

Surface Science 430 (1999) L553-L557

www.elsevier.nl/locate/susc

surface science

Surface Science Letters

Atomic force microscopy of Au deposition from aqueous HF onto Si(111)

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Abstract

Non-contact atomic force microscopy (AFM) was employed following emersion to examine Au nanoclusters deposited from aqueous mixtures of HF and 10^{-4} M KAu(CN)₂ onto Si(111). As the HF concentration is increased, the growth rates both parallel and perpendicular to the substrate of the approximately oblate Au hemispheroids increase. AFM images were obtained for times at which previously reported in situ second harmonic generation signals from the interface reach a maximum. At the time when the second harmonic enhancement is maximized during deposition from 0.500 (5.00) M HF, the Au nanoclusters have an average diameter of 94 (109) nm and an average height of 3.6 (9.5) nm. These cluster diameters can be understood qualitatively by the shift of the plasmon resonance due to depolarization as the cluster size increases, causing the resonant second harmonic enhancement at 532 nm to pass through a maximum at cluster diameters in the range 90–110 nm. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Atomic force microscopy; Electrochemical methods; Gold; Nanoclusters; Second harmonic generation; Semiconductor-electrolyte interface; Silicon; Surface chemical reaction

Deposition of noble metals onto Si involves interesting fundamental problems due to the highly complex interactions which occur, including interdiffusion and silicide formation [1] For example, deposition of Au onto Si has been thoroughly studied in vacuum, yet the system is still not wellunderstood, particularly the complicated reaction dynamics at elevated temperatures [1] Deposition of noble metals is also of great importance in the electronics and microelectronics industries. Cu interconnects are eventually expected to replace Al

Direct noble metal deposition onto Si also occurs as unwanted contamination during cleaning and preparation of Si wafers during microelectronics manufacture. Following dissolution of the native oxide in an HF etchant, metals more noble

due to its lower resistivity and better electromigration resistance [2–4]. Cu deposited by electrochemical means is currently used in the electronics industry for filling high-aspect-ratio through-holes in printed circuit boards [5,6] and for junction delineation [7]. In addition, electrochemically deposited Au is employed for the absorber layer in X-ray masks [8], for conductive coatings [9], and for electrical contacts [10–13].

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than hydrogen can be reduced and deposited onto bare Si, which is a strong reducing agent [14]. Scanning probe microscopy has shown that metals deposited from aqueous HF onto Si initially form features best described as nm-sized oblate hemispheroids [15–18].

Scanning microscopy of systems involving metal clusters deposited onto semiconducting and insulating substrates is often made difficult by weak cluster adhesion. Atomic force microscopy (AFM) is preferably performed in the contact mode, where either the cantilever deflection is held constant and the variation in the scanner height is measured, or where the sample height is held constant and the variation in the local force is measured. However, the AFM tip may interact with weakly bound metal clusters, in some cases displacing them.

This difficulty can be largely circumvented by performing AFM in the non-contact mode, where the cantilever oscillates near its resonance frequency with a small amplitude. When the tip interacts with the sample, the frequency and amplitude of the oscillation are altered, and imaging is achieved typically by holding the oscillation amplitude constant. Contact mode AFM is believed to sample short-range repulsive forces, while noncontact mode is believed to sample longer range attractive forces [19], although recent calculations challenge this assertion [20]. Non-contact AFM has been used by numerous investigators to image noble metal clusters on semi- or non-conducting substrates [21-25]. This report describes preliminary non-contact AFM studies of Au deposition from aqueous HF onto Si(111).

Prior to each experiment, the sample was cleaned by treatment in a 0.50 M HF etchant and typical SC-1 and SC-2 cleaning solutions. Hydrogen-terminated Si(111), which is known to be stable in air and water for extended periods, was prepared by immersing a cleaned Si(111) sample into 0.50 M HF and rinsing the surface. If created properly, this solid–liquid interface is probably the most ideal that can be prepared, exhibiting the lowest surface recombination velocity ever observed for a semiconductor-liquid junction [26]. Preparation of H-terminated Si(111) allows the Au deposition kinetics to be studied without com-

plications caused by the poorly understood dissolution kinetics of the native oxide.

Au was deposited onto H-Si(111) from aqueous solutions containing various concentrations of KAu(CN)₂ and HF with pHs ranging from approximately 0.4 to 1.9. Deposition of Au from aqueous HF onto Si may be described by the following overall half-reactions:

$$Au(CN)_2^- + e^- \rightarrow Au + 2CN^-, \qquad (1)$$

$$Si + 6F^- \rightarrow SiF_6^{2-} + 4e^-,$$
 (2)

with standard reduction potentials of approximately -0.595 and -1.37 V NHE, respectively [27]. Non-contact AFM studies were performed following emersion using a Burleigh Instruments Metris 2000 with a scanning range of 25 µm.

The current AFM studies were motivated by studies of Au deposition by surface second harmonic generation (SHG), which showed large enhancements due to formation of Au nanoclusters. Fig. 1 shows the variation of the SH signal during deposition of Au onto H-Si(111) from solutions containing 10^{-4} M KAu(CN)₂ [28,29]. The Nd:YAG pump laser was *s*-polarized during these experiments. All of the curves in Fig. 1 reach a maximum, whose temporal position and intensity depend on HF concentration, and subsequently decline.

The maxima in Fig. 1 arise from resonance between the surface plasmon of Au nanoclusters and the second harmonic photon (2ω) at 532 nm.



Fig. 1. Second harmonic signal as a function of time during Au deposition from 10^{-4} M KAu(CN)₂ at various nominal HF concentrations. Reproduced with permission from Ref. [28].

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Noble metal hemispheroids exhibit strong surface plasmons and can produce enormous resonant signal enhancements in surface-enhanced Raman spectroscopy (SERS) and surface second harmonic generation (SHG) [30–34]. The surface plasmon resonance occurs in the range 510–540 nm for Au colloids of 2.5–10 nm diameter, while the resonance is red-shifted for larger Au colloids [35–37]. The surface plasmon resonance is difficult to understand in detail, depending upon cluster size and shape [30], cluster density, and the dielectric function of the surrounding medium [38,39].

The current studies were undertaken to identify the approximate cluster size(s) associated with the maxima in Fig. 1. Surface plasmon-enhanced SHG from Na nanoclusters grown on dielectric substrates in vacuum has been studied as a function of cluter size, and maxima similar to those shown in Fig. 1 have been seen for 100–200 nm diameter clusters [40–42]. In the current study, Au cluster growth rates both parallel and perpendicular to the substrate were seen to increase with HF concentration, in agreement with previous investigators [18]. This suggests that fluoride-containing species are involved in the rate-limiting step of Au cluster growth [29].

Figs. 2 and 3 show non-contact AFM images taken following emersion of the samples from 0.500 and 5.00 M aqueous HF solutions at the maxima in the curves shown in Fig. 1. The mean equivalent cluster diameters obtained from these two images are 114 and 129 nm, respectively. If one deconvolutes the effects of the AFM tip from the apparent cluster sizes by simply subtracting the tip diameter, approximate cluster diameters of 94 and 109 nm are obtained from Figs. 2 and 3, respectively. The mean cluster heights are 3.6 and 9.5 nm, respectively, with quite narrow distributions.

The cluster diameters obtained from Figs. 2 and 3 can be qualitatively understood through the effects of cluster size on the surface plasmon resonance and the resultant electric field enhancement. Since the incident laser is polarized perpendicular to the plane of incidence, the electric field excitation is aligned with the long axis of the oblate hemispheroids. For this reason only one surface pasmon resonance will be excited.



Fig. 2. Non-contact AFM image following 610 s of Au deposition from 0.500 M HF.



Fig. 3. Non-contact AFM image following 193 s of Au deposition from 5.00 M HF.

The enhancement of the second harmonic signal, $S(\omega, 2\omega)$, which is observed can be approximately related to the electric field enhancements, $R(\omega)$ and $R(2\omega)$, at the fundamental and second

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harmonic frequencies as [34,43]:

$$S(\omega, 2\omega) \propto R(\omega)^2 R(2\omega).$$
 (3)

For noble metal hemispheroids, maxima in the absorption spectrum are closely related to maxima in the electric field enhancement arising from the surface plasmon resonance [44], although the exact relationships between the absorption and extinction maxima and the SERS and SHG maxima are expected to be complex [34,44,45]. In the current studies, the second harmonic signal should reach a maximum with the electric field enhancement at the second harmonic frequency 2ω , since no enhancement is expected at the fundamental frequency ω .

As the Au clusters grow, several effects will occur simultaneously. The surface plasmon resonance will shift to longer wavelengths and broaden as the electric field becomes depolarized across the cluster, and eventually radiation damping will cause the a decline in the electric field enhancement. We expect that the decline in the SHG signals observed in Fig. 1 is likely to be dominated by the shift in the maximum in the electric field enhancement with increasing cluster size. Since substrate interactions and size effects may slightly red- or blue-shift the surface plasmon resonance away from the second harmonic frequency 2ω , the cluster size at which the maximum electric field enhancement occurs will differ somewhat from that at which the absorption is maximized.

The spectra of clusters as large as those seen here can only be fully understood by an electrodynamic treatment. Quantitative results can most generally be obtained by the Discrete Dipole Approximation (DDA), where the metal cluster of interest is divided into a cubic array of finite dipole elements [44,46], and are beyond the scope of the current report. The origin of the surface plasmon resonance will be discussed here qualitatively.

The surface plasmon resonance and its dependence on cluster size have been discussed previously [46,47]. Neglecting finite size effects, the electric field (E_i) inside spheroidal clusters can be related to the applied field (E_0) according to [47]:

$$E_{i} = \frac{1}{1 + (\epsilon - 1)A} E_{0}, \tag{4}$$

where ϵ is the dielectric function and A is a constant describing the spheroid eccentricity, equal to 1/3 for spheres. A resonance is observed when the denominator in Eq. (3) vanishes, at which point the surface dipolar charge distribution can absorb and reradiate maximum electromagnetic radiation, behaving like a resonantly driven cavity.

However, for cluster sizes not insignificant with respect to the wavelength, the electric field becomes non-uniform within the cluster, and depolarization fields in different parts of the cluster become out of phase. These effects correspond to optical retardation of the internal field [48]. In this case the electric field inside spherical clusters is [48]:

$$E_{i} = \frac{1}{4\pi} \frac{(\epsilon - 1)(1 - k^{2}a^{2}/10)}{1 + (\epsilon - 1)A_{\text{eff}}} E_{0},$$
(5)

where

$$A_{\rm eff} - \frac{1}{3} - \frac{1}{3}k^2a^2 - \frac{2}{9}ik^3a^3.$$
 (6)

The second term in A_{eff} is associated with dynamic depolarization and the third term with radiation damping. This approach, which should be valid for Au spheres of less than 120 nm diameter [47], can also be generalized to spheroids [49].

This results in the electric field enhancement reaching a maximum with size, the effects of which have been seen experimentally in the spectrum of Au colloids, with the maximum absorption at 532 nm occurring for spherical clusters of approximately 60–80 nm diameter [50,51]. This is close to the size range seen in the current studies at which the surface second harmonic generation (SHG) reaches a maximum for oblate Au hemispheroids. Although the spectra of Au spheroids are considerably altered from those of Au spheres [51-55], the current results suggest that the size at which maximum enhancement occurs remains similar. This holds in the present case because the polarization of the incident electric field is aligned with a specific axis of the oriented hemispheroids.

Acknowledgements

This research has been supported by NSF grant CTS-9527497. Thanks to James Zobel and

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Burleigh Instruments for their assistance in obtaining the AFM images.

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