

**CADMIUM ELECTRODEPOSITION FROM AN
AQUEOUS 0.1 M CdSO₄ SOLUTION
PART 1: ELECTROCHEMICAL AND IN SITU AFM
STUDIES IN THE CASE OF n-Si(100)**

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Abstract: Electrochemical and in situ AFM studies of cadmium electrodeposition from an aqueous 0.1 M CdSO₄ solution have been carried out in the case of (100) n-type silicon single crystal. The mechanisms related to the initial stages of the nucleation and growth mechanism of cadmium have been studied as a function of different potential steps. Within appropriate potential ranges the initial deposition kinetics corresponded to a model including progressive nucleation and diffusion controlled cluster growth. Nucleation rate and the number of atoms in the critical nucleus were determined from the analysis of current transients at different overpotentials. A N_{crit} -value of 14 ± 1 atoms was determined in the following potential range: $-9 \text{ mV} \geq \eta \geq -11 \text{ mV}$. The response of the system at different waiting times at the equilibrium potential was also investigated.

Keywords: *electrodeposition; n-Si(100); nucleation and growth mechanism; anodic stripping curves.*

INTRODUCTION

The interest in thin films of cadmium is increasing considerably due to its use in the electrodeposition of CdX (X = S, Se, Te, O) compound thin films or nanostructures [1-7]. Since these thin films or nanostructures are grown from plating bath containing Cd^{2+} ions, it is of great interest to understand the fundamentals of cadmium electrodeposition. Although many works have been carried out on the cadmium electrodeposition on various substrates such as Bi, Sn and Pb (references cited in [8]), Ag [9], Au [8, 10], Cu [11], or GaAs [12], only a limited number of fundamental studies of Cd electrodeposition have been carried out on silicon single crystals. And generally, these studies are carried out in solutions corresponding to low concentrations of the metal ions Cd^{2+} (1 to 5 mM). In an earlier work [13], we examined Cd electrodeposition - from a solution containing 5×10^{-3} M Cd^{2+} ions - on n-Si(111) (1 – 5 Ωcm resistivity and 0° misorientation). It was shown that within appropriate potential ranges the initial deposition kinetics corresponded to a model including progressive nucleation on active sites and diffusion controlled cluster growth. Nucleation rate and the number of atoms N_{crit} in the critical nucleus were determined from the analysis of current transients at different overpotentials. A value of 6 was derived for N_{crit} with an accuracy of ± 1 in the overpotential range $-15 \geq \eta \geq -21$ mV. These results were compared with those of a detailed study in the system n-Si(100) / 5 mM CdSO_4 + 0.5 M Na_2SO_4 + 5×10^{-3} M H_2SO_4 [14]. In this case, a N_{crit} -value of 16 was determined in the overpotential range $-16 \text{ mV} \geq \eta \geq -19 \text{ mV}$. Though the overpotential ranges were close within experimental errors, the N_{crit} -values were different. It is of interest to extend our investigations in the case of aqueous CdSO_4 solutions with concentrations higher than 5 mM to understand the behavior of silicon single crystals in such concentrated aqueous solutions.

Generally, the technique used for deposition is as follows: the working electrode is prepolarized with respect to the reference in solution at a selected underpotential ΔE_i , where no current flows. At $t = 0$, the potential step raises the Fermi level to a potential corresponding to an overpotential $\eta = (E - E_{Me/Me^{z+}}) < 0$. The main electrocrystallization parameters besides those relative to the substrate are ΔE_i , η , the time of deposition and the solution composition (pH , concentration, etc.). The aim of the present work is to investigate the initial stages of nucleation and growth of electrodeposited Cd, from an aqueous 0.1 M CdSO_4 solution, in dependence of overpotential η on (100) n-type silicon single crystal. We also investigate the behavior of the system n-Si(100) / 0.1 M Cd^{2+} in dependence of different waiting times at $\Delta E_i = 0$ mV.

EXPERIMENTAL

The investigations were carried out in the system: n-Si(100) / 0.1 M CdSO_4 + 0.5 M Na_2SO_4 + 5×10^{-3} M H_2SO_4 ; $pH = 2.5$, $T = 298$ K.

The Silicon working electrode was made from n-type silicon wafers with the following features: (100) orientation, phosphorus-doped 20 – 40 Ωcm resistivity, MEMC Electronic Materials, Germany. The geometrical surface area of the electrode was approximately 1 cm^2 .

The n-Si(100) substrate was subsequently cleaned in trichloroethylen, acetone and methanol and etched for 1 min in 2% HF solution and 6 min in deaerated 40% NH₄F solution. The substrate was then mounted into a Teflon holder with its polished side in contact with the electrolyte. Ohmic contact was established on the back of the Si sample with a Ga/In eutectic.

The electrolyte was prepared from suprapure chemicals and fourfold-distilled water and deaerated by purified nitrogen prior to and during each experiment.

Conventional electrochemical measurements were performed in a three-electrode electrochemical cell with a Pt-counter electrode and a small Pt sphere covered with electrochemically deposited Cd used as the reference electrode and placed at a distance of 1-2 mm near the silicon-working electrode in order to ensure negligible ohmic drop in all experiments. All electrode potentials are referred to the equilibrium potential of the 3D Cd bulk phase $E_{3D\ Cd}$.

In situ electrochemical AFM studies were carried out in a three-electrode arrangement. Reference and counter electrode were a Cd wire and a Pt wire, respectively, inserted directly into the AFM cell.

RESULTS AND DISCUSSION

Voltammetric and in situ AFM studies

Figure 1 shows typical cyclic voltammograms of Cd deposition obtained at $T = 298\text{ K}$ with $|dE/dt| = 1\text{ mVs}^{-1}$ in the system n-Si(100) / 0.1 M Cd²⁺. In the system under investigation, no peak can be found in the UPD (underpotential deposition) range indicating a weak interaction (weak adhesion) of cadmium with n-Si(100). Current loop in the OPD (overpotential deposition) range, typical of a nucleation-growth process at electrode surfaces, is observed. The large current density in the OPD range results from the large Cd²⁺ concentration of the solution (0.1 M). Actually, in such systems (semiconductor substrates) where the binding energy of Me* adatoms on the substrate S, i.e. $(\Psi_{Me\ ads} - s)$, is lower than that of Me adatoms on the native substrate, i.e. $(\Psi_{Me\ ads} - Me)$, the 3D Me phase is formed in the OPD range on top of an unmodified substrate following a Volmer-Weber growth mechanism [15]. Further, anodic peak corresponding to the metal stripping can be seen in the positive voltammetric scan indicating that deposition and dissolution of Cd are reversible in this system.

We investigated the behavior of the system when the electrode potential was held constant for a certain time at the equilibrium potential $\Delta E_i = 0\text{ mV}$. Anodic stripping curves were then recorded at different waiting times. With increasing polarization time at this fixed underpotential, the anodic stripping charge associated with the dissolution of the deposited charge increases (peak O₁ in Figure 2).

* The notation Me denotes a metal

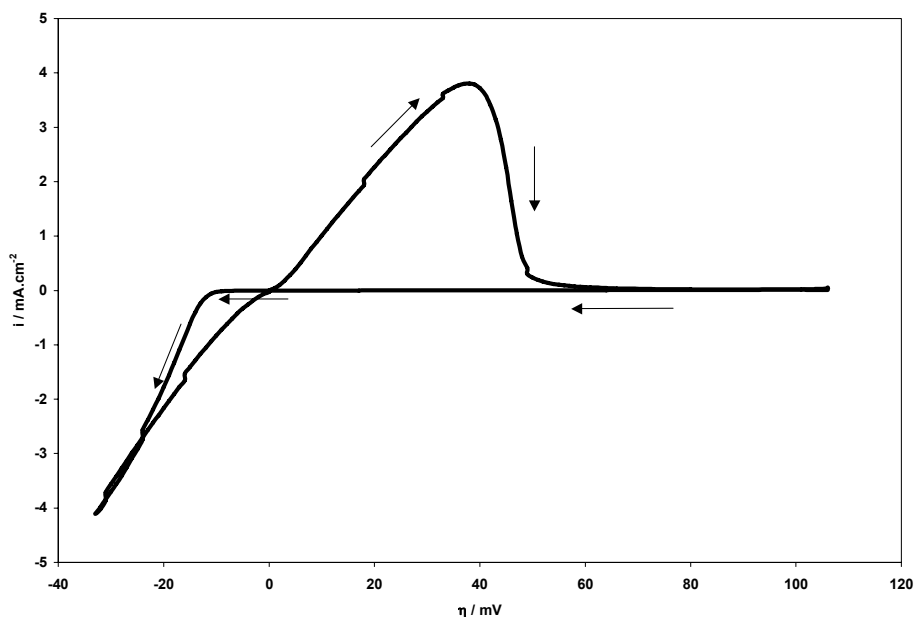


Figure 1. Cyclic voltammogram for Cd deposition and dissolution in the system $n\text{-Si}(100) / 0.1 \text{ M CdSO}_4 + 0.5 \text{ M Na}_2\text{SO}_4 + 5 \times 10^{-3} \text{ M H}_2\text{SO}_4$; $\text{pH} = 2.5$; $T = 298 \text{ K}$; $|dE/dt| = 1 \text{ mVs}^{-1}$

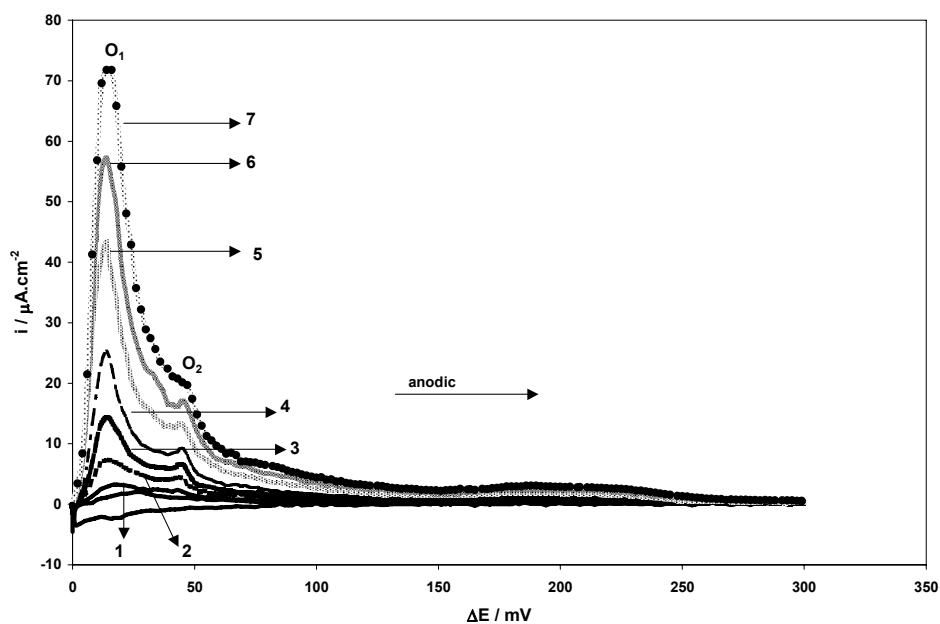


Figure 2. Anodic stripping curves obtained after different waiting times at $\Delta E_i = 0 \text{ mV}$. System: $n\text{-Si}(100) / 0.1 \text{ M CdSO}_4 + 0.5 \text{ M Na}_2\text{SO}_4 + 5 \times 10^{-3} \text{ M H}_2\text{SO}_4$; $\text{pH} = 2.5$; $T = 298 \text{ K}$; $|dE/dt| = 10 \text{ mV.s}^{-1}$. Waiting times: 1 (2 min), 2 (3 min), 3 (4 min), 4 (5 min), 6 (8 min), 7 (10 min).

We have undertaken the same experiment for a p-Si(100) and a n-Si(111) substrates. The same process also occurred with the system $n\text{-Si}(111) / 0.1 \text{ M Cd}^{2+}$, which indicates that the surface orientation doesn't account quantitatively for this process of charges

deposition at the equilibrium potential. The response of the system p-Si(100) / 0.1 M Cd^{2+} when the electrode was held constant at $\Delta E_i = 0$ mV was rather very poor. Even at a waiting time of $t = 10$ min, the anodic stripping current (peak O_1) could not exceed $8 \mu\text{A}/\text{cm}^2$. The system n-Si(100) / 0.1 M Cd^{2+} exhibited for the same waiting time of 10 min an anodic stripping current of about $70 \mu\text{A}/\text{cm}^2$. The poor response of the p type Si(100) - holes are the major carriers - compared with the n type Si(100) - electrons are the major carriers - could indicate that electrons are essentially involved in the process of charge deposition at the underpotential $\Delta E_i = 0$ mV. Another characteristic feature of the system n-Si(100) / 0.1 M Cd^{2+} is the presence in Figure 2 of a small anodic stripping peak O_2 .

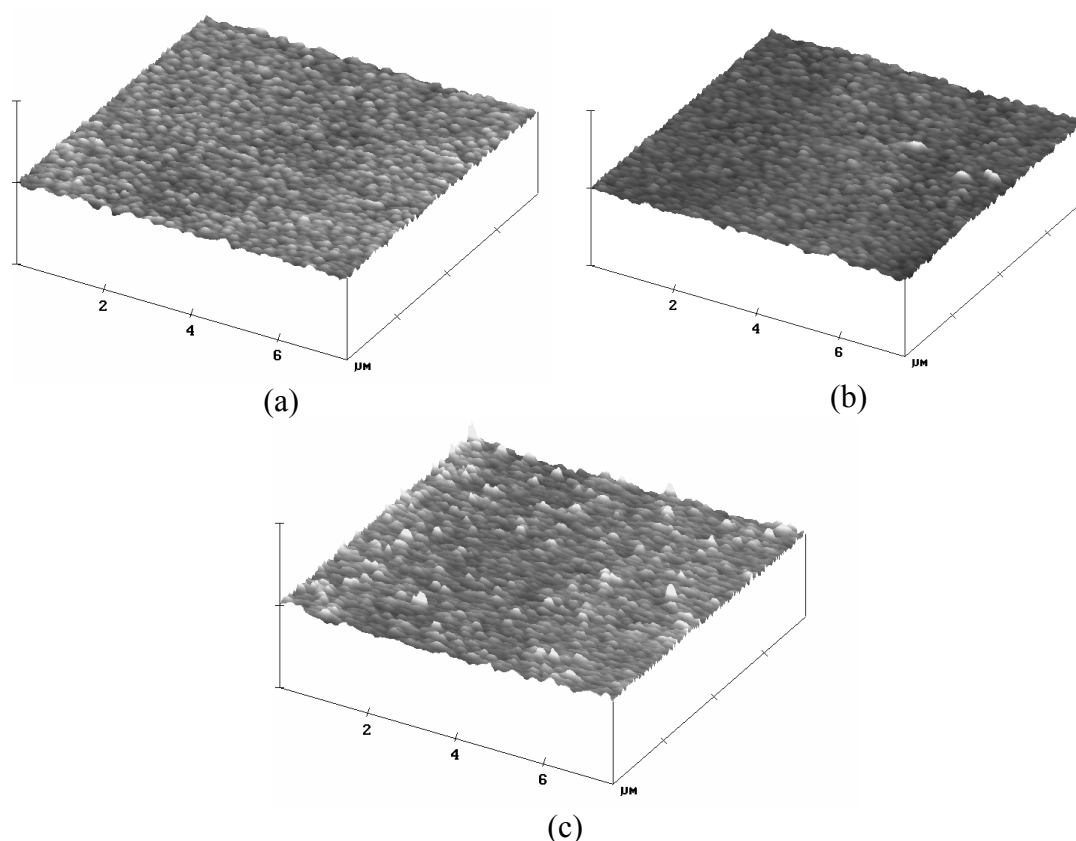


Figure 3. In situ AFM images showing the electrochemical Cd deposition on n-Si(100): (a) bare Si substrate at $\Delta E_i = 100$ mV, (b) Formation of hemispherical 3D Cd crystallites at $\eta = -8$ mV after $t = 20$ s in the OPD range, (c) Surface modification at the equilibrium potential $\Delta E_i = 0$ mV after a waiting time of 2 min.

System: n-Si(100) / 0.1 M $\text{CdSO}_4 + 0.5$ M $\text{Na}_2\text{SO}_4 + 5 \times 10^{-3}$ M H_2SO_4 ; pH = 2.5;

$T = 298$ K. Scales: horizontal axis X: $2 \mu\text{m}/\text{division}$; vertical axis Z: $60 \text{ nm}/\text{division}$

Electrochemical in situ AFM experiments were carried out in the AFM cell to observe the morphology of the deposits in the OPD and UPD ranges. We were not able to observe the initial stages of Cd deposition at surface steps and others surface inhomogeneities. We used therefore the following polarization: the substrate potential was held for 1 min at $\Delta E_i = 100$ mV in the UPD range; then the potential was suddenly fixed for 20 s at a low value of overpotential η in the OPD range. The substrate was

imaged under these conditions. This routine allows the direct observation of small hemispherical 3D Cd crystallites as can be seen in Figure 3b. When we compare the bare substrate at $\Delta E_i = 100$ mV (Figure 3a) with the same substrate polarized for a certain time (2 min) at the equilibrium potential $\Delta E_i = 0$ mV (Figure 3c), it is obvious that at this later potential there is a surface modification which results from a process of deposited charges (Cd^{2+}). This result is in agreement with those shown in Figure 2 where the amount of deposited charges increases with the waiting time. A central question then arises in the study of Cd deposition on the silicon electrode at the equilibrium potential: does this surface modification result from the formation of a surface alloy or a cadmium sulfate complex on the surface of the substrate? Since in situ AFM experiments do not provide any chemical information about the exact nature of the deposited charges, no attempt will be made here to analyze further this phenomenon. Experiments are under investigation in our Laboratory to understand the whole process and this will be the purpose of our next paper.

Current-time transients

Figure 4a shows current transients for Cd deposition on n-Si(100) 20 – 40 Ωcm resistivity. The deposition rate increases with overpotential η . The analysis of the transients was restricted only to their initial part in order to exclude overlapping effects of growing 3D Cd clusters and/or diffusion zones. The transient current density under these conditions is defined as i_{free} . Figure 4b shows the initial parts of the transients in a $(i_{free})^{2/3}$ vs. t plot. All the linear relationships were obtained with coefficients of determination R^2 greater than 0.9025. This indicates the goodness of fit of the data to a straight line [16]. The obtained linear relationships correspond to a nucleation and growth model including progressive nucleation and hemispherical diffusion to the growing 3D Cd clusters, where i_{free} is given by [17]:

$$i_{free} = -zF \frac{2}{3} \pi \nu_m^{1/2} J (2DC_{Cd^{2+}})^{3/2} [1 - \exp(-\frac{zF\eta}{RT})]^{3/2} (t-t_0)^{3/2} \quad (1)$$

where ν_m represents the molar volume of the bulk metal Cd, D the diffusion coefficient of Cd^{2+} ions, $C_{Cd^{2+}}$ the metal ion bulk concentration, and t_0 the induction period. The nucleation rate J in equation (1) is defined by [17]:

$$J(\eta) = A \exp[-\frac{\Delta G_{crit}(\eta)}{kT}] \quad (2)$$

where $\Delta G_{crit}(\eta)$ is the Gibbs free energy for the formation of a critical cluster containing N_{crit} atoms. The pre-exponential factor A includes the number of active nucleation sites as well as the attachment frequency of single atoms to nucleus. The nucleation rates J were derived from the slopes of these plots using equation (1) with $\nu_m = 13.0074 \text{ cm}^3 \text{ mol}^{-1}$ and $D = 7.19 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [18]. This later value is an approximated value of the diffusion coefficient D , since the exact value of D may differ from the one given above due to the concentrated 0.5 M Na_2SO_4 supporting electrolyte [19]. The influence of the concentrated 0.5 M Na_2SO_4 supporting electrolyte is a decrease of the value of D [19].

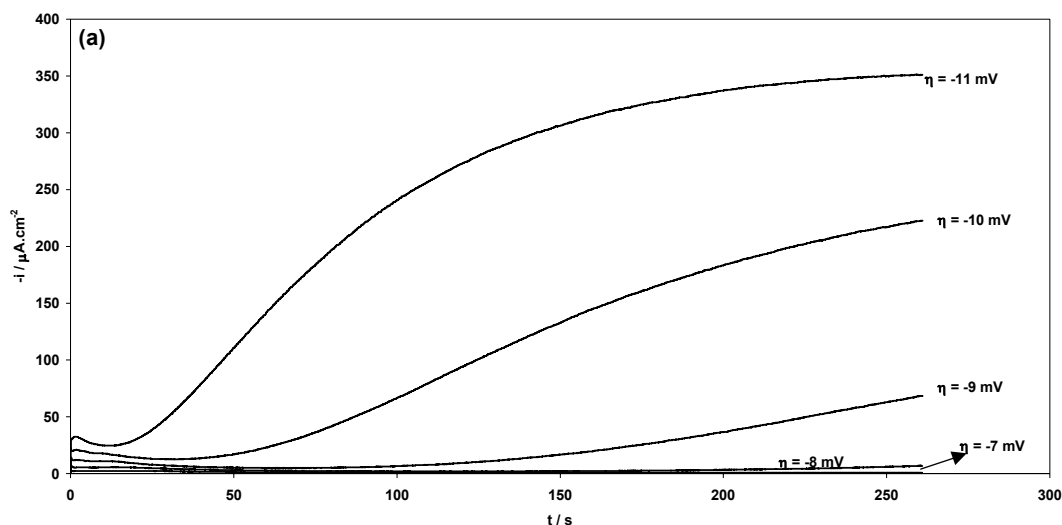


Figure 4a. Experimental current-time transients for Cd OPD at different overpotentials η in the system $n\text{-Si}(100) / 0.1 \text{ M CdSO}_4 + 0.5 \text{ M Na}_2\text{SO}_4 + 5.10^{-3} \text{ M H}_2\text{SO}_4$; $\text{pH} = 2.5$; $T = 298 \text{ K}$. Initial potential $\Delta E_i = E - E_{\text{Cd}/\text{Cd}^{2+}} = 0 \text{ mV}$

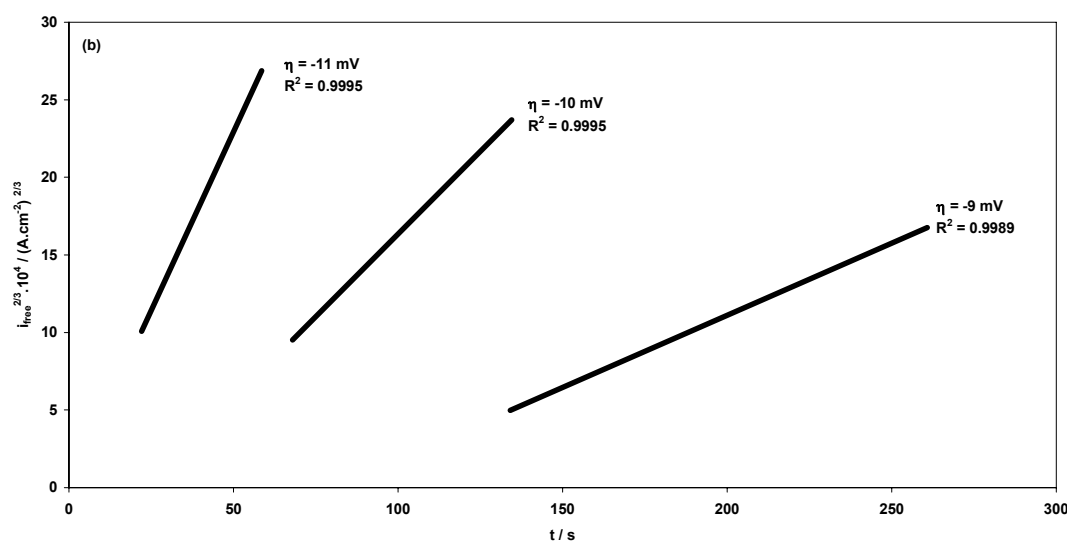


Figure 4b. $i_{\text{free}}^{2/3}$ vs. t plot of the initial parts of the transients shown in Figure 4a

Figure 5 shows the nucleation rate J as a function of the overpotential $|\eta|$ for the system under investigation. Linear $\ln J - |\eta|$ dependence is obtained in this overpotential range with a coefficient of determination R^2 greater than 0.9025 and in agreement with equation (2). The number of atoms N_{crit} in the critical cluster can be determined using equation (3)

$$N_{\text{crit}} = \frac{RT}{zF} \frac{d \ln J}{d |\eta|} \quad (3)$$

In this equation the weak overpotential dependence of the pre-exponential, A , in equation (2) is neglected because it affects N_{crit} only by less than 1 atom. From the slope

of the linear $\ln J - |\eta|$ dependence shown in Figure 5, a value of $N_{crit} = 14 \pm 1$ atoms was derived for the substrate in the overpotential range $-9 \text{ mV} \geq \eta \geq -11 \text{ mV}$ using equation (3). A decrease of the value of D from $7.19 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ down to $1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ doesn't change the number of atoms in the critical cluster (N_{crit}). The size of the critical cluster in 3D Cd phase formation process in the OPD range is mainly determined by Cd-Cd interaction. Furthermore, the low value of N_{crit} indicates that the nucleation process has to be described by an atomistic model instead of macroscopic theories [15, 17].

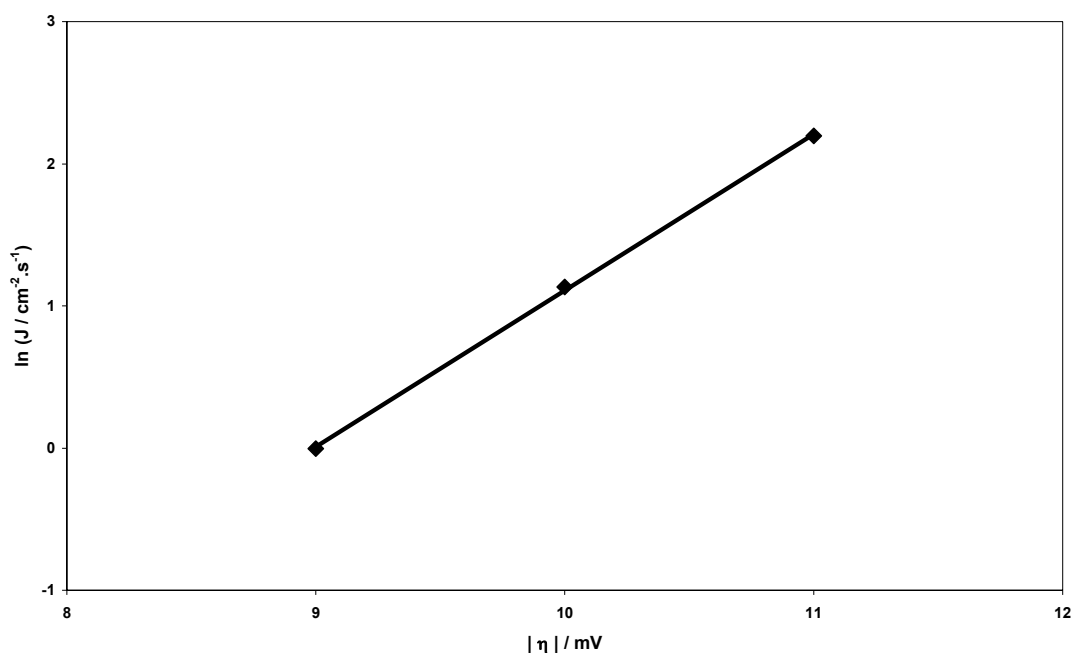


Figure 5. Nucleation rate J as a function of the overpotential η . System $n\text{-Si}(100) / 0.1 \text{ M CdSO}_4 + 0.5 \text{ M Na}_2\text{SO}_4 + 5 \cdot 10^{-3} \text{ M H}_2\text{SO}_4$; $\text{pH} = 2.5$; $T = 298 \text{ K}$. Coefficient of determination of the straight line: $R^2 = 0.9996$. $N_{crit} = 14 \pm 1$ atoms

A comparison of the results obtained in the present study with those obtained in the previous study of Cd electrodeposition from an aqueous 5 mM CdSO_4 solution [14] shows that the N_{crit} -values are close within experimental errors, but the overpotential ranges to reach the corresponding N_{crit} -values differ notably. While a relatively small cathodic overpotential range ($-9 \text{ mV} \geq \eta \geq -11 \text{ mV}$) is needed to reach the N_{crit} -value (14 ± 1 atoms) in the system $n\text{-Si}(100) / 0.1 \text{ M Cd}^{2+}$, a higher cathodic overpotential range ($-16 \text{ mV} \geq \eta \geq -19 \text{ mV}$) is needed to reach the N_{crit} -value (16 ± 1 atoms) in the system $n\text{-Si}(100) / 5\text{mM Cd}^{2+}$. In the case of electrodeposition of metals on semiconductor substrates, the influence of the space charge layer has to be taken into account [13]. 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 strongly depend on the relative position of the equilibrium potential $E_{Me/Me^{z+}}$, with respect to the flat band potential E_{fb} of the semiconductor substrate. The flat band potential of $n\text{-Si}(100)$ is about -0.16 V vs. SHE

(standard hydrogen electrode) [20]. The equilibrium potentials $E_{Cd/Cd^{2+}}$ are -0.46 V vs. SHE and -0.50 V vs. SHE for n-Si(100) / 0.1 M Cd^{2+} and n-Si(100) / 5 mM Cd^{2+} respectively. For both systems the condition $E_{Cd/Cd^{2+}} \ll E_{fb}$ is fulfilled so that an accumulation layer is formed at $E = E_{Cd/Cd^{2+}}$ and the deposition of the Cd bulk phase must occur at relatively small cathodic overpotentials, such as on metal substrates. This is indeed the case for both systems Si(100) / 0.1 M Cd^{2+} and n-Si(100) / 5 mM Cd^{2+} . The difference in the cathodic overpotential ranges could be related to the concentration of the metal ions Cd^{2+} . Since surface modification occurs at the equilibrium potential in the case of the first system (Figure 3c), this could lead to surface states which trap electrons more easily than in the second system. Therefore, a small cathodic overpotential range will be needed for the first system than it is for the second one.

CONCLUSIONS

Detailed studies have been carried out in the system n-Si(100) / 0.1 M Cd^{2+} using cyclic voltammetry, chronoamperometry and in situ AFM microscopy. The initial Cd deposition kinetics on n-Si(100) can be described by a model involving progressive nucleation on active sites and hemispherical diffusion towards the growing 3D Cd clusters. Within the investigated overpotential range (-9 mV $\geq \eta \geq -11$ mV), the number of atoms in the critical cluster was found to be $N_{crit} = 14 \pm 1$. The low value of N_{crit} indicates that the thermodynamics and kinetics of electrochemical nucleation must be described by the so-called small cluster or atomistic model [17]. The experimental results presented in this paper indicate clearly a process of deposited charges at the equilibrium potential, which lead to a surface modification and could explain why for the system n-Si(100) / 0.1 M Cd^{2+} a relatively small overpotential range is needed to reach the N_{crit} -value in comparison with the system n-Si(100) / 5 mM Cd^{2+} .

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