in current transients. A theoretical model taking into account the overlapping of diffusion zones has been developed by Gunawardena et al. [16]. According to this model the overall current transients for progressive and instantaneous nucleation can be described by

$$\left(\frac{i}{i_{\max}}\right)_{inst}^{2} = 1.9542 \frac{(t-t_{o})_{\max}}{(t-t_{o})} \left[1 - \exp\left(-1.2564 \frac{(t-t_{o})}{(t-t_{o})_{\max}}\right)\right]^{2}$$

$$\left(\frac{i}{i_{\max}}\right)_{prog}^{2} = 1.2254 \frac{(t-t_{o})_{\max}}{(t-t_{o})} \left[1 - \exp\left(-2.3367 \frac{(t-t_{o})^{2}}{(t-t_{o})_{\max}^{2}}\right)\right]^{2}$$

$$(5)$$

The products $i_{\text{max}}^2(t - t_0)_{\text{max}}$ are given, respectively, by $\int_{0}^{12} (t - t_0) dt$

$$= 0.1629 (zFc_{Me^{z+}})^2 \left[1 - \exp\left(\frac{zF\eta}{RT}\right) \right]^2 D$$
(6)

$$[t_{\max}^{2}(t-t_{o})_{\max}]_{\text{prog}} = 0.2598(zFc_{\text{Me}^{z}+})^{2} \left[1 - \exp\left(\frac{zF\eta}{RT}\right)\right]^{2} D$$
(7)

Fig. 7a represents as a typical example, a current transient for Tl deposition at an overpotential $\eta = -15$ mV. The corresponding $(i/i_{max})^2$ versus (t/t_{max}) plot in Fig. 7b shows, that at this relatively high cathodic overpotential the nucleation of Tl can be considered as instantaneous. Similar behavior was observed also in the case of Cd deposition at relatively high cathodic overpotentials. From experimental data and Eq. (6) diffusion coefficients of $D = 1.4 \times 10^{-5}$ and $D = 9.5 \times$ 10^{-6} cm² s⁻¹ were estimated for Tl⁺ and Cd²⁺, respectively. These values and Eq. (3) were used to derive nucleation rates J for Tl and Cd deposition at low cathodic overpotentials from the slopes of the $i_{\rm free}^{2/3}$ versus t plots presented in Figs. 5b and 6b. In the initial stages of Tl and Cd electrodeposition on n-Si(111) the driving force of nucleation, the supersaturation $\Delta \tilde{\mu}$, is related to the overpotential by Eq. (2). Thus, in Fig. 8 the corresponding nucleation rates J are presented as a



Fig. 7. System n-Si(111)/Tl⁺, SO₄²⁻, H⁺; T = 298 K, pH 2. (a) Current transient for Tl deposition at $\eta = -15$ mV ($t_0 = 0$). (b) $(i/i_{max})^2$ vs. $(t - t_0)/(t - t_0)_{max}$ plot of the transient in (a) compared with theoretical transients for progressive (dashes) and instantaneous (solid line) nucleation according to Eqs. (4) and (5).



Fig. 8. Nucleation rates *J* as a function of supersaturation $(zF|\eta|)$ for electrodeposition of Tl and Cd on n-Si(111) derived from experimental data in Figs. 5 and 6. Previous results obtained in the system n-Si(111)/Pb²⁺ are shown for comparison.

function of supersaturation $\Delta \tilde{\mu} = zF|\eta|$. Experimental data obtained previously in the system n-Si(111)/Pb²⁺ [9,10] are also shown for comparison.

The number of atoms $N_{\rm crit}$ in the critical nuclei can be determined using the equation

$$N_{\rm crit} = RT \frac{\mathrm{d}\ln J}{\mathrm{d}(zF|\eta|)} \tag{8}$$

This equation is general and can be applied without any restrictions for the size and form of the nucleus [1,17]. It allows an estimation of $N_{\rm crit}$ with an accuracy of about ± 0.5 . Relatively small $N_{\rm crit}$ -values of 18, 11 and 6 were derived from the slopes of the linear dependencies in Fig. 8 for Tl, Pb and Cd, respectively. The small values show that the so-called atomistic approach [18–20] has to be applied to describe the nucleation processes in these systems.

3.3. Deposition of metals with $E_{Me/Mez+} \gg E_{fb}$

Fig. 9 shows a cyclic voltammogram of the system n-Si(111)/Cu²⁺. The voltammogram is characterized by a relatively high critical cathodic overpotential for deposition and an absence of an anodic stripping peak. A similar electrochemical behavior was observed also by Cu electrodeposition on n-GaAs(100) [7,8] and n-Si(100) [12] and seems to be typical for many systems in which the equilibrium potential $E_{Me/Me^{z+}}$ is located in the band gap of the n-type semiconductor substrate and is more positive than the flat band potential E_{fb} . It is interesting to note, that in the absence of surface states, a formation of low dimensional metal phases by UPD is impossible in systems with $E_{Me/Me^{z+}} \gg E_{fb}$, even in the cases of a strong metal-semiconductor interaction.

Typical current transients for nucleation and growth of Cu on n-Si(111) at different overpotentials are shown in Fig. 10a. The obtained linear $i_{\text{free}}^{2/3}$ versus *t* relationships for the initial parts of the transients (Fig. 10b)



Fig. 9. Cyclic voltammogram in the system n-Si(111)/Cu²⁺, SO₄²⁻, H⁺ (pH 0.3), |dE/dt| = 5 mV s⁻¹; T = 298 K.



Fig. 10. System n-Si(111)/Cu²⁺, SO₄²⁻, H⁺ (pH 0.3). T = 298 K. (a) Current transients for Cu deposition at different overpotentials η ; (b) $i_{\text{free}}^{2/3}$ vs. t plot of the initial parts of the transients shown in (a).

correspond to a progressive nucleation and diffusion controlled cluster growth described by Eq. (3). Fig. 11a shows the current transient for $\eta = -509$ mV exhibit-

ing a maximum at large times. The normalized $(i/i_{max})^2$ versus $(t - t_o)/(t - t_o)_{max}$ plot of the transient presented in Fig. 11b is in good agreement with Eq. (5), corresponding to the model including progressive nucleation and cluster growth controlled by hemispherical diffusion. A Cu²⁺ diffusion coefficient of $D = 1.1 \times 10^{-5}$ $cm^2 s^{-1}$ was estimated from experimental data using Eq. (7). This value is in good agreement with literature data and was used to derive the nucleation rate J at different overpotentials from the slopes of the $i_{\rm free}^{2/3}$ versus t plots in Fig. 10b and Eq. (3). Nucleation rate as a function of supersaturation $zF|\eta|$ is shown in Fig. 12. Applying Eq. (8), a value of $N_{\text{crit}} = 1 \pm 0.5$ was estimated from experimental data in Fig. 12. In terms of the so-called small cluster nucleation model [1,18-20] this result indicates that under given conditions a single adatom or an adatom pair represent stable clusters which can grow spontaneously. N_{crit}-values ranging



Fig. 11. System n-Si(111)/Cu²⁺, SO₄²⁻, H⁺; T = 298 K, pH 0.3. (a) Current transient for Cu deposition at $\eta = -509$ mV ($t_0 = 280$ ms). (b) $(i/i_{max})^2$ vs. $(t - t_0)/(t - t_0)_{max}$ plot of the transient in (a) compared with theoretical transients for progressive (dashes) and instantaneous (solid line) nucleation according to Eqs. (4) and (5).



Fig. 12. Nucleation rate J as a function of supersaturation $zF|\eta|$ for Cu electrodeposition on n-Si(111) derived from experimental data in Fig. 10.

between 0 and 1 were recently found also in other systems characterized by $E_{\text{Me/Me}^{z+}} \gg E_{\text{fb}}$ [7,8,12]. Such low N_{crit} -values, however, are not specific for semiconductor substrates and are often obtained at high cathodic overpotentials (supersaturations) also by electrodeposition of metals on foreign metal substrates, glassy carbon and HOPG [1,20–28].

4. Conclusions

The studies of the early stages of electrodeposition of Tl, Cd and Cu on H-terminated n-Si(111) substrates presented in this paper demonstrate the important role of the relative position of $E_{Me/Me^{z+}}$ with respect to the substrate flat band potential E_{fb} . In systems with $E_{\rm Me/Me^{z\,+}} \ll E_{\rm fb}$ such as n-Si(111)/Tl⁺ and n-Si(111)/Cd²⁺ the deposition process occurs as on metal substrates and the initial nucleation and growth kinetics can be analyzed at relatively low cathodic overpotentials (supersaturations). On the contrary, in systems with $E_{\text{Me/Mez}+} \gg E_{\text{fb}}$, a study of deposition processes is usually possible only at relatively high cathodic overpotentials corresponding to high supersaturations. The relative position of the metal equilibrium potential with respect to the substrate flat band potential can be altered by a change of the concentration of Me^{z+} and/or pH as well as by complexation of Me^{z+} introducing complexing agents in the electrolyte solution [12]. Experimental results for electrochemical nucleation of Cd, Pb, Tl and Cu on various substrates are compared in Table 1. Results indicate that the main factors determining the size of the critical nuclei and the Gibbs energy of nucleus formation, are supersaturation and Me-Me interaction. The substrate influence seems to be related primarily to the density and activity of nucleation sites. The relatively small number of atoms in the critical nuclei, obtained even at low supersaturations (low cathodic overpotentials), show that thermodynamics and

Table 1

 $N_{\rm crit}$ -values for electrochemical nucleation of Cd, Cu, Pb and Tl on various substrates in different overpotential (supersaturation) ranges

Metal	Substrate	Overpotential range (mV)	Supersaturation range (kJ mol ⁻¹)	N _{crit} (atoms)	Ref.
Cd	n-Si(111) Pt	-15 to -21 -22 to -30 -30 to -38	2.89 to 4.05 4.25 to 5.79 5.79 to 7.33	6 2 1	This paper [22] [22]
	n-Si(111) n-GaAs(100)	-474 to -520 -510 to -570 -631 to -881	91.47 to 100.34 98.41 to 109.99 121.76 to 170.01	1 to 0 1 to 0 0	This paper [7] [8]
Cu	Au(111) Pd	-71 to $-82-40 to -54-54 to -82$	13.70 to 15.82 7.72 to 10.42 10.42 to 15.82	2 4 1	[30] [25] [25]
	Pt W	-82 to $-140-22$ to $-32-50$ to $-100-40$ to -55	15.82 to 27.02 4.25 to 6.17 9.65 to 19.30 7.72 to 10.61	0 11 0 4	[25] [31] [26] [31]
Рb	n-Si(111) Ag(111) Ag(100) C HOPG	$\begin{array}{r} -6 \text{ to } -10 \\ -15 \text{ to } -19 \\ -13 \text{ to } -18 \\ -50 \text{ to } -300 \\ -4 \text{ to } -7 \end{array}$	1.16 to 1.93 2.89 to 3.67 2.51 to 3.47 9.65 to 57.89 0.77 to 1.35	11 11 13 0 11	[9] [29] [29] [24] [9]
Tl	n-Si(111)	-3 to -7	0.29 to 0.68	18	This paper

kinetics of electrochemical nucleation must be generally described by the so-called small cluster or atomistic model [1,18–20].

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