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Electrochemical Nucleation and Growth of Silicon in Molten Fluorides

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As lithium is added to the bronzes of low sodium content, the degree of tilting of the octahedra increases, reducing the aperture size and increasing the activation enthalpy of motion. (iv) The sudden change in properties for sodium contents greater than about 0.7 is consistent with sodium ordering in the structure. (v) Mixed lithium-sodium bronze phases prepared at high temperature also contain mobile lithium ions, although no quantitative measurements on single crystals have yet been made.

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Electrochemical Nucleation and Growth of Silicon in Molten Fluorides

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ABSTRACT

The electrochemical nucleation and growth of silicon on vitreous carbon and graphite are characterized. The anode is a $copper: silicon\ alloy\ and\ the\ electrolyte\ is\ a\ molten\ solution\ of\ KF: LiF: K_2SiF_6\ at\ 750^\circ C.\ SEM\ examination\ of\ the\ initial\ stages$ of electrodeposition shows that the nucleation process is instantaneous and is followed by three dimensional growth. Because the nucleation is instantaneous, the initial nucleation density and the grain size of the deposited silicon can be controlled. Existing theoretical models for nucleation and their failure to model this system are also discussed.

The electrodeposition of metals from aqueous solutions and molten salts has been studied extensively. Particular interest in metal deposition on foreign substrates has led to nucleation studies (1-6) and the development of theoretical models to characterize the different nucleation and growth mechanisms.

This work characterizes the nucleation of silicon on carbon substrates in an electrochemical process for silicon purification. The silicon is electrorefined in a molten salt system and simultaneously electrodeposited on POCO® graphite substrates as thin sheets of polycrystalline material (7). One possible application of this process is to use the as-grown material as the active base in a photovoltaic cell. In this case, it is desirable to optimize the grain size of the deposited material through knowledge of the nucleation process. In this paper, empirical studies are described which provide a qualitative understanding of nucleation and, as a

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result, enable one to control the grain size of the electrodeposited material. Existing theoretical models for nucleation and their failure to model this system are also discussed.

Background

Nucleation and growth processes in electrodeposition are characterized by three parameters (2, 3): the growing radially), or three dimensional (hemispherical time dependence of the nucleation process. There are three fundamental growth modes: the growth can be one dimensional (a planar surface growing normal to itself), two dimensional (such as cylindrical nuclei growing radially), or three dimensional (hemispherical or spherical nuclei). Independent from the growth mode is the limiting growth mechanism. This rate-determining step in the growth process can be either the interface kinetics (such as adatom surface diffusion or incorporation), charge transfer kinetics, or the mass transfer of metal ions to the electrode surface. Finally, there are two broad categories for the time dependence of

the nucleation process. If all the nuclei form at essentially the same time, nucleation is termed "instantaneous." If nucleation continues to occur over a period of time, it is considered progressive.

The important parameter in optimizing grain size of deposited material is the time dependence of the nucleation. If nucleation is progressive, nuclei will continually form and grow, making grain size difficult to control. However, if nucleation is instantaneous, grain size is easily optimized. The number of nuclei which form is a function of potential (2) and with constant current growth conditions, this potential is related to the current density. Because no nuclei form after the initial nucleation process in instantaneous nucleation density. The density of nuclei determines how soon the nuclei coalesce and therefore determines the ultimate grain size (4).

The growth mode and time dependence of the nucleation process are most easily determined from observations of the initial shape and size of the heterogeneous deposit. The size of each nucleus is proportional to the time since its formation. Therefore, if the nuclei are of random size, nucleation is progressive, whereas if the nuclei are of equivalent size, nucleation is instantaneous (2, 8).

Another method for determining the time dependence of nucleation is to compare the results of potential step experiments with theoretical models. Experimentally, a potential step is applied to a bare electrode and a current-time response is measured. In processes other than deposition, the current decreases with time. However, for electrodeposition, once nucleation has occurred, the current usually increases due to an increasing surface area and a change from planar to two- or three-dimensional diffusion. This rising current can be modeled as a function of time and as such can be used to determine the nature of the nucleation process.

Models have been developed for systems involving different combinations of the characteristic parameters for nucleation and growth processes. Earlier models resulted in simple current-time relations of the form

$$I = Kt^{n}$$
 [1]

where K is a product of physical parameters (e.g., nucleation density N_0 , molecular weight of the deposited metal M, etc.) and n is generally some half integral number which is characteristic, but not unique, to the properties of the nucleation and growth process. For example, for the instantaneous nucleation and kinetics limited growth of three-dimensional nuclei, n = 2 (9).

These earlier models assume that only one process is rate controlling and that no overlap of nuclei occurs. More recent models (6) take into account the effects of overlap and ingestion of nucleation sites resulting in more complicated current-time relations. Alternatively, more than one mechanism may be rate controlling, such as the case of both kinetics and mass transfer control. In the following the potential step, currenttime response for a mixed control, and instantaneous nucleation process are derived by equating the currents due to mass flux (10)

$$I = n\mathbf{F}AkC \exp(H^2 t) \operatorname{erfc}(Ht^{\frac{1}{2}})$$
[2]

and the current due to mass accumulation for hemispherical nuclei

$$I = (2\pi n \mathbf{F} r^2 \rho / M) \frac{\partial r}{\partial t}$$
 [3]

where $H = k/D^{\frac{1}{2}}$, k is the reaction rate constant, D and C are the diffusion coefficient and the concentration of the electrodepositing species, M and ρ are the molecular weight and density of the depositing metal, and the other terms have their usual meaning. $r = (kCM/\rho) [\exp(H^2 t) \operatorname{erfc}(Ht^{\frac{1}{2}})H^{-2}]$

$$+ 2t^{\frac{1}{2}H^{-1}\pi^{-\frac{1}{2}}}$$
 [4]

which can then be substituted back into I to give

radius of the nucleus, as a function of time

$$I = (2\pi n \mathbf{F} k^3 C^3 A N_0 M^2 \rho^{-2}) \{\alpha^3 H^{-4}\}$$

$$+ 4t^{\frac{1}{2}\alpha^{2}H^{-3}\pi^{-\frac{1}{2}}} + 4t\alpha H^{-2}\pi^{-1}$$
 [5]

where $\alpha = \exp(H^2t)$ erfc $(Ht^{\frac{1}{2}})$. This equation, along with those of the form of Eq. [1], is used to analyze potential step transients for this system.

Experimental

A vitreous carbon crucible containing the anode (silicon source) and the molten salt electrolyte is situated in a resistively heated furnace at 750°C (see Fig. 1). The anode is solidified *in situ* from a hypereutectic solution of semiconductor grade silicon [16 weight percent (w/o)] and copper (99.999%). The electrolyte is a mixture of KF:LiF:K₂SiF₆ [46 mol percent (m/o):46 m/o:8 m/o] where the K₂SiF₆ is formed by reacting SiF₄ with excess KF. The LiF and KF are Suprapur[®] grade.

The KF and LiF are dried in situ at pressures less than 10^{-5} Torr by slowly heating from $100^{\circ}-300^{\circ}$ C. This drying procedure effectively prevents the formation of hydrolysis products that have a detrimental effect on the morphology of the silicon electrodeposit. The molten salt is further purified by a pre-electrolysis step. A potential of 2V is applied to a graphite electrode (relative to the crucible) until the current is less than 1 mA/cm².

The silicon reference electrode is formed in situ by depositing silicon on a 3 mm vitreous carbon rod. This electrode is stable for 2-3 days. Alternatively, an oxide-free, single crystal silicon wafer may be used as a reference electrode. The working electrode is the rounded end of a 3 mm rod of either graphite or vitreous carbon with a geometric area of 0.3-0.4 cm².

The chronoamperometric data are recorded with a Nicolet digital storage oscilloscope. For curve fitting the oscilloscope is interfaced with a Hewlett Packard 9825 computer.

Results and Discussion

Figure 2 shows a scanning electron micrograph of silicon nuclei grown on vitreous carbon. The size and shape of the nuclei determine the time dependence of nucleation and growth mode for the system. The nu-





Fig. 2. Scanning electron micrograph of silicon nuclei electroaeposited at 15 mA/cm². Deposition was 10 C of material on 1.5 cm² vitreous carbon. Imperfections in the vitreous carbon surface also appear.

clei are hemispherical, indicating that the growth is three dimensional. The nuclei are also all of equal size. They must have formed at essentially the same time, implying that the nucleation process is instantaneous. This means the grain size of the deposited silicon can be controlled by the initial current density.

The importance of the initial current density in controlling the grain size is illustrated in Fig. 3. These SEM micrographs show two as-grown silicon surfaces. Although both were grown at the same final current density, the initial current-time profiles were different. The current for the deposit in Fig. 3a was stepped directly from zero to the final growth current density of 70 mA/cm². As a result, nucleation occurred at a high current density, the nucleation density was large, and the grain size was small. The current for the deposit in Fig. 3b was stepped from zero to an intermediate current density of 40 mA/cm² and then ramped up to the final current density of 70 mA/cm². In this case, a lower nucleation density was established by a lower current density, and the resulting grain size was larger. This means that, by controlling the initial current-time profile, the grain size of the material can be controlled independently of the final growth conditions. One problem can arise if the initial current density is too low. In this case, there are areas where the nuclei do not coalesce, leaving voids in the material. Therefore, there is a compromise between maximizing the grain size and ensuring complete surface coverage.

Having established that nucleation is instantaneous and that the grain size can be controlled, potential step experiments were done to try to apply nucleation theory in this system. A series of potential-step, current-response curves are shown in Fig. 4. [Note that the process occurs on a time scale of msec, not sec, as is often encountered (1-3).] The curves can be broken down into several characteristic regions. Initially the current is large as a result of double layer charging and decays exponentially. In the ideal case, this should be followed by a nucleation current which increases with time. However, in this system, the onset of nucleation is swamped by a large prenucleation current which decays slowly in a diffusion limited $t^{-\frac{1}{2}}$ manner. In order to incorporate this large prenucleation current into the theoretical models, linear sweep cyclic voltammograms were examined to determine its cause.

The cyclic voltammogram, shown in Fig. 5, has several key features (11). The inflection point at approximately 0V is the reversible potential for silicon reduction relative to the silicon reference electrode. The





Fig. 3. Scanning electron micrographs of as-grown silicon deposits. Growth conditions: (a, top) current stepped to 70 mA/cm², (b, bottom) current stepped to 40 mA/cm² and then ramped to 70 mA/cm². Total coulombs in each case is approximately 300 C/cm².



Fig. 4. Cathodic current transients for silicon electrodeposition on 0.3 cm² vitreous carbon. Steps are from +1V to the final cathodic step potentials shown.

onset of silicon deposition is slightly offset from this reversible potential by the nucleation threshold, indicating nucleation is the initial rate-limiting step in deposition. The cathodic excursion is due to silicon deposition. The surface increase loop implies that the area of the growth surface is increasing. The increasing surface area results in a larger current on the reverse scan than on the forward (cathodic) scan, and may be



Fig. 5. Expanded cyclic voltammogram for silicon deposition on graphite vs. Si reference electrode with KF:LiF:K₂SiF₆ electrolyte, $T = 724^{\circ}$ C, scan rate = 50 mV/sec, and area = 0.4 cm². The cathodic limit, in this case, -50 mV, along with the scan rate determines the quantity of silicon deposited on the carbon electrode, which in turn is proportional to the height of the stripping peak anodic of the reversible potential. The anodic limit is +0.7V.

due to either two-dimensional or three-dimensional growth. Anodic to the reversible potential, there is a small cathodic current which was correlated with the prenucleation current. There are several possible explanations for this current. For example, the cathodic current is associated with the underpotential deposition (UPD) of silicon on graphite. UPD is the adsorption of a monolayer of metal atoms onto a foreign substrate at potentials anodic of the reversible potential. There are two theoretical criteria to determine if UPD should occur. One involves the difference in lattice parameters of the substrate and depositing species. For differences in unit cell dimensions greater than 1.5Å, it has been shown that monolayer formation, and therefore UPD, does not occur (12). However, conclusions made by comparing unit cell dimensions for silicon on polycrystalline graphite are questionable since graphite is anisotropic. Other work has related UPD to differences in work function (13). The UPD shift is shown to be half the difference in work functions of the substrate and depositing species. Work function data for silicon and carbon are inconclusive due to the wide spread in reported results (14). If the mean values are used, UPD should occur at approximately 0.2V anodic of the reversible potential, which is approximately what is observed in cyclic voltammograms. However, the presence or absence of UPD is inconclusive at this time.

Another possibility for the prenucleation current is the reduction of impurities. In similar experiments in which silicon is purposely excluded from the system, *i.e.*, with KF, LiF, and Cu only, a large current results in response to a potential step. This current may be due to a change in oxidation state of a species such as copper, or it may be due to the presence of oxides since there is some correlation between this prenucleation current and the height of an oxidation peak at +2.0V. These processes are likely to occur with silicon also present in the system.

Because the causes of the prenucleation current could not be conclusively determined, two methods were used to treat the step response data. In one method the prenucleation current was assumed to drop to zero once nucleation occurred and the data were treated in a straightforward manner. In the other method, the prenucleation current was extrapolated and then subtracted from the total current. This residual current was treated as the nucleation and growth current. In neither method did the current fit any of the simple models (Eq. [1]).

It is surprising that this system does not follow a simple diffusion-controlled model. Most molten salt



Fig. 6. Current time transients for (a) vitreous carbon and (b) graphite. Geometric areas are 0.3 cm^2 and potential steps are +1V to -100 mV.

systems are diffusion controlled since at elevated temperatures, the temperature activated processes (such as charge transfer) are rapid (2). However, in this system, a diffusion-limited current has not been observed in cyclic voltammetry (within the limits of the apparatus). This suggests the mixed control model Eq. [5] might better describe the system; however, it did not. Using a model which accounts for nuclei overlap, again assuming mixed control (6), also failed to fit the data with meaningful parameters. This suggests there are several processes occurring simultaneously in this system which cannot be understood or deconvoluted by existing theories.

To explore the effects of the substrate material on the nucleation process, potential step experiments were done on graphite and vitreous carbon. Though both materials are made of carbon, they have different properties, as seen by comparing incubation times for silicon nucleation (Fig. 6). The incubation times on graphite were an order of magnitude larger than those on vitreous carbon. One possible reason is that vitreous carbon has a greater number of highly active sites for nucleation. At the same initial current density, grain sizes will be smaller on vitreous carbon than on graphite due to its lower resistance to nucleation. Other possible explanations can be formulated, but no supporting data or observations exist.

Conclusions

We have shown that the electrochemical nucleation of silicon on vitreous carbon or graphite in a molten fluoride is instantaneous and is followed by three-dimensional growth. Though the growth process cannot be completely characterized theoretically, the fact that nucleation is instantaneous enables the grain size of the as-grown silicon to be controlled, and its growth parameters and polycrystalline structure to be optimized.

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Galvanostatic Pulse Plating of Copper and Copper (I) Halides from Acid Copper (II) Halide Solutions

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ABSTRACT

CuX (X = Cl or Br) is formed during the galvanostatic pulse plating of copper from acid solutions containing Cu^{2+} and X^- . The reaction $Cu^{2+} + Cu^{0+} + 2X^- \rightarrow 2CuX$ occurs in the relaxation period of the pulse. Copper (I) chloride andes for reserve seawater batteries may be made by this method. CuBr is oriented in the {220} plane when deposited on copper foil with the {200} plane uppermost. CuCl tends to dissolve in solutions containing Cl⁻ to give soluble copper (I) halides. Corrosion rates at pure copper were determined from the pulse-plating experiments.

Studies (1-3) of copper plating from acid baths by a variety of pulse methods have been made to improve efficiency and plate quality, especially in cathode geometries having small holes or pores (1). Different additives may also improve plate quality by complexing with ions in solution or by adsorption at the plating surface. This investigation was instituted to observe the effect of additives on pulse plating. Copper halides were chosen as model systems because of the availability of data and the body of previous work.

The corrosion of copper in solutions of copper(II) chloride has been studied by Hurlen (4, 5) who showed that layers of copper(1) chloride are formed which subsequently dissolve giving soluble species such as $CuCl_2^-$. The rate of copper(I) chloride formation is slow after an initial monolayer because of the need for solid-state movement of chloride ions to the underlying bulk copper. Numerous workers (4, 6-8) have studied the anodic behavior of copper in halide media. Copper dissolves to $CuCl_2^-$, $CuCl_3^{2-}$, and $CuCl_4^{3-}$ via films of CuCl.

Copper(I) chloride is used as an anode for reserve seawater batteries (9), which may be fabricated by mixing copper(I) chloride with an organic binder and graphite, or by dipping copper plates into molten copper(I) chloride (9). A method of manufacture by direct reaction at a copper electrode, as described in this paper, may provide electrodes which are more conducting, have a known discharge capacity, and ultimately be more economical.

Experimental

Materials

All materials were of Analar grade and used without further purification. Electrodes were 2 imes 2 cm copper foil (BDH 99.999%) or 2×2 cm platinum foil

• Electrochemical Society Active Member. Key words: pulse plating, battery anodes, corrosion.

(Johnson Matthey 99.99%) on which a thin layer of copper was plated from acid copper sulfate solution.

Methods

Corrosion of copper in solutions containing halide ions.-A clean copper foil was suspended from a balance (CI Electronics Microforce II) in a solution containing 1 mol dm⁻³ H₂SO₄, 0.34 mol dm⁻³ CuSO₄, and 0.1 or 0.34 mol dm^{-3} KCl or KBr. The solution was thermostated to $25^{\circ}C$ ($\pm 0.5^{\circ}C$). During the experiment, the level of the solution was adjusted relative to the electrode to correct for the buoyancy of the electrode. The increase in weight of the foil was measured (± 0.01 mg) with time. Similar experiments were attempted with solutions containing fluoride and iodide ions.

Pulse plating.—Copper was galvanostatically (300 mA) pulse plated from a series of electrolytes containing 1 mol dm⁻³ H₂SO₄, 0.1 to 0.34 mol dm⁻³ CuSO₄, and 0.05 to 0.34 mol dm $^{-3}$ KCl or KBr. A single compartment cell was used with a copper or platinum foil anode. The potential of the working electrode was monitored by an oscilloscope against a saturated calomel reference electrode connected with the Luggin capillary by a salt bridge. The cell was continuously purged with nitrogen during all experiments, and thermostated to $25^{\circ}C$ ($\pm 0.5^{\circ}C$). A train of square wave pulses was produced by a Chemical Electronics pulse generator (CE RB1) and the current controlled by a potentiostat (Thompson Associates 125) working in a galvanostatic mode. The range of pulse periods was 0.5-10 msec, and relaxation times of 10-1000 msec. For analysis of the deposited layer, plated platinum electrodes were used.

Analysis of plated layers.—Plated electrodes were washed with distilled water and dried in a nitrogen atmosphere to constant weight. For copper-plated