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Journal

Surface science, 258(1/3/2008)

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Publication Date

1991-06-01

Center for Advanced Materials

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Submitted to Surface Science

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June 1991

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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ACKNOWLEDGMENT

This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences of the U.S. Department of Energy under contract No. DE-AC03--76SF00098.

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Abstract

In-situ electrochemical scanning tunneling microscopy (ESTM) was employed to observe the surface of silver immersed in 1M KCl before and after an oxidation-reduction cycle (ORC). The roughness created by ORC was found to relax quickly. During the first two minutes marked decreases in surface area occur that are accompanied by the disappearance of nanometer size features. The rate of change in surface area decreases significantly after this time. Further decreases in surface energy are brought about by the growth of crystal planes which become apparent during the first three to five minutes. Some of these planes appear to be low index planes {111}; these have the lowest surface energy. The results of the present study suggest that the time evolution of surface enhanced Raman scattering (SERS) following an ORC of silver can be contributed to by changes in atomic scale roughness ($\leq 30\text{\AA}$) as well as submicroscopic roughness ($\sim 500\text{\AA}$).

Introduction

The surface of silver is known to be roughened by an oxidation-reduction cycle (ORC) in 1M KCl electrolyte. During oxidation a film of AgCl is formed on the surface of silver. The film is reduced to elemental silver during the electrochemical reduction portion of the ORC^[1,2]. The ORC gives rise to surface enhanced Raman scattering (SERS) from species near the silver surface. However, after the roughening process, the intensity of SERS decreases rapidly with time. A typical SERS intensity vs. time curve is shown in figure 1. The peak intensity decreases rapidly during the first minute after completion of ORC^[3]. Two types of roughness are thought to contribute to the enhancement^[4-11]. One involves roughness features of atomic dimensions that contribute to local mechanisms of enhancement such as charge transfer between surface states in silver and the adsorbate. It has been argued that the abrupt decay of the intensity of SERS in the first few minutes is caused by the disappearance of such atomic features (loss of SERS-active sites). On the other hand, roughness features on the order of 200-500 Å are necessary for the long-range mechanism of enhancement because they allow efficient coupling of the electromagnetic field and surface plasmons and they are not thought to change with time.

Recently Otsuka and Iwasaki^[12] have used the scanning tunneling microscope (STM) to image the surface of silver in air. From their *ex-situ* large-scale (~3x3 µm) STM images, they concluded that the roughened features (created by ORC) on a silver surface coalesced and that this smoothing had occurred during the 19 hours that the potential of the sample was held in the region in which no Faradaic processes take place. Previously they had also presented *in-situ* STM images (~1x1 µm) of the surface of silver after ORC^[13]. However, the time between successive images was 10 minutes, much longer than the time required for the decay of intensity of SERS (see figure 1). This is an important shortcoming if one wishes to study the time evolution of the surface morphology in the very first few minutes after ORC. Sakamaki *et al.*^[14] have performed *in-situ* electrochemical STM to follow changes in the morphology of the silver surface that occur during a single ORC. They found that an ORC can produce roughness on an atomic scale. However, they did not investigate the smoothing process after ORC.

The objectives of this study are to document by *in-situ* electrochemical scanning tunneling microscopy(ESTM) the changes that occur in the surface morphology of silver *immediately* following an ORC and to correlate the decay of intensity of SERS signals in the first few minutes after an ORC to changes in the surface morphology during the same time period.

Experimental

(A) Electrochemical Scanning Tunneling Microscope(ESTM)

The ESTM is shown in figure 2. It incorporates the original idea of Sonnenfeld *et al.*^[15] and includes an electrochemical cell. The microscope body is composed of two stainless steel plates parallel to each other and separated by three vertical fine screws. The single-tube piezoelectric scanner was mounted onto the upper stainless steel plate. The outer electrode of the tube scanner was cut into eight sectors. The upper four sectors are used for X,Y $\pm$ scanning plus the Z signal while the lower four are used for X,Y $\pm$ offset. The inner electrode of the tube scanner is used for Z offset. The vertical displacement constant, 20 Å/V, was calibrated by measuring the atomic step height of an {111} oriented gold film on mica. The X,Y transverse constants, 100 Å/V, were calibrated by imaging the atomic unit cell of highly oriented pyrolytic graphite(HOPG).

The sample holder and electrochemical cell were located on the bottom stainless steel plate. They were attached together and firmly held in position by two horizontal displacement screws and two spring plates. In this way, it is possible to move the sample area under the tunneling probe by several millimeters in the X,Y directions.

The two stainless steel plates were held together by a tripod of screws and four springs. It is very compact and rigid. The tip is mounted on the piezoelectric tube scanner and is placed near the side of the triangle whose vertices are the three screws. This produces a 20:1 reducing lever arrangement. The front two screws are used for coarse approach and the rear one is used for fine approach. It usually takes ~5 minutes of manual operation to advance the tip into tunneling position.

The tripod ESTM unit is suspended on an aluminum plate by four surgical tubes for vibration isolation. A chamber with four transparent plexiglass doors encloses the

ESTM and helps reduce acoustic noises. For further vibration isolation, the chamber is sitting on a sand box. A commercial STM control electronics (RHK Technology) is used for scanning and feedback. Data acquisition is done by a PC compatible computer equipped with a 12-bit 150 KHz analog-to-digital converter.

(B) Electrochemical Cell and Potential Control

The design of the ESTM combines the conventional three-electrodes of an electrochemical cell with a fourth electrode that serves as the tunneling probe. The cell itself is made of a Teflon block with an O-ring at the bottom that is used to prevent leakage of the electrolyte. The cell is attached to a sample holder by four screws. The total volume of electrolyte contained in the cell is ~1.6 ml. An EG&G Model 362 scanning potentiostat (Princeton Applied Research) is used to perform the cyclic voltammetry. A ring of platinum wire is used as the counter electrode and all the potentials were measured versus a Ag/AgCl, 1M Cl⁻ reference electrode.

In the ESTM potentiostatic circuitry, the tunneling bias (V_t) is inherently related to the potential of the sample (E_s) and the tip (E_t), i.e. $E_t - E_s = V_t$. Because one is interested in studying the electrochemical reactions at the sample, E_s is to be changed by the potentiostat. In our experiments the tunneling bias V_t is kept constant. As E_s changes, E_t is changed by the same amount. It is important to choose an appropriate value for V_t , such that E_t is always limited to a potential region with low faradic current (ideally, zero). Green *et al.*^[16] used this method. Siegenthaler *et al.*^[17] have recently discussed the ESTM potentiostatic circuitry in more detail.

(C) Tip Etching and Coating

We used a 0.5 mm diameter Pt-13%Rh wire as the tunneling probe. Its tip was sharpened by electrochemical etching in 6M NaCN + 2M KOH solution by an AC voltage. This method was applied by Heben *et al.*^[18] to sharpen Pt-Ir tips. After etching, the tip was rinsed in distilled water and dried in air. The radius of the tip was less than 1 μ m and crystallographic faceting was clearly visible along its length. The etched tip was then coated with Apiezon wax. The coating method was the same as described by Nagahara *et al.*^[19] Although the exposed tip area was not directly determined, its low value is suggested by the magnitude of the faradic leakage current

which was less than 100 pA in 1M KCl solution, with a positive bias of 300 mV during the ESTM operation.

(D) Sample Preparation and Oxidation-Reduction Cycle (ORC)

Polycrystalline Ag (99.99%) sheet was mechanically polished with 400 and 600 grit SiC grinding paper and fine polished with 6 and 1 μm diamond paste. All specimens were ultrasonically cleaned in distilled water and alcohol before ESTM imaging. The electrolyte 1M KCl was prepared from reagent grade potassium chloride(Baker) with Mega-Pure distilled water(Corning). The solution was purged with high purity nitrogen gas for three hours in a separate glass beaker and then transported through a clean pipette to the ESTM electrochemical cell. No further purging of solution was performed after this stage.

To perform the ORC, the sample was first held at a potential of -200 mV(non-Faradaic region). The potential was then raised at a rate of 2 mV/sec to its maximum value of 45 mV at which point the direction of potential change was reversed and it was lowered to its final value of -100 mV at a rate of -2 mV/sec. During the oxidation part of the cycle silver is oxidized to AgCl and during the reduction portion of the ORC, AgCl is reduced to elemental silver. Figure 3 is a plot of the current versus potential of the silver electrode during the ORC.

(E) ESTM Operation

During ORC the tip is moved away from the surface($\sim 1\mu\text{m}$) by using the piezo Z offset. Immediately after the ORC it was moved back into tunneling range. Two types of experiments were performed: (1) High magnification topographic imaging in which the scanning area was $\leq 500 \text{ \AA} \times 500 \text{ \AA}$ and the scanning speed was 0.1 sec/line. It took ~ 25 seconds to acquire one image. (2) Low magnification topographic imaging in which the scanning area was $3000 \text{ \AA} \times 3000 \text{ \AA}$ and the scanning speed was 1 sec/line. It took ~ 1 minute to acquire one image.

Results

(A) High Magnification Topographic Imaging

Figure 4 is a time sequence of images of the silver surface immediately following

the ORC. The left-hand side of figure 4 shows a 3D view of the surface and projected 2D views of the same images are presented on the right. The shading corresponds to an artificial light source shining from the left side at approximately 30° above the average surface plane. The time indicated for each image corresponds to the time elapsed after the ORC and the starting time for data acquisition. As shown in the figure, features $\sim 200 \text{ \AA}$ in size (marked by A) disappeared from the picture within 90 seconds and were replaced by an atomically flat plateau (marked by B). Morphological changes also occurred at two finger-like features (marked by C). The groove between the features was filled rapidly. In general, an overall smoothing of the surface occurred as evidenced by the decrease of vertical range with time (from $110 \text{ \AA}$ at $t = 0$ to $45 \text{ \AA}$ at $t = 110 \text{ sec}$). After the first two minutes, the surface features appeared quite stable and almost no further changes were observed. A sharp angle ($\sim 120^\circ$) was seen on one stable feature (marked by D). This particular angle also appeared in several other images and will be mentioned below.

Figure 5 is another example of the changes occurring following an ORC. An initial featureless hill (marked by A) in fig.5a was transformed to a hexagonal plane (marked by B) in fig.5d within two minutes. Small features (marked by C) in fig.5a were seen to disappear and merge into a step (marked by D) in fig.5b.

Growth of stable and atomically smooth planes is illustrated in figure 6. Again 3D and 2D ESTM representations of the surface are shown side by side. In fig.6a ($t=0$) the hill-like feature (marked by A) decomposes into two fragments in fig.6b ($t=31 \text{ sec}$). Also a flat area (marked by B) expanded with time. This was accompanied by the recession of other features (marked by C and D) in fig.6c-f. The overall vertical range decreased from $127 \text{ \AA}$ to $64 \text{ \AA}$ in ~ 4 minutes. Thereafter the smoothing rate decreased and no further changes were observed. From the projected 2D image in fig.6g three neighboring grains (marked by E, F, G) are seen to meet along three intersecting lines that are $\sim 120^\circ$ apart. This stable configuration presumably resulted from the equilibrium of surface tensions of the three grain boundary surfaces.

The images shown above indicate that smoothing and flattening of the $\geq 200 \text{ \AA}$ size features occur shortly after the completion of an ORC. However, fast changes occur in nanometer-size features as well, as shown before in figure 5a (feature marked by C). Figure 7 shows another example. Several small clusters ($\sim 30 \text{ \AA}$) are visible in the center of fig.7a ($t=0$). In the next image (fig.7b, $t=37 \text{ sec}$), these clusters have

disappeared and a step (marked by A) that was not present earlier has been formed. Initially the step was three atomic layers high and it subsequently diminished to one atomic layer in less than one minute. Presumably the clusters coalesced to form the step. Similar observations are also shown in figure 8. A small protrusion ($\sim 50\text{\AA}$) in fig.8a merged into the left terrace and many facets developed within minutes (fig.8g). Because of the angular shape of their borders (120° apart), their orientation is most likely $\{111\}$.

(B) Low Magnification Topographic Imaging

In order to better characterize the smoothing process, it is helpful to scan a large surface area. However, such images require a longer time to obtain (e.g. ~ 4 minutes for a $1\mu\text{m} \times 1\mu\text{m}$ image). Because the smoothing rate is very fast in the first few minutes, it is necessary to limit the imaging time (i.e. scanning area) in order to retain reasonable temporal resolution. The optimum conditions correspond to a scanning area of $3000\text{\AA} \times 3000\text{\AA}$, which is obtained in ~ 51 seconds. Figure 9 is a sequence of images taken in slightly over 2 hours. The changes in morphology were very obvious in the first 5 minutes. For example, one large mountain-like feature (marked by A) was transformed to a flat plateau (marked by B) and three bumps (marked by C) were formed at the bottom of fig.9c. Once again the overall smoothing of the surface is evidenced by the decrease in the vertical range (from $640\text{\AA}$ to $133\text{\AA}$). The surface appeared quite stable after 5 minutes. This is consistent with the results of the high magnification scanning experiments described above. After this time the smoothing process continued to occur at a slower rate. This can be seen by comparing fig.9d ($t=5$ mins) to fig.9e ($t=30$ mins). The three bumps at the bottom of the image merged into two bumps (marked by D). In fig.9g ($t=55$ mins) the bumps were extending and flattening straight into the upper region.

Discussion

(A) Smoothing Mechanism

The surface of silver was roughened by ORC that produced a structure of marked hills and valleys. According to the Gibbs-Thomson equation^[20], the chemical potential of an atom on a curved surface will be different from that on a flat surface by

$\Omega\gamma(1/R_1+1/R_2)$, where Ω is the atomic volume, γ is the isotropic surface energy and R_1 , R_2 are the two principal radii of curvature of the surface. The difference in chemical potential will cause material to redistribute in a direction of annihilating such difference until equilibrium is established. Therefore, hills will reduce their height and valleys will be filled. The smoothing phenomenon observed by ESTM of the roughened surface of silver is exactly due to such curvature effect.

From an atomistic point of view, the curved surface has a multitude of steps, kinks in the steps in addition to adatoms and small clusters of atoms. In this configuration the energetic content of the surface is very high because of the large number of broken bonds of the atoms with lower coordination. These atoms will diffuse to positions of higher coordination and lower energy: small clusters will dissolve and the adatoms will merge into steps. Steps on stable planes will adsorb the diffusing adatoms and expand. The final equilibrium structure is the result of the minimization of total surface energy leading to the Wulff's shape of a crystal. A detailed analysis of the equilibrium shape of crystals can be found elsewhere^[20-22]. These thermodynamic models predict facets composed of planes of low Miller indices such as {111}, {110}, {100} to form in inverse proportion to their surface energies.

From the results of *in-situ* ESTM, the smoothing rate was very fast in the first 2 minutes after electrochemical reduction was completed. It slowed down rapidly and the surface was relatively stable after 5 minutes. This is consistent with the measurements of surface capacitance made by other researchers^[23-27]. However, the ESTM revealed in a clear way that the morphological changes include the growth of crystal planes. From fig.4-8, it is seen that 5 minutes after the ORC the surface consists in part of atomically smooth planes(or plateaus) with edges or steps forming sharp angles of $\sim 120^\circ$. The orientation of these planes is likely to be {111}.

The transport of matter that is necessary for the observed smoothing may occur by two mechanisms, namely, surface diffusion and volume diffusion. The latter consists of dissolution through the electrolyte and re-precipitation on the surface. Jaenicke *et al*^[25] have followed the smoothing of silver in KI solution after ORC by measurement of surface capacitance. They concluded that the process of smoothing was caused by a dissolution/re-precipitation mechanism through the formation of surface complex ions of silver. However, from the present results of *in-situ* ESTM images, the smoothing

process can be explained by either surface diffusion or volume diffusion mechanisms.

(B) Surface Enhanced Raman Scattering

In summary, three important observations were obtained in the *in-situ* ESTM experiments: (1) The atomic scale roughness ($\leq 50\text{\AA}$), e.g. atomic clusters, disappeared by coalescing to form steps during the first few minutes after completion of the electrochemical reduction portion of ORC. (2) The average corrugation of the surface decreased in the same time period. The vertical height of surface features diminished by $\sim 100\text{\AA}$ and $\sim 500\text{\AA}$ in respective higher and lower magnification imaging, resulting in a surface composed of flat, low Miller index planes. (3) The distribution, within the plane parallel to the surface, of sizes of large-scale features did not change appreciably.

The strong decay of intensity of SERS in the first few minutes is thought to be caused by the loss of SERS-active sites, i.e. the disappearance of atomic roughness features^[3,28,29]. The long range features ($200\text{-}500\text{\AA}$) are thought to remain stable. However, the results of ESTM have shown that the smoothing process involves changes of features whose sizes range from $\sim 30\text{\AA}$ to $1000\text{\AA}$. Although the distribution of the dimensions measured in the plane of the surface remains mostly unchanged, the vertical amplitude of these features decreases considerably. Consequently the electromagnetic contribution to SERS may decrease by as much as several orders of magnitude^[30]. These results indicate that the decay of intensity of SERS may result from changes in the large-sized features as well as from changes in the atomic-size features.

Conclusions

In-situ ESTM was used to study the smoothing process of silver surface that was roughened by an ORC in 1M KCl. The results clearly demonstrate the ability of ESTM to follow the changes in surface structure of an electrode under potential control. The smoothing occurred very rapidly within the first few minutes and growth of low index planes was also observed. Both small-scale features ($\sim 30\text{\AA}$) and large-scale features

(~500Å) changed during the smoothing process. The local ("chemical") and long-range ("electromagnetic") enhancement mechanisms would change in similar times scales. It is therefore not possible based on these results to dismiss any one of these two mechanisms in favor of the other. The driving force for the smoothing is the reduction in surface energy. This is achieved by a combination of a decrease in surface area and growth of crystal planes.

Acknowledgements

The authors want to thank the staff of the machine shop in the Materials Science Division of the LBL. Without them it is impossible to construct the main body of ESTM. Special thanks to Dr. M. Heben and Professor N. Lewis at California Institute of Technology for their helpful advice in tip etching and coating. One of the authors (J.-S. Chen) also likes to express his gratitude to Dr. G. Neubauer and Dr. J. Gui for many helpful discussions during the course of this work.

This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences of the US Department of Energy, under Contract No. DE-AC03-76SF00098.

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Figure Captions

- Figure 1. Time evolution of the intensity of the 240 cm^{-1} stretching mode of $\text{Ag}^0\text{-Cl}^-$ measured during and after ORC of silver in 1 M KCl. ORC terminated at -0.1V at $t \sim 40$ seconds. Potential was held constant thereafter.
- Figure 2. Tripod electrochemical scanning tunneling microscope(ESTM). Tip approach is done manually through a 20 : 1 reducing lever arrangement of three fine screws. The front 2 screws are for coarse adjustment, while the rear one is for fine approaching.
- Figure 3. Cyclic voltammogram showing an oxidation-reduction cycle (ORC) of the silver polycrystal in 1 M KCl. Potential is cycled from -200 mV to 50 mV (vs. Ag/AgCl,Cl^-) at a rate of 2 mV/sec .
- Figure 4. A 3D and 2D representation of a sequence of images($500\text{\AA} \times 500\text{\AA}$) of the surface of polycrystalline silver after an ORC. The time indicates the starting time of data acquisition and the time elapsed after the completion of ORC. Each image takes ~ 25 seconds to obtain. Roughness features($\sim 250\text{\AA}$) disappear and surface smoothing takes place within 2 minutes. Notice the 120° angles formed by the border line at the right side of feature D in (d). This is characteristic of crystallographic directions in $\{111\}$ plane.
- Figure 5. A hexagonal shape feature(marked by B in 5e) was developed from the original featureless hill(marked by A in 5a) within 2 minutes. The size of image is $500\text{\AA} \times 500\text{\AA}$.
- Figure 6. 3D and 2D representation of a sequence of images($500\text{\AA} \times 500\text{\AA}$) taken after ORC. The height decreases from $127\text{\AA}$ to $64\text{\AA}$ in ~ 4 minutes. Surface smoothing occurs by loss of material from the hill-like feature A, by expansion of the flat area B and by receding of features C & D.
- Figure 7. Small clusters ($\sim 30\text{\AA}$ in size) in the center of 7a disappear while a step is formed in 7b in less than one minute. The size of image is $500\text{\AA} \times 500\text{\AA}$.
- Figure 8. A sequence of $300\text{\AA} \times 300\text{\AA}$ images that show: (1) A small bump marked by the arrow merging into the left terrace and (2) Many facets that have developed in ~ 7 minutes. The top and right edges of these facets form 120° angles characteristic of the $\langle 110 \rangle$ directions in planes of $\{111\}$ orientation.

Figure 9. Large scale topographic images($\sim 3000\text{\AA} \times 3000\text{\AA}$) showing evolution over a period of ~ 2 hours after the ORC. A mountain-like feature (marked by A in 9a, $\sim 640\text{\AA}$ in height) quickly dissolves into a flat plateau (marked by B in 9b, $\sim 200\text{\AA}$ in height) in one minute.

Figure 1

(a) Front View of Tripod ESTM

(b) Top View of the Base Plate

Figure 2

Cyclic Voltammogram

Figure 3

(a) $t = 0$

(b) $t = 37 \text{ sec}$

(c) $t = 72 \text{ sec}$

(d) $t = 110 \text{ sec}$

XBB 913-1997

Figure 4

(a) $t = 0$

(e) $t = 156 \text{ sec}$

(b) $t = 36 \text{ sec}$

(d) $t = 114 \text{ sec}$

(c) $t = 75 \text{ sec}$

Figure 5

XBB 913 1998

(a) $t = 0$

(b) $t = 31 \text{ sec}$

(c) $t = 61 \text{ sec}$

(d) $t = 92 \text{ sec}$

Figure 6

XBB 913-1999

(e) $t = 125 \text{ sec}$

(f) $t = 165 \text{ sec}$

(g) $t = 210 \text{ sec}$

XBB 913-2000

Figure 6 (cont)

(a) $t = 0$

XBB 913-2001

(b) $t = 37 \text{ sec}$

Figure 7

(a) $t = 0$

(b) $t = 60 \text{ sec}$

(c) $t = 135 \text{ sec}$

(d) $t = 203 \text{ sec}$

(e) $t = 240 \text{ sec}$

(f) $t = 300 \text{ sec}$

(g) $t = 400 \text{ sec}$

Figure 8

XBB 913-2002

(a) $t = 1$ min

(e) $t = 30$ min

(b) $t = 2$ min

(f) $t = 45$ min

(c) $t = 3$ min

(g) $t = 55$ min

(d) $t = 5$ min

(h) $t = 127$ min

XBB 913-2003

Figure 9

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