

Reductive spectrophotometry of divalent tin sensitization on soda lime glass



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ABSTRACT

Rapid and facile evaluation of tin (II) sensitization could lead to improved understanding of metal deposition in electroless (EL) plating. This report used a balanced redox reaction between 3,3',5,5'-tetramethylbenzidine dihydrochloride (TMB-HCL) and *N*-bromosuccinimide (NBS) to evaluate effects of sensitization conditions (i.e., sensitization time, analyte concentration, aqueous immersion, and acid content) on the accumulated mass of surface-associated divalent tin ion. The accumulated mass of tin (II) increased as the sensitization time increased up to 30 s in proportion to aqueous tin (II) chloride concentrations between 2.6 and 26 mM at a trifluoroacetic acid (TFA) content of 68 mM. The average mass peaked at 7.3 nanomoles (nmol) per cm² after a 5 s aqueous immersion post-sensitization, and then decreased with increasing aqueous immersion post-sensitization. The total average tin (II) + tin (IV) accumulated on soda lime glass measured by inductively coupled plasma optical emission spectrometry (ICP-OES) was 17% higher at 30 s sensitization, suggesting a fraction of the tin (II) present may have oxidized to tin (IV). These results indicated that *in situ* spectrophotometric evaluation of tin (II) could support development of EL plating for electronics, catalysis, and solar cells.

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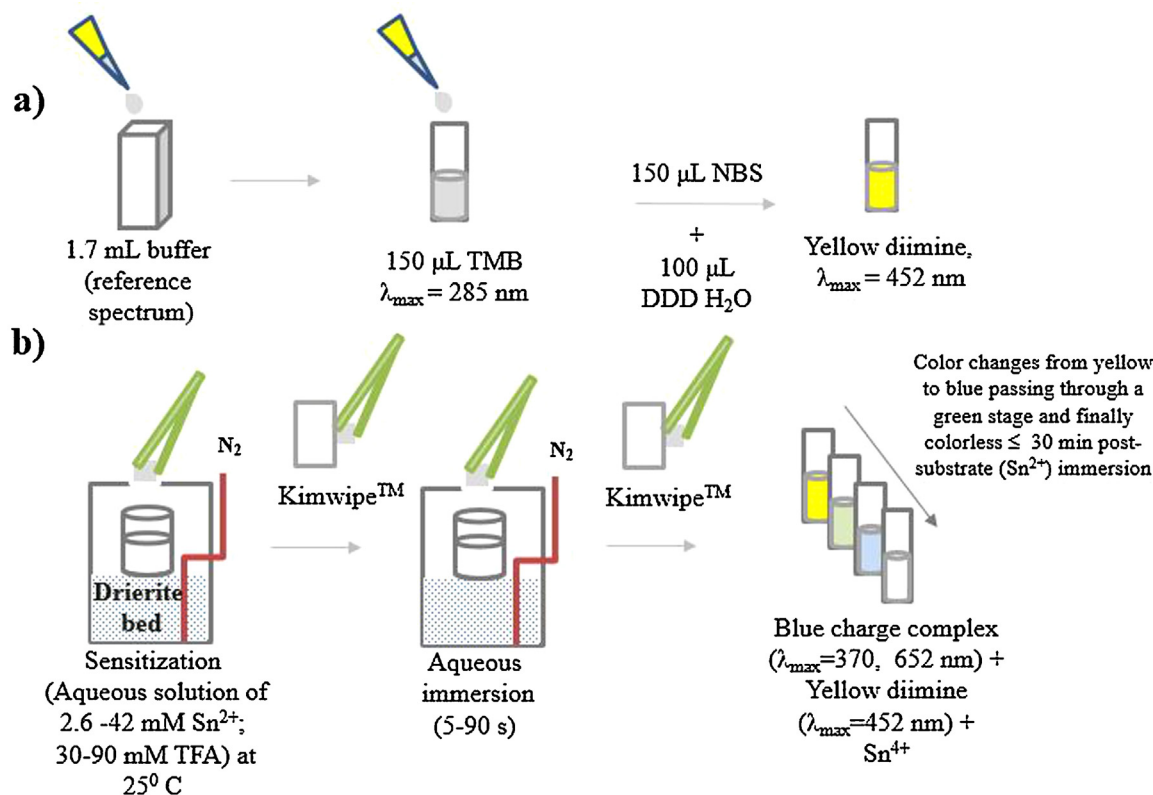
1. Introduction

Electroless (EL) deposition of thin metal films offers an economic, non-vacuum alternative to chemical deposition or sputtering [1]. It has been used to prepare submicron electrical interconnects [2], polystyrene/silver (PS/Ag) microspheres for filling applications in anisotropic conductive films [3], reductive platinum (Pt) catalyst [4], silicon and germanium semiconductors with copper (Cu) nanofilms [5], and functionalized polymer surfaces with gold (Au) nanoparticles [6]. EL Au plating was recently used to create ordered arrays of metal nanoparticles [1,7]. Such arrays support coupling between lattice diffraction with localized surface plasmons for use in functional waveguides [8], nanoantennae [9], enhanced fluorescence sensors [10], biosensors [11], or surface enhanced Raman spectroscopy (SERS) [12]. EL plating is commonly initiated by tin (II) sensitization followed by substrate activation and metallization [13]. Tin (II) behaves as a strong stabilizing and reducing agent to create catalytic sites with less than 20 atoms on glass substrates [4]. Control of the equilibrium state and dynamics of the sensitization step could improve uniformity and reproducibility of thin metal films with enhanced optical features [14].

Spectrometric [15–17] and electrochemical [18–20] methods have been used to quantitate tin (II) in solutions. But they have not been applied to quantitate the mass of tin (II) deposited on substrates to sensitize EL plating. The effects of tin sensitization, and activation steps on EL plating along with substrate properties have been evaluated by Rutherford backscattering [21–23], radiochemical tracer analysis [24,25], Mossbauer spectroscopy [26], X-ray fluorescence spectrometry [27] and X-ray photoelectron spectroscopy (XPS) [28]. Challenges of these methods [13,29] underscore a need for rapid, *in situ* evaluation of tin (II) deposited during sensitization with respect to operational variables, e.g., sensitization time, analyte concentration, aqueous immersion, and acid content.

This work characterized the effect of sensitization conditions on the mass of surface-associated tin (II) deposited on soda lime glass by balancing the redox activities of a color reagent and reductant, 3,3',5,5'-tetramethylbenzidine dihydrochloride (TMB-HCL), and a strong oxidant, *N*-bromosuccinimide (NBS). Jang and Roper first used aqueous acid solutions in which formaldehyde, HCHO, and NBS were balanced with TMB-HCL to quantitate dissolved Au (I) [30]. Subsequently, Wei et al. combined equal volumes of equimolar solutions of TMB-HCL and NBS to measure dissolved tin (II) from 0.05 μg/mL (lower limit of quantitation, LOQ) to 0.34 μg/mL (upper limit of quantitation, UOQ) [29]. To reproducibly quantitate tin (II) deposited on soda lime glass, the present work modified this method, including extending the quantifiable range to UOQ of 1.7 μg/mL by tripling volumes of both redox reagents. A calculated lower limit of detection (LOD) of 0.046 μg/mL was achieved. Inductively coupled plasma optical emission spectroscopy

Abbreviations: EL, electroless; TMB-HCL, 3,3',5,5'-tetramethylbenzidine dihydrochloride; NBS, *N*-bromosuccinimide; TFA, trifluoroacetic acid; ICP-OES, inductively coupled plasma optical emission spectrometry; SERS, surface enhanced Raman spectroscopy; LOQ, lower limit of quantitation; UOQ, upper limit of quantitation; LOD, lower limit of detection; DDD, distilled.



Scheme 1. Basic procedure for determination of tin (II) on soda lime glass using reductive spectrophotometry: a) Assay preparation; b) Substrate sensitization and tin (II) measurement. (For interpretation of the references to color in this scheme text, the reader is referred to the web version of this article.)

(ICP-OES) confirmed tin (II) deposition increased with sensitization time, and corroborated the mass of tin measured using redox spectrophotometry. It also indicated ~ 17% of deposited tin may have oxidized to the tetravalent ion at 30 s sensitization. This new method to quantitate deposited tin (II) *in situ* could be useful for facile evaluation of EL plating in industrial applications such as electronics, catalysis, and solar cells.

2. Materials and methods

2.1. Reagents

Soda lime glass microscope slides, acetone (CH_3COCH_3 , 99.5%) and acetic acid (H_3CCOOH , 99.7%) were purchased from VWR (Philadelphia, PA, USA). Sodium hydroxide pellets (NaOH , 99.9%) were purchased from Mallinckrodt (St. Louis, MO, USA). 3,3',5,5'-tetramethylbenzidine dihydrochloride (TMB-HCL; $\text{C}_{16}\text{H}_{20}\text{N}_2 \cdot 2\text{HCl}$, 98.0%) was purchased from Electron Microscopy Sciences (Hatfield, PA, USA). *N*-bromosuccinimide (NBS; $\text{C}_4\text{H}_4\text{BrNO}_2$, 99.0%), and tin standard solution (Sn 1000 $\mu\text{g}/\text{mL}$) were purchased from Alfa Aesar (Ward Hill, MA, USA). About 50–100 gm of NBS was recrystallized in 95 °C distilled, deionized H_2O before use. Anhydrous tin (II) chloride (SnCl_2 , 99.99%), nitric acid (HNO_3 , 70%) and trifluoroacetic acid (TFA; $\text{C}_2\text{HF}_3\text{O}_2$, 99.0%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Aqueous solutions were prepared using distilled, deionized and degassed (DDD) H_2O .

2.2. Apparatus

Absorbance across the spectral range of 300–750 nm was measured using USB4000 UV–vis fiber-coupled spectrometer from Ocean Optics (detector range: 200–1100 nm; Dunedin, FL, USA). The light source, a deuterium lamp (215–500 nm) and a halogen

lamp (500–2500 nm), was purchased from Avantes (Avalight-DH-S BAL, Broomfield, CO, USA). A Branson Sonifier 250 from VWR (Philadelphia, PA, USA) was used to dissolve TMB-HCL and NBS in DDD H_2O . A glove box to handle tin (II) chloride was purchased from Vacuum Atmospheres Company (Hawthorne, CA, USA). The SPECTRO ARCOS ICP-OES was purchased from SPECTRO Analytical Instruments, Inc. (Mahwah, NJ, USA), and was outfitted with an interface for radial plasma observation. Charged coupled devices (CCDs), and a Paschen-Runge mount assembly covering a wavelength range of 160–770 nm composed the optical system of the ICP-OES.

2.3. Reductive spectrophotometric method

2.3.1. Calibration of tin (II) concentration

The light source was initially blocked in order to record a dark background. Then the spectrum of a 1.7 mL of acetate buffer [0.2 M , $4.3 \leq \text{pH} \leq 4.5$ at 25°C] in a polystyrene cuvette with a path length of 1.0 cm was taken as the reference. This was followed by the addition of 150 μL TMB-HCL (0.3 mM), 150 μL NBS (0.3 mM), between 50 and 100 μL [= (100– x) μL] of DDD H_2O , and between 0 and 50 μL of tin (II) [= x μL] at 2 mM analyte concentration to create a 2.1 mL assay. The solution was mixed for 30 s by repeatedly drawing 1 mL of the solution into the pipette, and then releasing it back into the cuvette, followed by recording its absorbance spectrum. A second absorbance spectrum of the assay was taken 3 min post-tin (II) addition. The calibration curve was generated by increasing the microliter volume of tin (II) added to the mixture (i.e., $x=0$, 1, 2, 3, 4, 5, 6, 8, 10, 15, 30 and 50 μL), and decreasing the corresponding microliter volume of H_2O [= (100– x) μL], respectively, to maintain constant assay volume. Detailed procedures for preparing solutions, and generating the calibration curve are available as Supporting information (Sections S2 and S3).

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