

Spectroelectrochemical Study of the Effect of Organic Additives on the Electrodeposition of Tin

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Adsorption behavior and the effect of organic additives on tin electrodeposition process were studied utilizing combined electrochemical and surface enhanced Raman spectroscopy (SERS) techniques. The adsorption behavior of polyethylene glycols with and without hydrophobic head group was correlated with the morphology of the deposit. SERS experiments suggest that the head group part of the molecule remains adsorbed at all potentials studied. The potential dependence of the adsorption is primarily due to the hydrophilic tail in the Triton X100 family of compounds. The head groups of Triton X compounds are not required for adsorption but significantly enhance it. Triton X also enhances phenolphthalein adsorption on gold or silver surfaces and weakly interacts with it through some kind of supramolecular interactions. The coadsorption of Triton X100 and phenolphthalein significantly changes the grain size and the deposit structure of the electroplated tin as compared to Triton X alone. © 2003 The Electrochemical Society. [DOI: 10.1149/1.1554724] All rights reserved.

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Organic additives are commonly used in the electrodeposition of tin from acidic solutions.¹⁻⁴ Surfactants and grain refiners are added to plating baths to influence the deposit morphology, brightness, and grain refinement.⁵ These addition agents are an important component of plating baths for the deposition of tin with desirable properties and morphology suitable for electronic and other practical applications. While the use of organic reagents in electrodeposition process is commonplace, the specific activity of the reagents is only generally understood in terms of adsorption at the cathode surface during the deposition. The manner in which small amounts of organic species affects the physical morphology of a metal deposit remains unclear. Adsorption on the metal surface is believed to be the main generic way of these additives influencing the electrodeposition process. Numerous experimental works discuss the effect of additives on metal electrodeposition.⁶⁻⁸ A major limitation of these studies is the inability to characterize accurately the adsorption of ionic and molecular species at the electrode surface during the electrodeposition.

Surface enhanced raman spectroscopy (SERS) is a vibrational spectroscopy that provides 10⁶ times stronger Raman signals of the species adsorbed on a metal surface as compared to normal Raman spectroscopy. In addition, SERS is highly surface selective, that is, typically only the molecules (or parts of them) that are in direct contact with the surface are enhanced and show up in the spectra. SERS has been widely used to obtain the information on what species are adsorbed, what their orientations are on the surface, and how strong is the adsorption.⁹ These studies, however, have been mainly limited to relatively small and simple molecules, which are normally not used in electroplating. Hope and Brown used SERS to study adsorption of polyethylene glycol (PEG) at a polarized copper electrode.¹⁰ They found the adsorption to be potential dependent. Unfortunately, direct measurements of adsorption behavior of organic molecules on tin electrode by SERS is very difficult because the enhancement effect is limited for gold, silver, or copper electrodes. Nevertheless, valuable insights can be gained by correlation of adsorption behavior measured by SERS on gold or silver electrodes with electrochemistry of tin and morphology of tin deposit.

In this paper, we used SERS to study the adsorption of additives used in tin electroplating. As a model system we used combination of Triton X-100 and its derivatives with phenolphthalein. Such system is known to produce smooth and reflective coating in both pure tin and tin/lead electroplating.¹¹ Schematic structures of Triton X-100 and phenolphthalein are shown in Fig. 1. Table I lists the

nature and length of the surfactants used in this study. The major questions we tried to address in our study were orientation of these molecules on the electrode surface as a function of applied potential, effect of the length on adsorption strength and electrochemisty, role of the hydrophobic head of the molecule, and effect of mutual interaction between Triton X-100 and phenolphthalein.

Experimental

The effect of organic additives on the electrodeposition of tin from aqueous 1 M methanesulfonic acid (CH_3SO_3H) and 0.5 M tin methanesulfonate $(SnCH_3SO_3)$ electrolyte was characterized by electrochemical methods in a standard three-electrode cell. The 0.5 L cell was comprised of a rotating copper disc electrode, platinum wire counter electrode, and Ag/AgCl reference electrode.

Raman spectra were collected by Renishaw 1000S microscope equipped with custom build three-electrode spectroelectrochemical cell. 633 nm unpolarized red excitation and 180° geometry was used to gather the data. Pt wire was used as a counter electrode and Ag/AgCl equipped with a Luggin capillary was used as a reference electrode. Gold and silver working electrodes were roughened using optimized literature procedures^{12,13} and 0.1 M KCl solutions in deionized water (Millipore). The potential of the electrode was controlled by a EG&G M273 potentiostat. All chemicals were purchased from Aldrich and used as received.



Figure 1. Schematic structures of the Triton X family of surfactants and phenolphthalein.

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Table I. Length and chemical nature of the molecules studied.

	Hydrophobic head	Number of ethylene oxide groups in the tail
Igepal CA520	C ₈ Ph	5
Triton X-100	C ₈ Ph	10
Igepal DM970	$(C_9)_2$ Ph	150
PEG1	none	7
PEG2	none	14
PEG2	none	77
PEG4	none	101
PEG-PPG	none	~85

Results and Discussion

Electrochemistry of tin electrodeposition, Triton X class of surfactants.-Typical voltammograms for the electrodeposition of tin in methanesulfonic acid with and without Triton X-100 are shown in Fig. 2. The onset of reduction current occurs at ca. -0.42V. Without Triton X-100, a current density peaked at ~ 0.5 V. No diffusion limiting current plateau was seen in the curve, and as potential decreased, current density started increasing rapidly again. Such behavior is usually associated with dendritic crystal growth, which greatly increases surface area of the electrode. The addition of Triton X-100 to the solution suppressed the dendritic growth of the tin deposit and a cyclic voltammogram (CV) revealed two distinct peaks. The current in the first peak at ~ 0.5 V did not depend on tin concentration in the solution and it was reasonable to associate appearance of this peak with adsorption of Triton X-100 on the growing tin layer, which strongly inhibited the tin reduction current. This process can be reversible, as seen from the inset in Fig. 2. The second peak at -0.75 V depended strongly on the tin concentration indicating that it is a diffusion limiting current.

The effect of agitation on the reduction of tin in the presence of Triton X-100 is shown in Fig. 3. At 100 rpm, in the forward scan reduction current reached plateau at ca. -0.75 V and remained almost constant up to ca. -1.2 V. At more negative potentials it slightly increased due to onset of hydrogen evolution. In the backward scan a current density was significantly lower than in the forward scan. At 400 revolutions per minute (rpm), the limiting current density was approximately twice higher than at 100 rpm, consistent with convective-diffusion considerations. The current density remained constant up to ~ 1 V, then increased slowly with potential. In the backward scan, current density was slightly higher than in the forward scan. At 800 rpm, as expected, the limiting current density in the forward scan further increased, but unexpectedly the differ-



Figure 3. Effect of electrode rotation speed on electroreduction of tin.

ence between the current densities in the forward and backward scans grew even larger. These results could indicate that effect of Triton X-100 on reduction current of tin weakened at negative potentials and at higher agitation. In order to further validate this assumption we measured current density transients at constant applied potential of -1.2 V at different electrode rotation speeds, see Fig. 4. At 200 rpm, a current density transient revealed typical behavior under potentiostatic control, *i.e.*, an initial current density dropped quickly to \sim 50 mA/cm² and remained constant throughout the experiment. At 400 rpm, after an initial drop to $\sim 80 \text{ mA/cm}^2$, the current density grew slowly with time for about 50 s and then increased sharply to $\sim 300 \text{ mA/cm}^2$. At higher rpm, similar current density transients were observed. However, time required for current density to increased sharply, and decreased as rotation speed increased. At 800 rpm, no initial current density drop was seen and a current rapidly increased with time throughout the experiment. The morphology of tin deposit formed under such condition is shown in Fig. 5a.

The effect of the size of the Triton X-type molecule on electrochemistry of tin is shown in Fig. 6, which compares CVs of tin reduction obtained with Igepal DM 970 and Igepal CA 520 instead of Triton X-100. All molecules have a similar hydrophobic head but different lengths of hydrophilic tail (Table I). Note that both curves are very similar to that measured with addition of Triton X-100, indicating that the length of the hydrophilic tail has only slight effect on the kinetics of tin electrodeposition. Similar results were obtained under agitation conditions.



Figure 2. Voltammograms for reduction of tin with and without addition of Triton X-100.



Figure 4. Current density transients for electroreduction of tin at different electrode rotation speeds.

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Figure 5. Surface morphology of tin deposit obtained from solutions with addition of (a) Triton X-100, (b) block copolymer of ethylene oxide and propylene oxide, and (c) Triton X-100 and phenolphthalein.

Effect of polyethylene glycols.—In order to understand the functional role of the head group on the electrochemistry and electrodeposition we performed similar experiments with PEGs which lack the above head group. Figure 7 shows CVs for tin reduction in



Figure 6. Voltammograms for reduction of tin with addition of Igepal DM 970 and CA 520.

the presence of PEG of different lengths and with no agitation. In general, the curves revealed features similar to those for Triton X type molecules. In the presence of PEG1 (n = 7) observed current densities were higher than those for Triton X-100 and cyclic voltammetry showed significant hysteresis. With increase in the molecular weight of PEG the passivation effect on tin electrodeposition became stronger but observed current densities remained relatively high and the quality of the obtained deposit was unsatisfactory. Introduction of more hydrophobic propylene oxide units into the body of the PEG molecule strongly enhanced absorption strength of PEGs as evidenced by suppression in the tin current. Thus, block copolymer containing *ca.* 30% of polypropylene glycol (PPG) strongly suppressed tin electrodepositon current in both stagnate solution and agitated at 800 rpm, as seen in Fig. 8. The tin deposits obtained from this solution were smooth with fine grains, as seen in Fig. 5b.

Effect of phenolphthalein.—Phenolphthalein is used in electroplating baths in order to improve the surface morphology of the deposits.¹¹ Because of its very low solubility in water, phenolphthalein is added to the solution together with surfactants, such as a Triton X type. Figure 9 shows a CV for reduction of tin in the presence of both phenolphthalein and Triton X-100. Without agitation, the voltammogram was very similar to that for Triton X-100 used alone. However, at 800 rpm the difference between two systems became evident in the absence of hysteresis characteristic for Triton X-100. Moreover, in potentiostatic test at applied potential of



Figure 7. Voltammograms for reduction of tin with addition of PEG with different molecular weights.



Figure 8. Voltammograms for reduction of tin with addition of block copolymer PEG-polypropylene glycol.

-1.2 V, constant current density of ~140 mA/cm² was established throughout the experiment, demonstrating that the mixture of Triton X-100 and phenolphthalein can provide control for tin electrodeposition in much wider range of current densities than Triton X-100 alone. This can be taken as an indication that the mixture of Triton X-100 and phenolphthalein is more strongly adsorbed at the surface of tin electrode than Triton X-100 alone. The surface morphology of tin deposit obtained from the electrolyte containing both additives is shown in Fig. 5c. A comparison with Fig. 5a shows a dramatic improvement brought by phenolphthalein.

Electrochemical data presented so far suggest that the activity of the organic additives is a strong function of applied potential and agitation. However, what exactly happens on the surface of the electrode when these parameters vary remains unknown. Adsorption/ desorption is believed to be the main mechanism by which the additives influence the observed electrochemistry and morphology of the obtained deposits. However, classical electrochemistry provides very indirect ways of measuring the adsorption strength and coverage. In order to better understand the connection between the adsorption of the species studied and their effect on electrochemistry and electrodeposition process, we performed a series of SERS measurements as a function of applied potential.

Surface enhanced Raman spectroscopy, Triton X class of surfactants.—The SERS spectra of the Triton X class of surfactants could be exemplified by the spectra of Igepal 520 on a gold surface. Figure 10 shows the SERS spectra obtained using saturated (*ca.*



Figure 9. Voltammograms for reduction of tin with addition of Triton X-100 and phenolphthalein.



Figure 10. SERS spectra of 0.003 M solution of Igepal 520 in 0.1 M H_2SO_4 at (top) +0.23 V and (bottom) at -0.5 V. Bands marked with a star are assigned to the phenyl ring moiety, and bands marked with a pound sign assigned to the isooctane moiety. On the bottom spectrum, only the bands that changed significantly in intensity are marked.

0.003 M) solution of Igepal 520 in 0.1 M sulfuric acid at OCP (*ca.* +0.23 V) and at -0.5 V *vs.* saturated calomel electrode. By comparison of the spectrum at OCP with the bulk Raman spectra reported in the literature, we were able to assign all the Raman bands either to the isooctane (marked by #) or a phenyl ring (marked by a *) part of the molecule.¹⁴ For a number of bands the exact assignment is impossible because the vibrations originating from the different parts of the molecule accidentally have the same frequencies. These bands have multiple assignments in Table II. The bands that reported in the literature to originate exclusively from the poly-

Table II. Raman bands assignments according to Ref. 12. Bands assigned exclusively to the polyoxyethylene tail of the molecule are shown in bold.

Frequency, cm ⁻¹	Assignment ¹
3067	Ph
2927	C_8
2876	C_8
1607	Ph
1466	Ph, C_8 , OE^a
1447	Ph, C_8
1289	Ph, OE
1241	Ph, OE
1183	Ph
1129	OE, C ₈
1094	Ph
1060	OE
1040	OE
1006	Ph
964	Ph, C ₈
922	Ph
906	C_8
886	OE
868	C ₈ , OE
837	Ph, OE
796	Ph, OE
746	C_8
714	C_8
679	Ph
637	Ph
584	Ph
566	OE
525	Ph, OE
472	Ph

^a OE is oxyethylene unit.



Figure 11. Suggested orientation of Igepal 520 on a gold surface at (a) +0.23 V and (b) -0.5 V vs. SCE. Oxygen atoms are in red; hydrogen atoms are not shown for clarity.



Examining spectra of Igepal 520 obtained at -0.5 V shows that most of the bands observed at OCP remained either unchanged at all or enhanced. In addition to the old bands, there are three new bands at 1060, 1040, and 566 cm^{-1} . These new bands are unequivocally assigned to the polyoxyethylene tail of the molecule. They began to show up at -0.2 V, reached a maximum at *ca*. -0.5 V, and then decreased at more negative potentials. The SERS bands of the hydrophobic head showed up at any potential studied (-0.8 to +0.4V) and reached maximum intensity also at *ca*. -0.5 V. The terminal ν (C-OH) band at 886 cm⁻¹ was not observed at all which suggests that the end of the tail is not in direct contact with the surface at any potential. The bands at -0.5 V are shifted toward the lower wavenumbers by up to 8 cm⁻¹ as compared to those at +0.23 V. This could be explained by larger reduced mass of the molecule due to stronger interaction with the relatively heavy metal atoms, which in turn suggests stronger (tighter) adsorption of the head groups at -0.5 V. Larger coverage (adsorption) normally leads to the positive shifts in the Raman frequencies because the new molecules would have to occupy higher energy sites on the metal surface; therefore, it can not explain the observed negative shifts in Raman frequencies. Also, the bands at -0.5 V are considerably broader than the corresponding bands at +0.23 V and, again, suggests stronger metal-tosurfactant interaction (adsorption) at -0.5 V.



Figure 12. SERS spectra of phenolphthlein at +0.2 V and at -0.4 V. Bands marked with a star are assigned to the phenolic moiety, bands marked with the pound sign are assigned to the lactone ring moiety.

SERS of polyethylene glycol on Ag electrode.-Dilute (7g/L, 0.002 M) solution of PEG4 (Table I) in 0.1 M sulfuric acid shows no SERS signal on silver or gold electrodes at OCP (+0.2 V). However, boosting up the concentration of PEG4 to 0.06 M (ca. 200 g/L) does lead to the appearance of the Raman bands characteristic of bulk PEG. Just like with the Triton X family, the SERS intensity was observed at ca. -0.4 V. The characteristic ν (C-O) band at 1064 cm^{-1} is clearly enhanced at -0.4 V vs. relatively more positive potentials. The main difference between the two compounds is that Triton X has an anchor group (the hydrophobic head) whereas PEG4 does not. Therefore, the hydrophobic head group of Triton X is not required for the adsorption at -0.5 V but it significantly enhances it, especially at potentials anodic of -0.4 V. PEG4 does not form micelles but shows similar behavior of ν (C-O) bands at the same potentials as Triton X compounds. Interpretation of the potentials dependent Raman spectra of Igepal 520 leads us to propose the following adsorption mechanism of Fig. 11a and b. Immediately, it suggests that the functional group that fulfills the role of adsorption is largely the hydrophobic head group. Equally important is that the hydrophilic tail group participates also in the adsorption at more negative potentials at which the electrodeposition of tin takes place. The relative importance of the head and the tail group is potential dependent, indicating the dynamic nature of the surfactant/surface interactions.

The apparent potential dependent change in the surface orientation of Igepal 520 observed by SERS helps to explain the CV in Fig. 1. The orientation shown in Fig. 11b (-0.5 V) leads to a much higher effective surface coverage than that in Fig. 11a (0.23 V). The net effect of this molecular "flip" which takes place on a surface is a stronger adsorption and higher surface coverage which would lead to the decrease in the observed tin current at *ca.* -0.5 V.

SERS of phenolphthalein.—Grain refiners are used in electroplating baths in conjunction with the surfactants to improve the surface morphology. The presumed mechanism of grain refiners action is adsorption on high energy sites of the metal surface. Figure 12 shows the SERS of one of the commonly used grain refiners, phenolphthalein, on a roughened gold surface at +0.2 V (OCP) and at -0.4 V. The most striking feature in Fig. 12 is the total absence of normally very strong ν (C=O) bands at 1740 cm⁻¹ present in the bulk Raman or IR spectrum of phenolphthalein. This indicates that the lactone C=O group is not close to the surface at both potentials. Bands that are enhanced at -0.4 V are bands associated with the two phenolic groups.¹⁶⁻¹⁸

This data suggest that at -0.4 V, the adsorption becomes stronger with the molecule moving closer to the metal surface. Bands from the furan ring (lactone part) are either too weak to be detected or totally absent at both potentials. Quinone tautomer form of phenolphthalein is present to some degree at -0.5 V but not at +0.2 V

as judged by a weak band at 1680 cm^{-1} . Similar analysis of the data obtained on a roughned silver surface suggested different orientation of phenolphthalein with the lactone group in direct contact with the metal surface.

SERS of Triton X-100 and phenolphthalein together.—SERS spectra obtained from a solution containing both Triton X-100 and phenolphthalein shows only the Raman bands due to phenolphthalein even though the Triton X-100 is present at a much higher concentration. This indicates that phenolphthalein adsorbs more strongly than does Triton X-100. Also, in the presence of Triton X-100, phenolphthalein bands are much more intense as compared with an experiment with no Triton X-100. This indicates synergetic interactions between the two species. In the presence of Triton X-100, the band positions of phenolphthalein are shifted by *ca.* -5 to +15 cm⁻¹, which suggests weak supramolecular interaction between the two chemicals.

In view of these findings it is reasonable to suggest that in this solution, the layer of phenolphthalein molecules is in direct contact with the metal surface and the Triton X-100 is on top of that layer of the phenolphthalein. This model helps to explain the apparent absence of the hysteris in the CV shown in Fig. 9. That is, the phenolphthalein layer acts as glue which helps the Triton X-100 to stay on the surface of the metal even at the very negative potentials.

Conclusions

Combined electrochemical and SERS study provided new insights on adsorption behavior of organic additives used for tin electroplating. Triton X-100 is adsorbed on the electrode surface in the wide range potential. A hydrophobic head group serves as an anchor of the molecule to the metal surface. At negative potentials, around -0.5 V, the molecule turns its long hydrophilic tail to the surface, increasing the effective surface coverage. The head groups of Triton X compounds are not required for adsorption but significantly enhance it. PEGs are also adsorbed to the metal surface, but apparently the effective coverage is relatively low, which results in a rough tin deposit. Triton X-100 facilitates adsorption of phenolphthalein and interacts weakly with it through some kind of host-guest interactions. The coadsorption of Triton X-100 and phenolphthalein modifies the grain size and the deposit structure to impart a uniform and smooth surface.

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