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Electrodeposition of Tin onto a Well-Defined Pt(111) Surface from **Aqueous HBr Solutions**

Studies by LEED and Auger Electron Spectroscopy

John L. Stickney, *^{,1} Bruce C. Schardt, Donald A. Stern, Andrzej Wieckowski,² and Arthur T. Hubbard*

Department of Chemistry, University of California, Santa Barbara, California 93106

We wish to report an instance in which the energetic driving force for electrosorption, in this case the substantial affinity of tin-oxygen monolayers for the Pt surface, was sufficient to cause spontaneous deposition of monolayer quantities of material upon immersion (of Pt into Sn(II) solutions) at open circuit. Since the electrodeposition of Sn species occurred without flow of current in the external circuit, the deposited species were detected, identified, and quantitated by Auger electron spectroscopy (1) along the lines of previous work from this laboratory (2).

Experimental procedures were as described in Ref. (3). After cleaning and annealing, the electrode was examined by LEED and Auger spectroscopy to directly verify surface structural and compositional purity. Electrode potentials were measured with respect to a Ag/AgBr $(10^{-3}M)$ KBr) half-cell, standardized against a Ag/AgCl (1M NaCl) reference, and are reported vs. the latter.

Immersion of the Pt(111) surface into $10^{-4}M$ SnCl₂ in 10⁻²M HBr at open circuit produced a Sn-containing deposit having the Auger spectrum shown in Fig. 1B. Integration of Auger spectra revealed that Sn species were present at a packing density, θ_{sn} (Sn atoms per Pt surface atom), of 0.90, Table I, and oxygen species, $\theta_0 = 1.3$. (Packing densities in Table I were calculated from Auger data without correction for self-scattering and therefore represent lower limits.) As would be expected for (3), the Pt Auger signal decreased sharply, to 29% of the clean surface value, as a result of the spontaneous deposition process. Oxygen was not detected after the immersion of Pt(111) from 10⁻²M HBr near 0V in the absence of Sn(II), Table I. Therefore, the presence of a large oxygen signal

*Electrochemical Society Active Member. ¹Present address: Department of Chemistry, University of

Georgia, Athens, Georgia 30602. ²Present address: Department of Chemistry, University of Illinois, Urbana-Champaign, Urbana, Illinois 61801.

is related to the presence of Sn. Substantial Br was present whereas Cl was negligible, as expected on the basis of solution composition. Inspection of thermodynamic data for Sn and its compounds suggests an explanation for the presence of an oxygen Auger signal. Sn²⁺ is slightly unstable in water in favor of species such as Sn(OH)₂. For instance, based upon the usual tabular values of standard potentials, ΔG° is -3.78 kcal/mol for the reaction

$$2\mathrm{Sn}^{2^{+}} + 2\mathrm{H}_{2}\mathrm{O} \rightleftharpoons \mathrm{Sn}(\mathrm{OH})_{2} + \mathrm{Sn}^{4^{+}} + \mathrm{H}_{2} \qquad [1]$$

The pathway of oxidized tin deposition may involve electrodeposition of metallic Sn, Eq. [2], with the disproportionation (4) and the underpotential as the driving forces, followed by

Table 1. Auger spectroscopic data^a

Surface treatment	Sn from Auger data ^b	O from Auger data ^b	Br from Auger data ^b	Pt Auger signal at 160°V, relative to clean Pt(111)
Open-circuit immersion Voltammetric scan	0.90 1.40	1.26 3.90	0.16 0.00	0.29 0.00
Immersion at 0.6V Pure 0.01M HBr supporting electrolytes	1.10 0.00	2.94 0.00	0.23 0.44	0.05 0.75

^a Experimental conditions: $10^{-4}M$ SnCl₂ in $10^{-2}M$ HBr at $23^{\circ} \pm 1^{\circ}C$. Auger beam current, 1A at 2000 eV, 11° incidence from the surface plane; Ag/AgCl (1M NaCl) reference electrode.

^b Auger electron yield factors, G_{sn} (435 eV) –36.3 × 10⁻¹⁹ cm², $G_0 = 6.12 \times 10^{-19}$, and G_{Br} (1400 eV) = 0.44 × 10⁻¹⁹ from Ref. (5). Auger data were not adjusted for self-scattering.

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Fig. 1. Auger spectra: A. Clean surface; B. After immersion at open circuit in tin solution; C. After scans shown in Fig. 3; D. After immersion at controlled potential, 0.600V.



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corrosion of the metallic Sn, Eq. [3]

$$Sn + 2H_2O \rightarrow Sn(OH)_2 + H_2$$
[3]

Or, the Pt surface may be catalyzing the direct conversion of Sn^{2+} to the oxidized tin deposit. Participation of Sn^{4+} , as in Eq. [1], is consistent with the observation that the open-circuit potential was relatively positive, 0.3V, at the time of immersion, declining to the steady value, -0.15V, over a period of about 2 min.

The packing densities of Sn and O increased to more than $\theta_{sn} = 1.4$ and $\theta_0 = 3.9$ when the potential was scanned positive of -0.1V in the Sn(II) solution, Fig. 3. Also, the O/Sn ratio increased, Table I, from 1.4 following open-circuit immersion, to 2.8 after anodization. That is, the average oxidation state of the Sn was doubled by anodic electrolysis in the Sn(II) solution. Similarly, immersion of the clean Pt(111) surface at 0.60V led to an oxidized Sn surface layer containing $\theta_{sn} = 1.1$, $\theta_0 = 2.9$, and a O/Sn ratio of 2.7. A second voltammetric cycle (dotted curve in Fig. 3) revealed that the surface had become passivated toward all but H₂ and O₂ evolution.

LEED patterns obtained following immersion and various stages of electrolysis were diffuse, as illustrated by Fig. 2B. Evidently, both the oxidized Sn layer and the oxidized Pt surface were disordered. The Sn results are thus in contrast to those reported for electrodeposition of Ag, Cu, and Pb, which displayed highly ordered superlattice at Pt(111), Pt(100), and Pt(s) (6(111) \times (111)) electrode surfaces (2, 3, 5-10).

A previous study presented Mössbauer spectroscopic evidence for residual SnO_2 on Pt electrode surfaces at positive potentials (11). Another previous study reported Auger spectra for SnO_2 surfaces cleaned by Ar^+ ion bombardment (12). The O/Sn signal ratio in that study was about two-thirds that for the anodized surfaces in this work, suggesting that surface enrichment of Sn may have occurred as a result of ion bombardment in that earlier work.

Spontaneous deposition, displayed to an exceptional degree by Sn^{2+} at Pt, was observed also for Ag⁺ at Pt(111),



Fig. 2. LEED patterns: A. Pt(111) (1 × 1), clean surface, 140 eV; B. Pt(111) (diffuse), after immersion in tin solution, 251 eV. Downloaded on 2015-02-24 to IP 35.8.191.249 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).



Fig. 3. Current potential scan: solid curve = first scan, dotted curve = second scan, 2 mV/sec.

Pt(100), and Pt(s) (6(111) \times (111)) (3, 5-10). The extent of spontaneous deposition of Ag depended on the crystallographic orientation of the Pt substrate surface and the nature of the supporting electrolyte, being greatest for surface-inactive electrolytes and the relatively open Pt(100) structure. Since spontaneous deposition occurs without flow of current in the external circuit, and since anodic stripping of the deposited material tends to be complicated, these results illustrate some of the hazards of the study of metal monolayer deposition and related phenomena by electrochemical methods alone.

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Chemical Etching of Ion Implanted Amorphous Silicon Carbide

J. A. Edmond, J. W. Palmour, and R. F. Davis

Department of Materials Engineering, North Carolina State University, Raleigh, North Carolina 27695-7907

Silicon carbide (SiC) is a wide bandgap semiconductor having a high breakdown electric field, saturation drift velocity, melting temperature, and thermal conductivity and a low dielectric constant (1). It is currently being grown and perfected, in bulk and thin film forms, for use or potential use in high temperature device operations and electro-optical applications, as well as for high power and high speed switching devices.

In the amorphous state, SiC (a-SiC) has principally been used with amorphous Si in the development of heterojunction solar cells (e.g., Ref. (2)). Additionally, it has been employed as a passivation dielectric material (3) and as a light emitting diode (4).

Etching of monocrystalline SiC has been studied by a number of investigators (1, 5-8). Typical applications include selective etching for the formation of device structures, surface cleaning, and defect delineation. Various methods employed for etching this material include molten salt, gas-phase, thermal, molten metal, and electrolytic (see an essentially complete list of etchants and a discussion of their efficacy in Ref. (1), pp. 659-667) as well as reactive ion etching (7). However, crystalline SiC is strongly resistant to chemical attack. With the exception of slow decomposition in hot H_3PO_4 (6), no acids are known to chemically attack SiC. However, its two components, Si and C, individually react readily with (1:1) HF:HNO₃ and hot HNO₃, respectively.

Chemical etching of a-SiC has not been extensively investigated. Chang et al. (3) recently measured the rate of this process for B or P in situ doped hydrogenated a-SiC films prepared using radio-frequency glow discharge. The etch solutions employed were concentrated HF acid (49%), buffered HF, and hot (453 K) H_3PO_4 . Etch rates were determined as a function of the C source utilized during film preparation. The results pertinent to the present work show that, for P doped samples, the etch rate was 5 nm/min, when using the concentrated HF acid solution. Additionally, McHargue et al. (8) have compared etch rates of amorphous surface layers produced in both poly- and monocrystalline α -SiC by ion implantation of Cr. The etchant used was a boiling saturated solution of (1:1) K_3 Fe(CN)₆ and KOH. Etch rates for the amorphous layers produced in the polycrystalline and monocrystalline α -SiC were 134 and 80 nm/min, respectively. A summary of results is given in Table I.

In the present research, amorphous surface layers have been produced via ion implantation of ³¹P⁺, ²⁷Al⁺, and ²⁸Si⁺ and ${}^{12}C^+$ at liquid N₂ temperatures in single crystal (100) β -SiC thin films. These were previously fabricated by epitaxial growth at 1658 K on (100) Si, using a dual process of chemical conversion of the Si surface, followed by film growth via chemical vapor deposition (CVD) (9).

Because of the high thermal annealing temperature required to recrystallize an amorphous layer in β -SiC

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