

OFFICE OF NAVAL RESEARCH

GRANT or CONTRACT: N00014-91-J-1919

96PRO-2855
Robert Nowak

Technical Report No. 21

Electrochemical Digital Etching: Atomic
Level Studies of CdTe(100)

Tom A. Sorenson, Belinda K. Wilmer and John L. Stickney

Submitted to a Symposia Volume

on

"Electron Spectroscopy and ATM/AFM Analysis of Solid Liquid Interfaces"

to be published by the American Chemical Society

Department of Chemistry
University of Georgia
Athens, GA 30602-2556

19960711 083

6/22/96

Reproduction in whole, or in part, is permitted for any purpose of the United States Government.

This document has been approved for public release and sale;
its distribution is unlimited.

1996 QUALITY INSPECTED 1

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 6/25/96	3. REPORT TYPE AND DATES COVERED Technical 6/1/95 - 5/31/96		
4. TITLE AND SUBTITLE Electrochemical Digital Etching: Atomic Level Studies of CdTe(100)		5. FUNDING NUMBERS G-N00014-19-J-1919 Dr. Robert J. Nowak 96PRO-2855		
6. AUTHOR(S) Tom A. Sorenson, Belinda K. Wilmer and John L. Stickney				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) John L. Stickney Department of Chemistry University of Georgia Athens, GA 30602-2556		8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report # 21		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Chemistry Division 800 North Quincy Street Arlington, VA 22217-5660		10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release and sale; its distribution is unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Atomic level control in the etching of CdTe(100) is being investigated, in an attempt to develop an electrochemical digital etching procedure. In principle, surface atoms on the crystal should show higher reactivity than those contained on the interior, due to their decreased coordination. Electrochemical oxidation in 50 mM K ₂ SO ₄ resulted in removal of the surface Cd atoms and a tellurium enriched surface, as observed by Auger electron spectroscopy. Subsequent reduction at -1.8V reduced the surface excess of Te, and returned the surface composition to stoichiometric. Selection of an appropriate potential for the oxidation of surface cadmium atoms was complicated by the observation that bulk CdTe is oxidized at potentials close to that used to oxidize the surface cadmium atoms.				
14. SUBJECT TERMS Digital etching, layer by layer etching, CdTe, LEED, Auger, electrochemical etching			15. NUMBER OF PAGES 17	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT UL	

6/5/96

Electrochemical Digital Etching: Atomic Level Studies of CdTe(100)

T. A. Sorenson, B. K. Wilmer, and J. L. Stickney

Department of Chemistry, University of Georgia, Athens, GA 30602

Atomic level control in the etching of CdTe(100) is being investigated, in an attempt to develop an electrochemical digital etching procedure. In principle, surface atoms on the crystal should show higher reactivity than those contained on the interior, due to their decreased coordination. Electrochemical oxidation in 50 mM K_2SO_4 , resulted in removal of the surface Cd atoms and a tellurium enriched surface, as observed by Auger electron spectroscopy. Subsequent reduction at -1.8 V reduced the surface excess of Te, and returned the surface composition to stoichiometric. Selection of an appropriate potential for the oxidation of surface cadmium atoms was complicated by the observation that bulk CdTe is oxidized at potentials close to that used to oxidize the surface cadmium atoms.

Etching of CdTe single crystals can be categorized as dry etching and wet etching. Dry etching is performed using techniques such as argon ion sputtering in ultrahigh vacuum (UHV) (1,2) and plasma etching using CH_4/H_2 (3,4). Wet etching has been demonstrated using a variety of solutions including: $HNO_3/K_2Cr_2O_7/Ag^+$ (5), Ce^{4+} (6,7), $S_2O_4/NaOH$ (8), 15% HNO_3 (8), $Cr_2O_7^{2-}/HNO_3$ (1,8) and Br_2/CH_3OH (1,9). Interest in CdTe for solar energy conversion has led to a number of studies of the CdTe/electrolyte interface (8,10-12), and development of

photoelectrochemical etching (13-15). In general, the above studies focused on macroscopic etching as a microfabrication process or surface cleaning technique for CdTe.

As the dimensions of semiconductor structures approach the atomic scale, atomic level control becomes increasingly important. With regards to etching, a technique known as digital etching has begun to be studied (16-22). Digital etching makes use of surface limited reactions to etch a material one atomic or molecular layer at a time. Gas phase digital etching generally involves an initial surface limited adsorption step, of a precursor gas. The resulting surface is then subjected to a beam of energetic particles: photons, electrons, ions, etc. The yield of volatile species resulting from the bombardment is then limited to a monolayer by the limited amount of preadsorbed gas. The process is repeated, in a cyclic manner, until the desired etch depth is achieved. Digital etching has been demonstrated on silicon and gallium arsenide using fluorine, chlorine, selenide, and hydrogen as gaseous adsorbates and Ar^+ ions, electrons, and photons (from XeF and KrF lasers) as energetic particles.

Research in our laboratory involves studies of the electrochemical atomic layer processing of compound semiconductors. A major project involves atomic layer epitaxy (ALE). ALE is the formation of a compound one atomic layer at a time using surface limited reactions, and the electrochemical analog of ALE (ECALE) is presently under development in this group. This study concerns development of the electrochemical analog of digital etching, where a compound is dissolved one atomic layer at a time (23,24). The present article is an atomic level study of electrochemical digital etching.

A schematic illustration of electrochemical digital etching is shown in Figure 1. The principle is that potentials are used for which only the top atomic layer of a particular element is

electrochemically removed, in a surface limited reaction. Removal of just the top atomic layer is facilitated by those atoms being in a lower coordination state on the surface, than corresponding atoms in the bulk of the compound. If the surface is terminated by a layer of cadmium atoms (Figure 1A), careful selection of an oxidative potential should result in the anodic dissolution of the top cadmium atoms, while leaving a tellurium terminated surface (Figure 1B). Interior Cd atoms are not removed as they are tetrahedrally coordinated. The resulting tellurium terminated surface can then be reductively etched by selection of an appropriate reduction potential, leaving a cadmium terminated surface and completing one digital etching cycle (Figure 1C). The cycle is then repeated until the desired etch depth is achieved. The use of an electrochemical etching cycle, with both oxidation and reduction components has been well demonstrated by Kohl et. al., in the etching of InP (25). The present studies, however, focus on the development of a cycle based on removal of a single monolayer per cycle, using surface limited reactions.

Experimental

Undoped cadmium telluride single crystals, cut and oriented to the (100) plane, were obtained from II-IV Incorporated. Before use, the CdTe single crystals were chemically etched in 1% $\text{Br}_2/\text{CH}_3\text{OH}$. An ohmic contact was established by soldering an indium strip on the top of the crystal. The crystal was held between two molybdenum plates, tightened by 0-80 bolts. Al foil was sometimes wrapped around the In strip to help with conduction and prevent the crystal from falling out. Tungsten wires were connected to the molybdenum bars to facilitate electrical

contact to the CdTe(100) crystal and allow thermal annealing in the UHV surface analysis instrument.

All experiments in this paper were performed in an UHV surface analysis instrument equipped with a Phi model 3017 Auger electron spectroscopy subsystem and Phi model 15-120 low energy electron diffraction (LEED) optics. The instrument was also equipped with an electrochemical antechamber used to perform the etching experiments (1,26,27). A standard, in-house built, three electrode potentiostat was used for all electrochemical experiments. All potentials are reported versus a Ag/AgCl(3M KCl) reference electrode obtained from Bioanalytical Systems, Inc. During electrochemical experiments, solution levels were kept at least 2 mm below the In strip and Mo plates. The electrolyte solution used was 0.050 M K_2SO_4 for all electrochemical experiments followed by a rinse in 1mM H_2SO_4 , to remove excess electrolyte prior to transfer to vacuum. All solutions were made with Nanopure water and were purged with argon for at least fifteen minutes. All chemicals were high purity (Fisher) and used without further purification. The CdTe electrode was illuminated during oxidations using a Fiber-Lite Model 190 (Dolan-Jenner Industries, Inc.), with a W-halide bulb on high intensity, focused on the electrode through a viewport. All reductions were performed in the dark.

Results and Discussion

The surface structure of CdTe(100) has been the focus of a number of recent studies. A cadmium terminated CdTe(100) surface, for instance, displays a $c(2\times 2) + (2\times 1)$ reconstruction (28-34), while a tellurium terminated surface displays a (2×1) reconstruction (29-32). Prior to each electrochemical study, the CdTe(100) crystal was ion bombarded and annealed, resulting in an

unreconstructed (1X1) LEED pattern (Figure 2). Why a (1X1) is observed in the present studies, as opposed to a c(2X2) or a (2X1) is not clear, but may result from variations in the pretreatment procedures. The corresponding Auger spectrum (Figure 3A) shows a Cd/Te ratio of 1.32, calculated from the heights of the cadmium peak at 376 eV and tellurium peak at 483 eV. Figures 4A and B show voltammetry for the electrochemical reduction and oxidation, respectively, of this surface in 50 mM K_2SO_4 . When the potential was scanned negative of open circuit in the dark, only a slight reductive current due to hydrogen evolution was observed, with no detectable change in the Cd/Te ratio. Scanning the potential positively, however, with the surface illuminated, resulted in an oxidation feature consisting of a small peak at about +0.1 V, on top of an exponentially increasing background. When the resulting oxidized surface was immersed in fresh electrolyte and scanned negatively in the dark, a surface limited peak, at approximately -1.65 V, was observed on a small background of hydrogen evolution (Figure 4C).

To characterize the oxidation process a series of experiments were performed in which the ion bombarded and annealed CdTe(100) crystal was immersed at increasingly positive potentials, for five minutes each time. Examples of the chronoamperograms obtained are shown in Figure 5 and are very similar in shape to those observed in previous studies of photoelectrochemical etching (14). Two features are evident, a steady state current that increases with increasing potential, and a transient current that decays to the steady state current after about 60 seconds, for potentials positive of -0.25 V. Auger spectra taken after each immersion indicated that Cd was preferentially dissolved, leaving a Te enriched surface. Figure 3B shows the Auger spectrum recorded following oxidation at +0.25 V, and a Cd/Te ratio of 1.08.

Subsequent reduction of the Te enriched surface was accomplished by immersing the oxidized CdTe(100) single crystal in a fresh aliquote of the 50mM K_2SO_4 solution at -1.8 V. The resulting chronoamperogram is shown in Figure 6. Similar behavior was observed for Te reduction following the oxidation steps. That is, an initial reduction peak was observed, which decayed to background after 1 minute. Auger spectra obtained after these reduction steps all indicated that the initial stiochiometry of the CdTe(100) surface had been restored, that Cd/Te ratios were equivalent to those observed for the ion bombarded/annealed surface (Figure 3C).

Figure 7 shows the dependence of the charge passed, converted to monolayers of the corresponding elements, as a function of the potential used during the oxidation step. The total oxidation charge (triangles pointing down) increased dramatically between -0.25 V and -0.12 V. In addition, the charges for the transient (squares) and constant background (circles) features in Figure 5, are plotted in Figure 7. For potentials more positive than -0.25 V, charge due to the transient actually decreased as the potential increases, while the charge due to the constant background oxidation increased markedly. Charge passed in the subsequent Te reduction step at -1.8 V (triangles pointing up) followed the transient oxidation charge.

Given the data presented above, it appears that at potentials between open circuit (-0.5 V) and -0.25 V, cadmium is oxidized in a surface limited manner, with a 0.5 monolayer removed at -0.25 V. Reduction of the resulting Te layer was consistent with the amount of Cd removed, and restores the original surface. However, at more positive oxidation potentials, a second oxidation process began, the constant background oxidation, which appeared to involve oxidation of both Cd and Te. The potential for oxidative stripping of bulk tellurium from a gold electrode has been shown to begin around 0.2 V (27,35), possibly explaining the steep increase in charge at that

potential in Figure 7. Why the total charge increases abruptly at -0.12 V is not clear, given a formal potential for Te of 0.2 V. On the other hand, the formal potential for Cd is close to -0.7 V, and though it is clear that Cd is stabilized by bonding with Te to form CdTe, by -0.125 V a sufficient over potential should exist to strip Cd atoms away from Te atoms in the lattice, leaving the Te under-coordinated and destabilized. The resulting Te atoms should be susceptible to underpotential oxidation, explaining the loss of both Cd and Te.

Creation of a pitted morphology after several cycles of etching is indicated by examination of the LEED patterns after each step. No change in the symmetry of the LEED patterns was observed after either the oxidative or reductive steps, but each step resulted in an increase in diffuse intensity, indicating surface disordering or roughening. In addition, the mirror like finish, initially obtained with the $\text{Br}_2/\text{CH}_3\text{OH}$ etch, was significantly less reflective after three or four experiments. It is quite possible that the co-dissolution of Cd and Te, at potentials above -0.25 , is occurring more extensively at specific sites, rather than homogeneously across the surface.

Conclusion

An electrochemical method for digitally etching CdTe(100) is being investigated. In principle, two potentials are needed, one where surface atoms of Cd are oxidatively removed in a surface limited reaction, and one where surface atoms of Te are reductively removed in a surface limited reaction. Finding an optimal potential for cadmium oxidation is complicated by the observation that some tellurium is oxidatively etched at potentials 0.3 V negative of where bulk Te is stripped (underpotential stripping). This appears to be due to destabilization of the Te by stripping the Cd

atoms to which it was coordinated. Results from this study indicate that a potential near -0.25V would be optimal for surface limited removal of Cd without removal of the Te. The reduction of tellurium at -1.80V, on the other hand, has been shown to be an easily controlled surface limited reaction, which can restore the stiochiometry of the CdTe(100) surface following an oxidative step.

Acknowledgments

Acknowledgment is made for financial support of this work to the Department of Navy, Office of Naval Research, under Grant No. N00014-91-J-1919 and to the National Science Foundation under Grant No. DMR-94000570. Their support is gratefully acknowledged.

Literature Cited

1. Villegas, I.; Stickney, J. L. *J. Electrochem. Soc.* **1991**, 138, 1310.
2. Solzbach, U.; Richter, H. J. *Surface Sci.* **1980**, 97, 191.
3. Pearton, S. J.; Ren, F. *J. Vac. Sci. Technol. B* **1993**, 11, 15.
4. Neswal, M.; Gresslehner, K. H.; Lischka, K.; Lubke, K. *J. Vac. Sci. Technol. B* **1993**, 11, 551.
5. Lu, Y. C.; Route, R. K.; Elwell, D.; Feigelson, R. S. *J. Vac. Sci. Technol. A* **1985**, 3, 264.
6. Iranzo Marin, F.; Debeimme-Chouvy, C.; Vigneron, J.; Triboulet, R.; Etcheberry, A. *Jpn. J. Appl. Phys.* **1995**, 34, L1344.
7. Iranzo Marin, F.; Vigneron, J.; Lincot, D.; Etcheberry, A.; Debeimme-Chouvy, C. *J. Phys. Chem.* **1995**, 99, 15198.
8. Ricco, A. J.; White, H. S.; Wrighton, M. S. *J. Vac. Sci. Technol. A* **1984**, 2, 910.
9. Lincot, D.; Vedel, J. *J. Electroanal. Chem.* **1984**, 175, 207.
10. Lincot, D.; Vedel, J. *J. Cryst. Growth* **1985**, 72, 526.
11. Lincot, D.; Vedel, J. *J. Electroanal. Chem.* **1987**, 220, 179.
12. Tanaka, S.; Bruce, J. A.; Wrighton, M. S. *J. Phys. Chem.* **1981**, 85, 3778.
13. Tenne, R.; Marcu, V.; Yellin, N. *Appl. Phys. Lett.* **1984**, 45, 1219.
14. Muller, N.; Tenne, R. *Appl. Phys. Lett.* **1981**, 39, 283.
15. Marcu, V.; Tenne, R.; Yellin, N. *Appl. Surf. Sci.* **1987**, 28, 429.
16. Horilke, Y.; Tanaka, T.; Nakano, S.; Iseda, H.; Sakaue, A.; Shindo, S.; Miyazaki, S.; Hirose, M. *J. Vac. Sci. Technol. A* **1990**, 8, 1844.
17. Ishii, M.; Meguro, T.; Gamo, K.; Sugano, T.; Aoyagi, Y. *Jpn. J. Appl. Phys.* **1993**, 32, 6178.

18. Bourne, O. L.; Hart, D.; Rayner, D. M.; Hackett, P. A. *J. Vac. Sci. Technol. B* **1993**, 11, 556.
19. Takatani, S.; Kikawa, T. *Appl. Phys. Lett.* **1994**, 65, 2585.
20. Meguro, T.; Hamagaki, M.; Modaressi, S.; Hara, T.; Aoyagi, Y.; Ishii, M.; Yamamoto, Y. *Appl. Phys. Lett.* **1990**, 56, 1556.
21. Luviksson, A.; Xu, M.; Martin, R. M. *Surface Sci.* **1992**, 277, 282.
22. Aoyagi, Y.; Shinmura, K.; Kawasaki, K.; Nakamoto, I.; Gamo, K.; Namba, S. *Thin Solid Films* **1993**, 225, 120.
23. Lei, Q. P.; Stickney, J. L. *Mat. Res. Soc. Symp. Proc.* **1992**, 237, 335.
24. Willmer, B. K. B.; *ECAL Processing of Compound Semiconductors and Scanning Probe Microscopy of Mg(0001)* Masters Dissertation, University of Georgia, 1995, pp. 1-50.
25. Kohl, P. A.; Harris, D. B.; Winnick, J. *J. Electrochem. Soc.* **1990**, 137, 3315.
26. Soriaga, M. P.; Harrington, D. A.; Stickney, J. L.; Wieckowski, A. In *Ultrahigh-Vacuum Surface Analytical Methods in Electrochemical Studies of Single Crystal Surfaces*; Conway, B. E.; Bockris, J. O'M.; White, R. E., Eds. Modern Aspects of Electrochemistry, Number 28; Plenum Press, New York, 1995; pp. 1-60.
27. Suggs, D. W.; Stickney, J. L. *Surface Sci.* **1993**, 290, 362.
28. Veron, M. B.; Sauvage-Simkin, M.; Etgens, V. H.; Tatarenko, S.; Van Der Vegt, H. A.; Ferrer, S. *Appl. Phys. Lett.* **1995**, 67, 3957.
29. Tatarenko, S.; Bassani, F.; Klein, J. C.; Saminadayar, K.; Cibert, J.; Etgens, V. H. *J. Vac. Sci. Technol. A* **1994**, 12, 140.
30. Tatarenko, S.; Daudin, B.; Brun, D.; Etgens, V. H.; Veron, M. B. *Phys. Rev. B* **1994**, 50, 18479.
31. Wu, Y. S.; Becker, C. R.; Waag, A.; Bicknell-Tassius, R. N.; Landwehr, G. *J. Appl. Phys.* **1991**, 69, 268.
32. Wu, Y. S.; Becker, C. R.; Waag, A.; Kraus, M. M.; Bicknell-Tassius, R. N.; Landwehr, G. *Phys. Rev. B* **1991**, 44, 8904.
33. Seehofer, L.; Etgens, V. H.; Falkenberg, G.; Veron, M. B.; Brun, D.; Daudin, B.; Taterenko, S.; Johnson, R. L. *Surface Sci.* **1996**, L55.
34. Seehofer, L.; Falkenberg, G.; Johnson, R. L.; Etgens, V. H.; Tatarenko, S.; Brun, D.; Daudlin, B. *Appl. Phys. Lett.* **1995**, 67, 1680.
35. Gregory, B. W.; Suggs, D. W.; Stickney, J. L. *J. Electrochem. Soc.* **1991**, 138, 1279.

Figure Captions

Figure 1: Schematic illustrating the electrochemical digital etching process on CdTe(100).

Figure 2: LEED image showing (1X1) pattern of CdTe(100) that resulted from ion bombarding with 0.5 keV Ar⁺ ions for 20 minutes followed by annealing for 5 minutes. Electron beam energy 52.9 eV.

Figure 3: Auger spectra of CdTe(100) taken at various points in the electrochemical digital etching cycle. A) Argon ion bombarded, annealed surface. Cd/Te = 1.32. B) Surface resulting

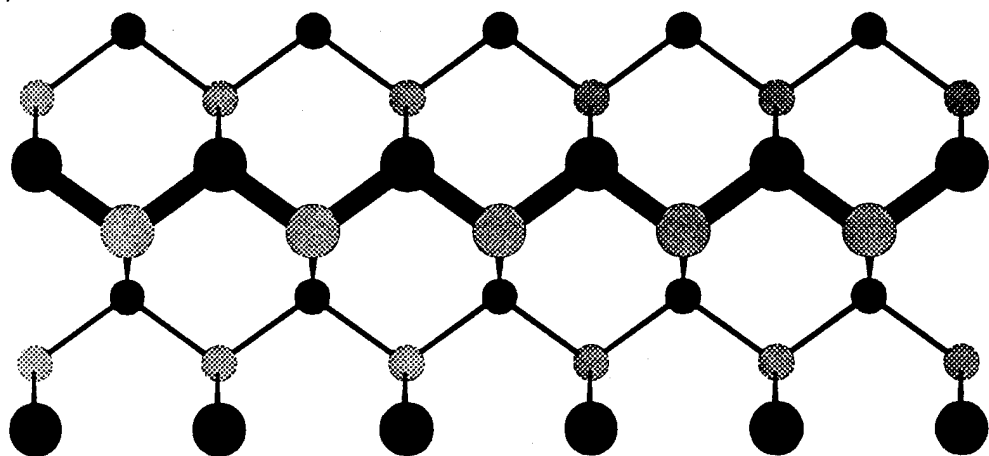
from oxidation at +0.25V for 5 minutes. Cd/Te = 1.08. C) Surface resulting from reduction at -1.8V for 2 minutes. Cd/Te = 1.34.

Figure 4: Voltammograms on an argon ion bombarded, annealed CdTe(100) surface in 50 mM K_2SO_4 , pH = 5.6. A) Reduction from the open circuit potential to -2.0V. B) Oxidation from the open circuit potential to +0.30V and reversing to -0.55V under illuminated conditions. C) Reduction following B) from open circuit potential to -1.8V and reversing to -0.50V.

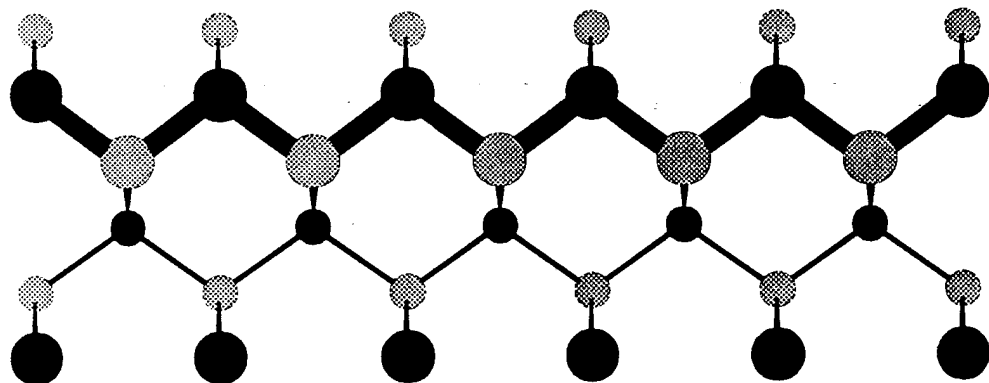
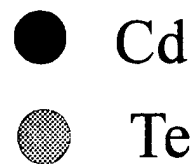
Figure 5: Chronoamperograms of ion bombarded, annealed CdTe(100) in 50 mM K_2SO_4 at different oxidative potentials for 5 minutes. A) +0.25V. B) 0.0V. C) -0.25V.

Figure 6: Chronoamperogram showing the reduction of the previously oxidized CdTe(100) surface in 50 mM K_2SO_4 at -1.8V.

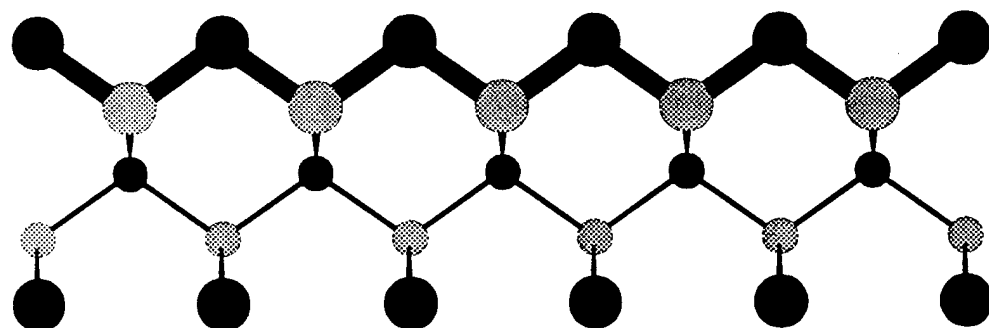
Figure 7: Graph showing the charge passed, converted to monolayers, as a function of potential used for oxidation. Total oxidative charge has been separated into two components: transient oxidation and background oxidation. In addition, the subsequent reduction charge for Te is listed as well.



A



B



C

Figure 1



Figure 2

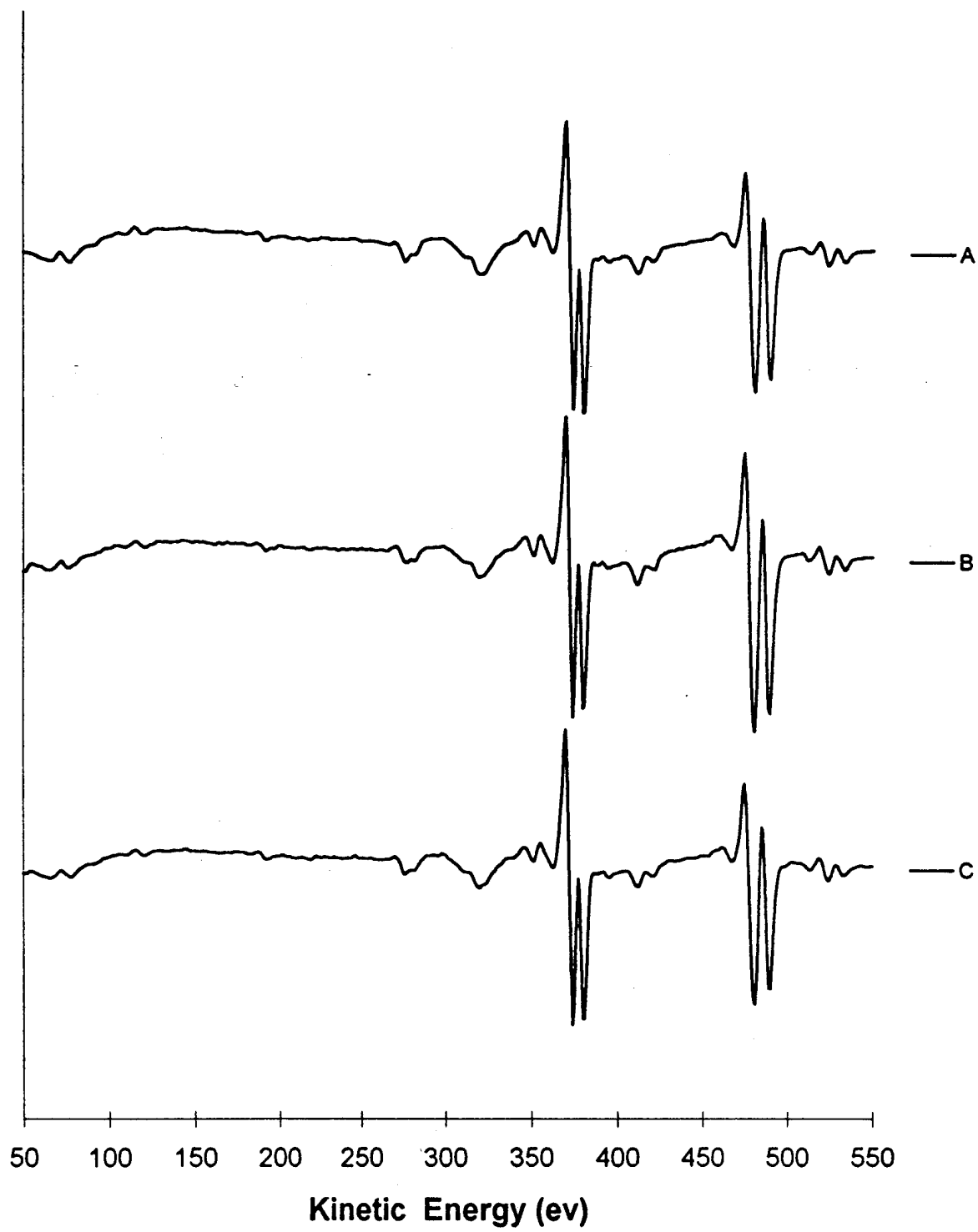


Figure 3

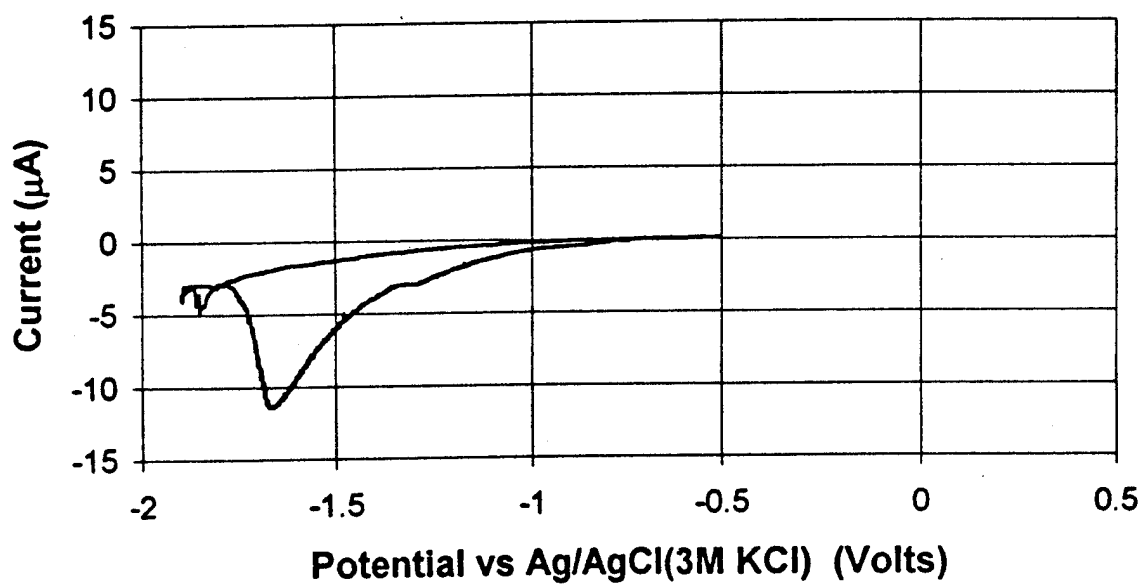
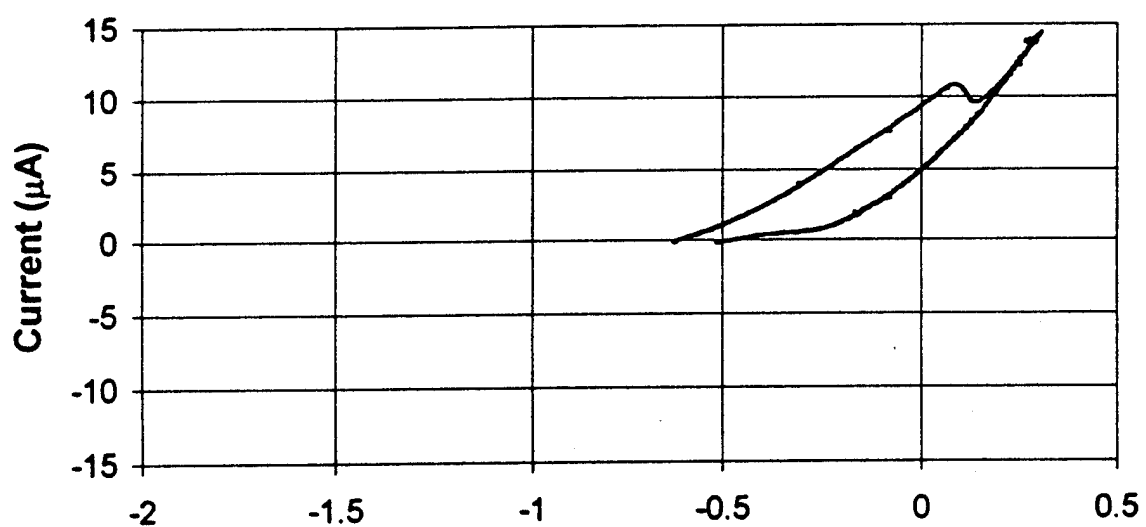
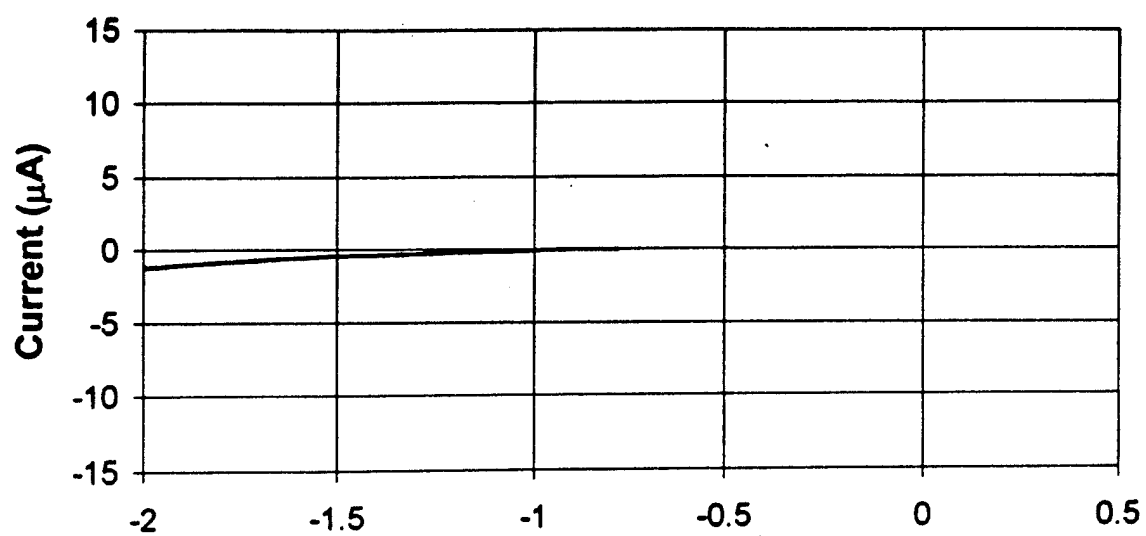


Figure 4

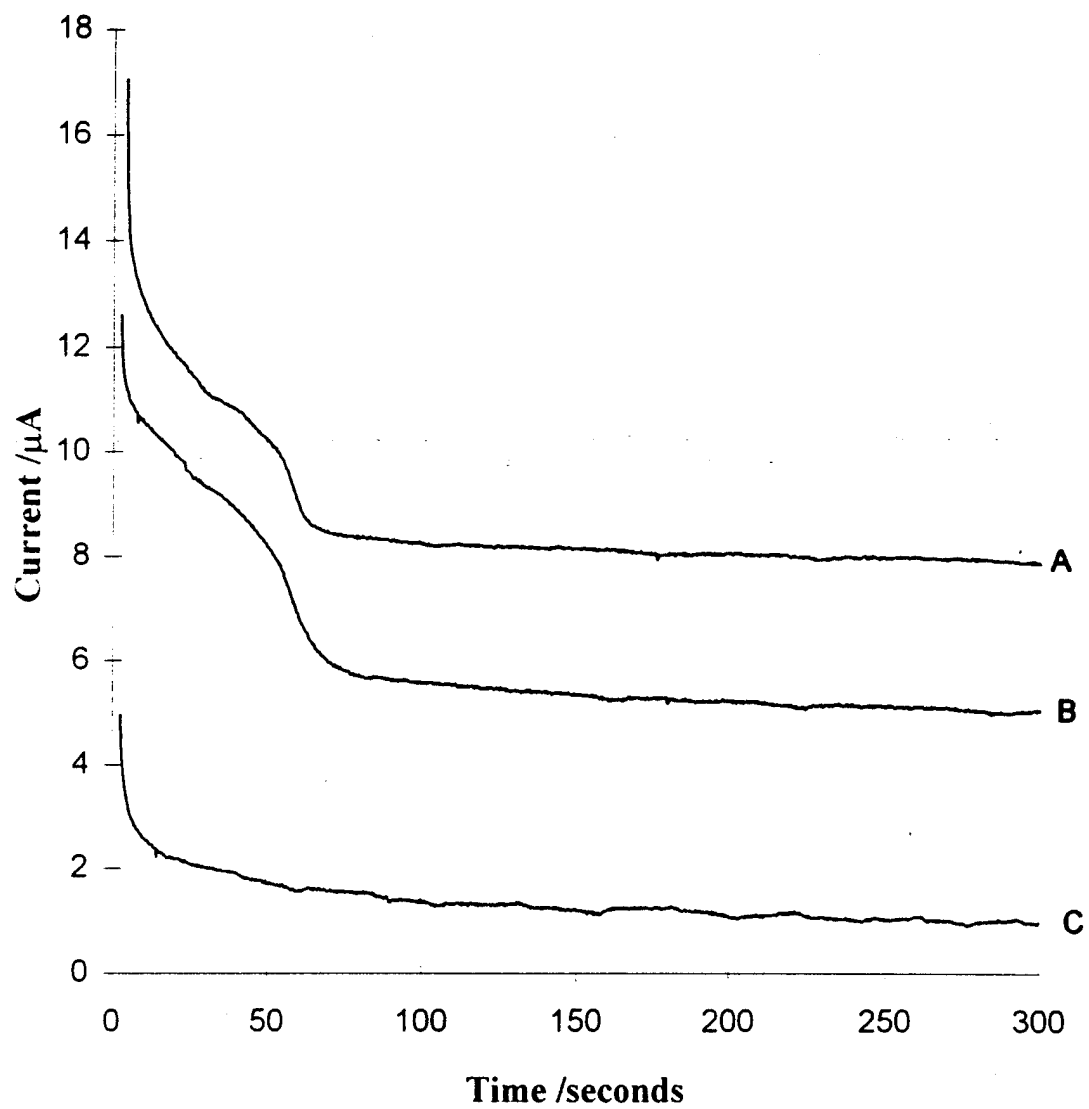


Figure 5

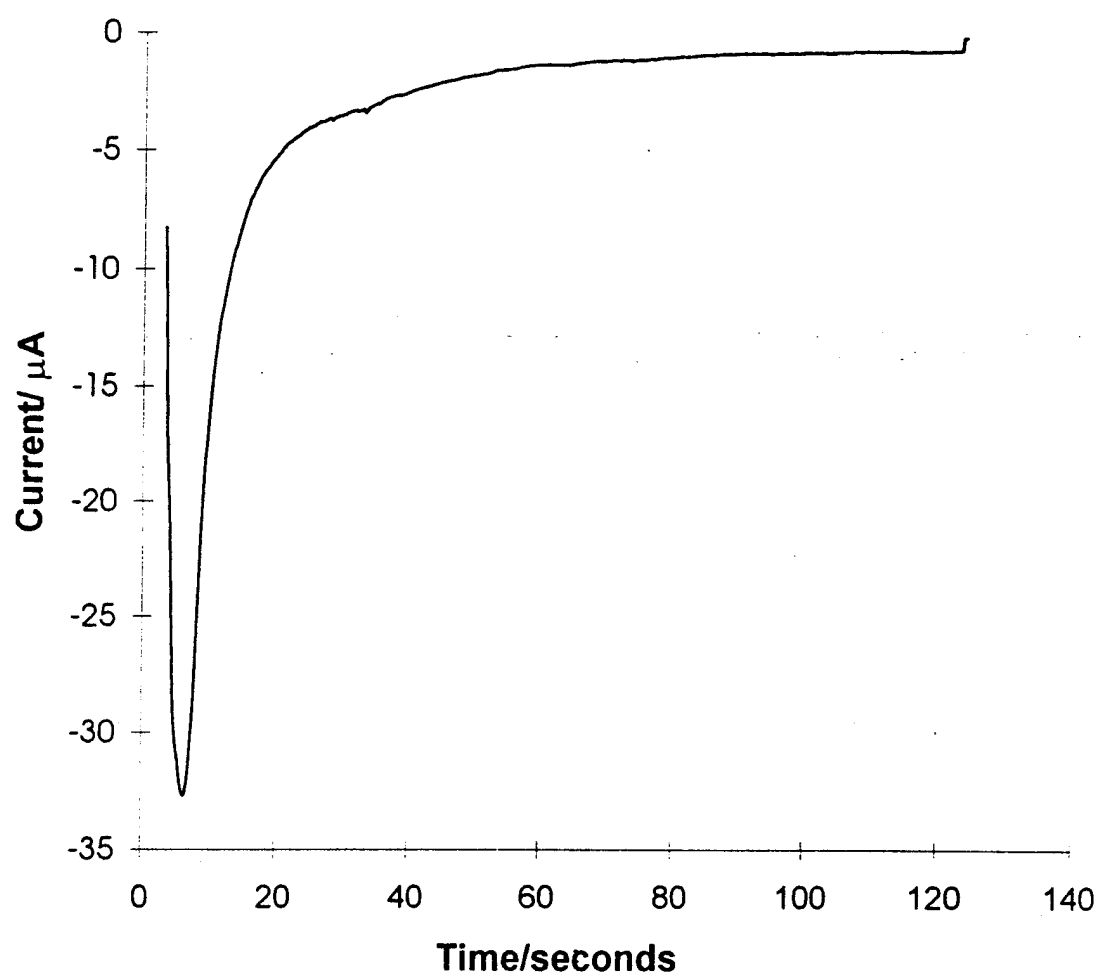
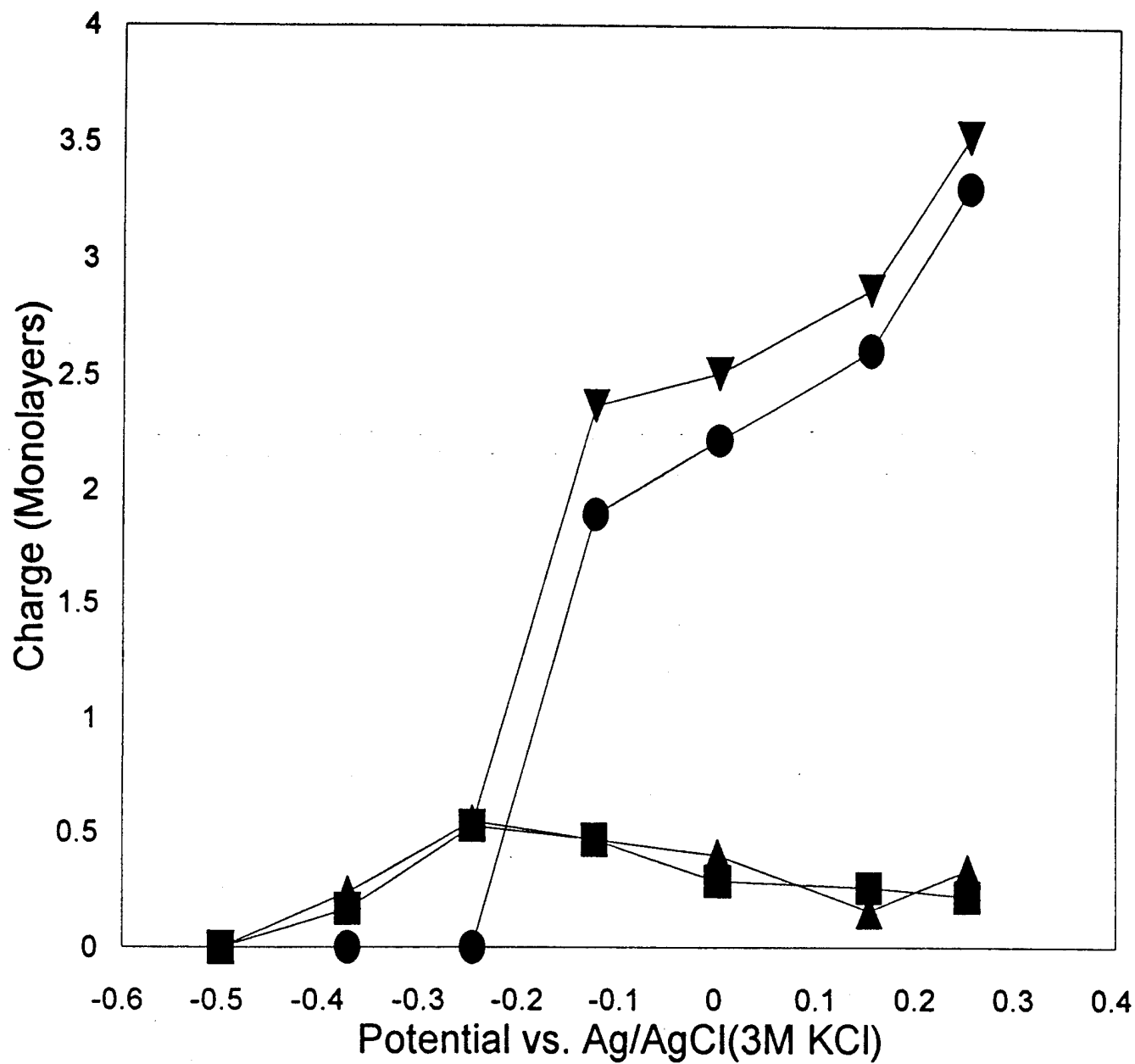


Figure 6



■ Transient Oxidation Peak ● Background Oxidation

▼ Total Oxidation ▲ Subsequent Reduction

Figure 7