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ELECTROCHEMICAL DEPOSITION INDUCED STRESS MEASUREMENTS ON A MICROCANTILEVER INVESTIGATED WITH CYCLIC VOLTAMMETRY

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Abstract

Electrochemical cyclic voltammetry for solution-based metallic deposit characterization is a standard method in solid-liquid interfacial surface science. We have carried out cyclic voltammetry on a microcantilever along with adsorption-induced cantilever deflection monitoring for investigating the surface stresses introduced by a deposited metal layer. Specifically, we have investigated the deposition of lead onto polycrystalline gold-coated microcantilevers. Confining the electrodeposition to one side of the cantilever causes it to undergo bending due to differential surface stress. Monitoring of adsorption induced surface stress along with electrochemical deposition current gives one an additional macroscopic characterization technique. This technique can be used for determining certain non-charge transfer processes that accompany electrochemical deposits, such as adsorbate rearrangements and phase transitions. Additionally, these types of studies should prove beneficial in the use of microcantilevered structures for various sensing applications.

Key Words: Adsorption, cantilever, electrochemical deposition, solid-liquid interface, voltammetry, sensor.

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Introduction

A considerable amount of information concerning the solid-liquid interface can be obtained by both macroscopic and microscopic surface sensitive techniques such as: cyclic voltammetry (CV); capacitance measurements; impedance analysis; ultraviolet-visible optical methods (e.g., ultraviolet-visible spectroscopy with optically transparent electrodes, ellipsometry, specular reflectance spectroscopy, photothermal and photoacoustic spectroscopy); several vibrational spectroscopy methods (e.g, infrared, vibrational Raman, resonance Raman and surface enhanced Raman spectroscopies); electron spin resonance spectroscopy; photocurrent spectroscopy; mass spectroscopy; Mossbauer spectroscopy; surface plasmon spectroscopy; surface conductance measurements; photo-emission; grazing incidence X ray scattering (GIXS); scanning tunneling (STM) and atomic force (AFM) microscopies and quartz crystal microbalances [2, 4, 5, 6, 7, 10, 16, 17, 18, 23, 24]. Another method for investigating the solid-liquid interface involves tension studies of electrochemically deposited metals. Near the start of this century, Stoney [25] performed optical microscope measurements of stainless steel beam deflections for single-sided beam deposits of nickel. Potential of zero charge (PZC) measurements of metal/solution interfaces using solid electrodes was investigated in the 1960's by T.R. Beck [3] using a extensometer to determine the PZC of a gold ribbon in 0.1 M KCl. Additionally, Fredlein *et al*. [8, 9] performed differential surface stress measurements of small beams monitored by optical deflection techniques for the determination of the PZC in gold electrodes in 0.1 M KCl, as well as in various concentrations of $HClO_4$. Pangarov and Kolarov [21] have performed similar measurements of platinum films in H_2SO_4 utilizing optical interference fringes from the bending of a 10 cm long lever. More recently, PZC measurements of gold films in 0.1 M KCl were reported by Raiteri and Butt [22] using a laser-optical deflection method with microfabricated cantilevers coated with gold. Utilizing the same method, Arai and Fujihira [1] presented results for the PZC of gold electrodes in solutions of NaOH, $HClO_4$ and NaF. In a similar fashion, O'Shea *et al*. [20] investigated the PZC of Au(111) in O.1 M KCl. Monitoring metallic deposition induced stress on solid substrates is another type of study

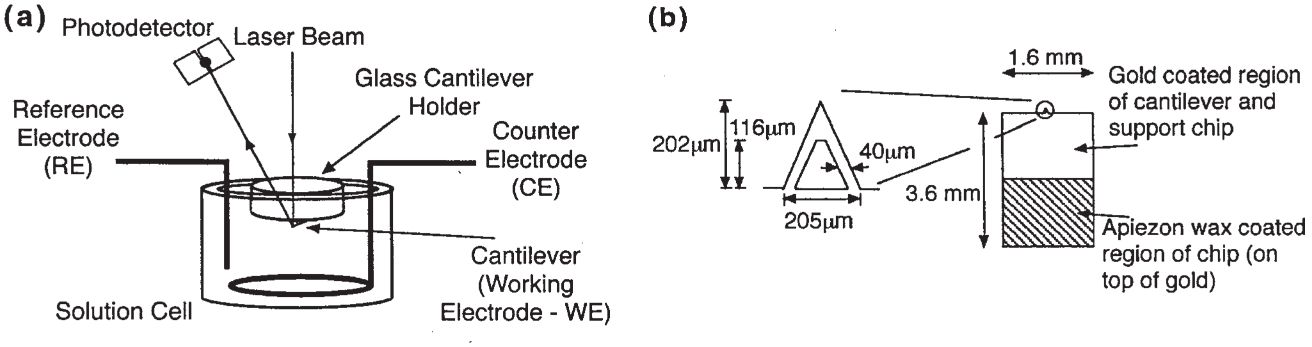


Figure 1. (**a**) A view of the electrochemical cell used for experiments. A lead reference electrode was used for results along with a platinum counter electrode. The confinement volume of the cell was approximately 2 mL. (**b**) A view of the shape of the cantilever support chip along with the geometry of the cantilever.

that has been performed by several groups. Haiss and Sass [15] have used a electrochemical STM tunneling tip over a Au(111) layer on mica for investigating buckling while depositing underpotential layers of copper, as well as studying the influence of OH at the Au(111) surface. Similar metallic studies were performed by O'Shea *et al.* [20], who reported preliminary results utilizing a laser-deflection method for monitoring uncalibrated bending of micro-fabricated cantilevers coated with gold and subsequently coated with lead from solution.

In this communication, we report the first results of calibrated end-deflection of microfabricated cantilevers versus both electrochemical potential and current. From this, we obtained a quantitative measure of the deflection rate of the cantilever in the lead deposition potential region, as well as the thickness of lead on polycrystal-line gold {Au(poly)} over which thin film stress will cause measurable cantilever bending.

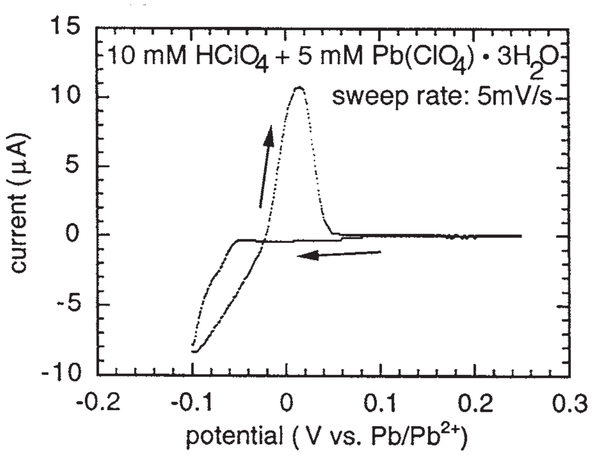
Materials and Methods

Results for this experiment were acquired with a commercially available AFM set-up (see Fig. 1a; Digital Instruments, Santa Barbara, Calif.). The electrochemical cell used was made of a section of a tube of approximately 19 mm outer diameter and 17 mm inner diameter. The cell was cleaned prior to each experiment by washing twice with acetone, methanol and 18 MΩ ultra-pure water from a Nanopure water system (Barnstead, Inc., Debuque, Iowa). Monitoring of the cantilever deflection was performed by a laser deflection monitoring technique standard to the previously mentioned instrument. With this set-up, cantilever displacement was monitored through a change in the slope of the cantilever at the position of the laser spot (see Fig. 1). Commercially available micro-fabricated "V" shaped Si_3N_4 cantilevers with a nominal vertical direction force constant of 0.12 N/m were utilized (Digital Instruments). The manufacturer-deposited gold layer on the top surface of the cantilever (opposite to the AFM scanning tip) was removed with aqua-regia. On the bottom side, a flash layer of chromium (approximately 4 nm) followed by a 40 nm film of Au(poly) were deposited in an electron-beam evaporator with a base pressure of approximately 10^{-6} Torr. Insulation from foreign metals within the glass AFM solution cell was accomplished by using Apiezon wax (Apiezon Products, Ltd., London, UK) as a coating for the metal clip that was used to confine the AFM cantilever chip within the cell. Additionally, one-half of the gold-coated cantilever chip was insulated from direct contact with the solution with wax (see Fig. 1b).

A solution of 18 MΩ H_2O with 10 mM $HClO_4$ + 5 mM $Pb(ClO_4)_2 \cdot 3H_2O$ was used for experimental results. Before data was acquired, the solution was degassed for at least 30 minutes in a double-humidified (bubbled) ultrapure helium set-up. Electrochemical control was maintained using a standard three-electrode geometry with a lead-wire reference electrode (RE) and a platinum-wire counter electrode (CE) as shown in Figure 1. A BAS Instruments Model CV-27 potentiostat (BAS Instruments, Lafayette, Indiana) was used for control with electrochemical potential and cell currents being read into a Stanford Research Instruments SR-850 analog-to-digital converter (16 bits in ± 1O V; Stanford Research Instrum., Sunnyvale, Calif.) at a rate of 4 Hz for temporal measurements. All electrochemical potentials are given against the Pb/Pb^{2+} reference potential scale.

Cantilevers were individually calibrated prior to electrochemical cycling. These measurements were performed in solution by bringing the cantilever to a rigid substrate (glass microscope slide), and then deflection versus z-displacement traces of the interaction between the tip and sample were acquired. It was assumed that in the small force region (forces on the order of 1O-20 nN), the deformation of the tip-sample

Figure 2 (at right). Typical cyclic voltammogram for lead deposition on Au(poly). Arrow pointing to the left indicates electrochemical potentials swept negative (anodic). Deposition processes in this system are indicated as negative currents occur. As the potential is swept positive (cathodic), the lead will be stripped from the electrode (cantilever) and indicated as a positive current on the y-axis.



junction was much smaller than the force constant of the lever. Therefore, for a unit deflection of the z-piezoelectric toward the cantilever, an identical magnitude deflection of the cantilever at the tip position was assumed. This, in turn, resulted in a measure of the sensitivity of the lever to a discrete loading force at the position of the sensing tip. For the results here, the sensitivity was determined to be 740 nm/V. One important point must be made when considering the quantitative measurements of the cantilever deflection. For the case of a thin-film-stressed cantilever, as present in this system, the electrochemically-induced deflection curves are considerably different from the tip-loaded deflection. In the thin-film-stress case, Stoney [25] has shown that the deflection curve (under the assumption that the film is less than 10 percent of the lever thickness) is a circular arc, while, with an end-loaded cantilever, the deflection curve is given by a third-order polynomial. Raiteri and Butt [22] describe a method for correcting for this difference. Another important consideration is that the slope, rather than deflection, is recorded by laser-beam deflection [9]. In the results of this communication, it is not necessary to compute a surface stress as has been done in previous communications. Instead, we report results that emphasize the temporal correlation of the point when the deflection begins and stops with the electrochemical current in the cell. Therefore, in this paper, deflections will be limited to measurements of the end deflection of the cantilever.

Results and Discussion

In Figure 2, a graph of a typical cyclic voltammogram (CV) is given for the system. From a lack of a clear underpotential deposition peak in the CV, an Au(poly) surface appears to be the dominant orientation of gold upon the chip/cantilever electrode surface. Instead of determining a PZC for this system as has been reported by other groups, we are primarily interested in the effects of metallic deposition upon cantilevers in this report. When comparing two identical experiments, one with lead in the perchloric acid solution and one without, there was a considerable difference in the deflection of the cantilever near electrochemical potentials where lead deposits (see Fig. 3). In Figure 3a, a graph of two different cantilever deflection experiments is given where the electrochemical potential has been cycled negatively at a rate

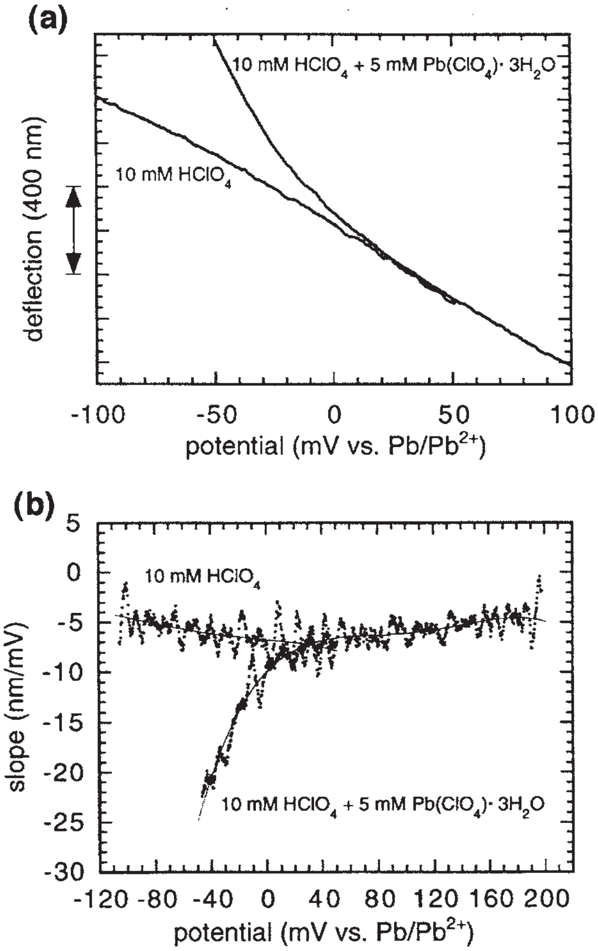


Figure 3 (above). (**a**) Graph of the end-deflection of the cantilever as a function of electrochemical potential (negatively swept) for both lead-free and lead-containing perchloric acid support electrolyte solutions (sweeps performed at 1 mV/s). (**b**) The numerical and functionally fitted derivative of the deflection with respect to electrochemical potentials for the deflection curves shown in (a).

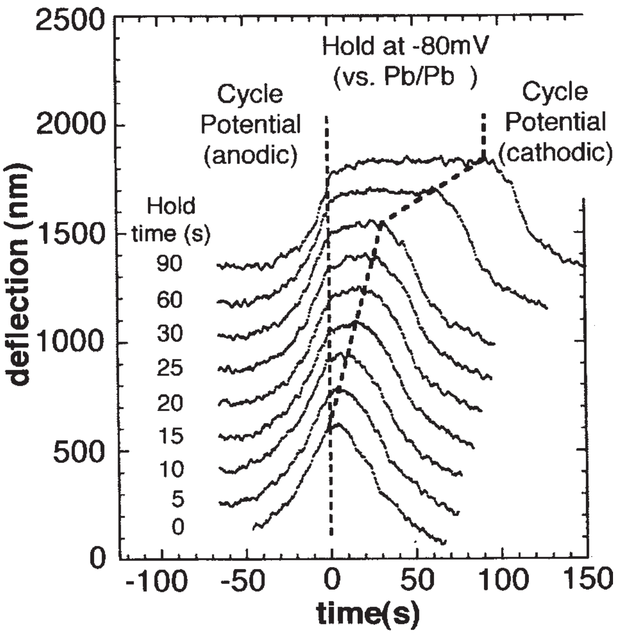


Figure 4. Graph of the negatively swept potential at a rate of 0.5 mV/s between +5O mV (versus Pb/Pb^{2+}), indicated as time = -65 seconds on the graph, and the hold potential of -80 mV (versus Pb/Pb^{2+}), indicated at time = 0 seconds on the graph. A vertical dotted line was used as a guide to the point when the hold potential was reached. The other dotted line was used to indicate the time range over which the electrochemical potential was held. Beyond this time, the potential was swept positively at the same rate as before.

of 5 mV/s. As would be expected, a substantial cantilever deflection (from a tensile stress induced in the gold film/cantilever structure) originating from the lead within the solution begins near 0 mV (vs Pb/Pb^{2+}). As a further display of this, Figure 3b shows a plot of the slope of the deflection versus electrochemical potential for the curves in Figure 3a. From this graph, it was determined that the magnitude of the cantilever deflection rate for the lead-free solution was 5-8 nm/mV in a potential range of +20 mV to -100 mV. On the other hand, for the lead-containing solution, the magnitude of the deflection rate was observed to increase approximately linearly from 8 nm/mV (at +20 mV) to 25 nm/mV (at -50 mV).

One interesting aspect of these results is the fact there is a considerable difference in the onset potential for lead deposition as determined by voltammetry and cantilever deflection. That this might be attributable to predeposition of lead preferentially upon surface steps in electrochemical environments has been reported before, and it is possible that there might be rearrangements of this material prior to the bulk deposition of lead in this system [11-14]. Along these lines, it is also possible that with the high step density present with this Au(poly) film, there might be an enhancement of this preferential adsorption effect as compared to a Au(111) surface.

When the electrochemical potential applied to the cantilever was cycled negatively and held at a potential where lead was deposited, it was observed that there was a period of time where the cantilever bent (from a tensile stress in the gold film/cantilever structure) with an approximately linear rate followed by a subsidence of bending throughout the remaining part of the hold period. This effect was invariably observed regardless of the hold time. It was determined that when the electrochemical potential was cycled negatively at a rate of 5 mV/s, to a hold potential of -80 mV (vs Pb/Pb^{2+}) (indicated as time = 0 in Fig. 4), there was a period of approximately 18 seconds where the deflection rate of the cantilever was linear with a magnitude of 3.18 ± 0.71 nm/s, and for the remaining hold time after this, the slope was -0.16 ± 0.13 nm/s, as determined by the five longest hold time cycles. In addition to this, it was observed that during the entire time period when the potential was held, the charge passing through the electrochemical cell to the cantilever was continuous (implying that the current was uniform). This fact negates the possibility of the subsidence of cantilever deflection being attributed to a change in the conductive properties of the lever or to a local depletion of lead in solution from the immediate region surrounding the cantilever.

An indication of the thickness of lead upon the gold substrate over which thin-film stress influences the system was obtained from these results as well. Upon integrating the electrochemical current over the negatively swept potential from 0 mV (vs Pb/Pb^{2+}) to -80 mV (vs Pb/Pb^{2+}), as well as the 18-second time period where the cantilever deflection occurred with the held electrochemical potential (integration of the voltammetric current was performed with sufficiently positive potentials to allow for subtraction of the offset value measured within the cell), it was determined that the lead layer thickness was 3.4 ± 0.73 nm. Therefore, for lead layers thicker than this value, no additional end-bending of the cantilever and therefore buckling of the cantilever from thin film stress introduced by this deposited layer were observed. This layer thickness is of the typical order for thin film stress phenomena [19].

Summary

In this paper, we have presented results for electrochemically deposited lead upon gold-coated, silicon-nitride cantilevers. Voltammetric investigations coupled with end-monitored cantilever deflection were used to determine the rate and amount of cantilever deflection when bulk deposition of lead was initiated for blank and lead-containing solutions. For this, two different potential cycling schemes were used for the study: one where the potential was

continuously cycled between potentials where the lead was deposited and stripped, and another, where the potential was swept and held at a potential where lead was bulk deposited. For the continuously swept situation, a deflection slope (deflection rate with respect to change in electrochemical potential) of 5-8 nm/mV was observed for the lead-free solution in the potential range of 0 mV to -120 mV, while an increasing deflection rate with lead deposition overpotential was observed in the range 0 mV (5 nm/mV) to -5O mV (25 nm/mV). For the sweep and hold experiment, it was determined that there was a time span of 18 seconds over which the cantilever bends at a uniform rate of 3.18 ± 0.71 nm/s, when the electrochemical potential was swept at 5 mV/s and held at -80 mV. After this time period, the deflection slope was determined to be -0.16 ± 0.13 nm/s. A ratio of 16.57:1 between the end deflection of the cantilever and the thickness of lead deposited on the cantilever was obtained as well.

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References

[1] Arai T, Fujihira M (1996) Effects of electric potentials on surface forces in electrolyte solutions. J Vac Sci Technol B **14**: 1378-1382.

[2] Bard AJ, Faulkner LR (1980) Electrochemical Methods. John Wiley and Sons, New York. Chapter 14.

[3] Beck TR (1969) "Electrocapillary curves" of solid metals measured by extensometer instrument. J Phys Chem **73**: 466-468.

[4] Bruckenstein S, Shay M (1985) Experimental aspects of use of the quartz crystal microbalance in solution. Electrochem Acta **30**: 1295-1300.

[5] Deakin MR, Buttry DA (1989) Electrochemical applications of the quartz crystal microbalance. Anal Chem **61**: 1147A-1154A.

[6] Deakin MR, Melroy O (1988) Underpotential metal deposition on gold, monitored in situ with a quartz microbalance. J Electroanal Chemistry **239**: 321-331.

[7] Deakin MR, Li TT, Melroy OR (1988) A study of the electrosorption of bromine and iodide ions on gold using the quartz crystal microbalance. J Electroanal Chem **243**: 343-351.

[8] Fredlein RA, Bockris JOM (1974) An "electrocapillary" study of the gold-perchloric acid solution interface. Surf Sci **46**: 641-652.

[9] Fredlein RA, Damjanovic A, Bockris JOM (1971) Differential surface tension measurements at thin solid metal electrodes. Surf Sci **25**: 261-264.

[10] Greef R, Peat R, Peter LM, Pletcher D, Robinson J (1985) Instrumental Methods in Electrochemistry. John Wiley and Sons. Chapter 1.

[11] Green MP, Hanson KJ (1991) Alloy formation in an electrodeposited monolayer. Surf Sci **259**: L743-L749.

[12] Green MP, Richter M, Xing X, Scherson D, Hanson KJ, Ross PN, Carr R, Lindau I (1988) In-situ STM studies of electrochemical underpotential deposition of Pb on Au(111). J Microsc **152**: 823-829.

[13] Green MP, Hanson KJ, Scherson DA, Xing X, Richter M, Ross PN, Carr R, Lindau I (1989) In situ scanning tunneling microscopy studies of the underpotential deposition of lead on Au(111). J Phys Chem **93**: 2181-2184.

[14] Green MP, Hanson KJ, Carr R, Lindau I (1990) STM observations of the underpotential deposition and stripping of Pb on Au(111) under potential sweep conditions. J Electrochem Soc **137**: 3493-3498.

[15] Haiss W, Sass JK (1995) Adsorbate-induced surface stress at the solid/electrolyte interface measured with an STM. J Electroanal Chem **386**: 267-270.

[16] Kanazawa KK, Gordon JG (1985) Frequency of a quartz microbalance in contact with liquid. Anal Chem **57**: 1770-1771.

[17] Konash PL, Bastiaans GJ (1980) Piezoelectric crystals as detectors in liquid chromatography. Anal Chem **52**: 1929-1931.

[18] Melroy O, Kanazawa K, Gordon JG, Buttry D (1986) Direct determination of the mass of an underpotentially deposited monolayer of lead on gold. Langmuir **2**: 697-700.

[19] Nix WD (1989) Mechanical properties of thin films. Metallurg Trans A **20A**: 2217-2245.

[20] O'Shea SJ, Welland ME, Brunt TA, Ramadan AR, Rayment T (1996) Atomic force microscopy stress sensors for studies in liquids. J Vac Sci Technol B **14**: 1383-1385.

[21] Pangarov N, Kolarov G (1978) "Electrocapillary" curves on solid metal obtained by holographic interferometry. J Electroanal Chem **91**: 281-285.

[22] Raiteri R, Butt HJ (1996) Measuring electro-chemically induced surface stress with an atomic force microscope. J Phys Chem **99**: 15728-15732.

[23] Schumacher R, Pesek JJ, Melroy OR (1985) Kinetic analysis of electroless deposition of copper. J Phys Chem **89**: 4338-4342.

[24] Siegenthaler H (1992) STM in electrochemistry. In: Scanning Tunneling Microscopy II. Springer Series in Surface Science, Vol. 28. Wiesendanger R, Guntherodt HJ (eds.). Springer-Verlag, Berlin, Germany. pp. 7-49.

[25] Stoney GG (1909) The tension of metallic films

deposited by electrolysis. Proc Royal Soc (London) A **82**: 172-175.

[26] Young WC (1989) Roark's Formulas for Stress and Strain. 6th Edn. McGraw-Hill, Inc., New York. Chapter 7.

Discussion with Reviewers

R. Nyffenegger: Regarding observed differences between the onset of deposition, even though underpotential deposition (UPD) is not easily observable on polycrystalline surfaces (as mentioned by the authors in **Results and Discussion**), it still exists. So why can UPD not be the reason for the observed difference?
Authors: If it were UPD in origin, we would have observed an inflection in the cantilever deflection vs electrochemical potential as seen by Brunt *et al*. [27] on their Ag on Au(111) surface study. We did not observe such an inflection. We agree that the UPD would influence the deflection trace, but we did not see the UPD indication in the voltammetry either, which, we suspect, is indicative of the substrate preparation.

R. Nyffenegger: At some point, there is a transformation from kinematically controlled deposition regime to diffusion controlled deposition. Can that be seen in the experiment?
Authors: Good question. We worried about the possibility of this and was concerned over the potential influence it would have on the results. But, because we simultaneously monitored the electrochemical current through the cell during the hold time, and we observed that there is a constant current vs time transferred through the cell (indicative of a kinematically controlled situation still), this is not the observed leveling of the deflection vs time trace.

N.J. Tao: Why was one half of the cantilever glass chip coated with apiezon?
Authors: Unfortunately, with the Bioscope and other electrochemical cells from Digital Instruments, there is a pesky wire holding the cantilever chip in place within the cell that is typically composed of a potentially contaminating metal. We though we should cover it up along with half of the cantilever chip to eliminate this problem. Additionally, from the work one of us (PIO) performed in Switzerland, it was found that Apiezon wax is "clean" material for up to 2 weeks in this concentration of perchloric/lead solution (unpublished observations).

N.J. Tao: Was the AFM cantilever deflection measurements done in a HE gas chamber? If not, was there any effect from the dissolved O_2 in the deflection measurements?
Authors: No, we did not do this under a situation to maintain the O_2 purged solution (Note: we mentioned in the text that we purged prior to the experiment). From prior experiments, I have found that there is a time period of a half hour or so that once a solution is purged, it will be okay. As can be seen from the voltammetry, there was not a significant effect of the oxygen in this result. We did not study the influence of the oxygen on the system (waiting long enough to see this in the voltammetry). It might be interesting to come back for a further study. Typically, the electrochemical experiments shown there take a short time to acquire once everything is set-up.

N.J. Tao: After striping off the deposited Pb layer, does the cantilever deflection return to the original value (before deposition)?
Authors: The reviewer brings to light an interesting point that was one of the initial reasons for continuing this work. It turns out that for the initial sweeps of the electrode, there is considerable difference in the deflection traces while the CV's are fairly consistent. This was one of my first indications of a rearrangement on the electrode surface.

Additional Reference

[27] Brunt TA, Chabala ED, Rayment T, O'Shea SJ, Welland ME (1996) Measuring surface stress induced by electrode processes using a micromechanical sensor. J Chem Soc, Faraday Trans **92**: 3807-3812.