Kinetic Analysis of Au deposition from Aqueous HF onto Si(111) by Surface Second Harmonic Generation

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Deposition of Au from aqueous HF onto Si(111) has been studied by Rutherford backscattering (RBS) and surface second harmonic generation (SHG), which at 532 nm is nearly resonant with the surface plasmon of Au nanoclusters. The RBS measurements indicate that Au deposition is rate-limited by diffusion, while the SHG measurements indicate that Au cluster growth is rate-limited by either a surface reaction involving a fluoride-containing species or electron transfer. This apparent contradiction can be reconciled by proposing that initial deposition in the form of AuCN is followed by a slow electroless reduction of Au(I) accompanied by Si oxidation. By addition of HCl and KF, the solution phase equilibria can be separately manipulated, motivating further SHG experiments which indicate that HF and not HF_2^- is the kinetically active fluoride-containing species. The apparent reaction order for Au cluster growth with respect to HF is approximately 1/2, and the reaction order for Au cluster growth with respect to $Au(CN)_2^-$ is near zero in the concentration range 10^{-4} to 10^{-5} M.

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Deposition of noble metals onto Si is important from both a fundamental and a practical viewpoint. Interesting fundamental questions arise due to the complex interactions between Si surfaces and noble metals, including rapid interdiffusion and metastable silicide formation.¹ For example, deposition of macroscopic Au films onto Si substrates yields a complex layered structure in the following sequence: Si substrate, a diffuse 15-20 Å thick alloy mixture of Au and Si, a region of pure Au, and a 1-2 monolayer thick metal-rich Au–Si alloy on top.¹ Many aspects of this system are not well understood, including the complicated reaction dynamics at elevated temperatures, which remain controversial.

Deposition of noble metals is also important in the electronics industry in two different respects, growth of conducting films and unwanted metallic contamination. Future generations of microelectronic devices are expected to have Cu interconnects due to its lower resistivity and better electromigration resistance with respect to Al.²⁻⁴ Electro- and electroless deposition of Cu are already in widespread use in printed circuit manufacture, particularly for filling high-aspectratio through-holes.^{5,6} Electro- and electroless Au deposition have a number of applications, including fabrication of the absorber layer in X-ray masks,⁷ conductive coatings,⁸ and electrical contacts.⁹⁻¹²

Noble metal deposition onto Si is also important during aqueous processing of Si wafers during microelectronics manufacture. Since bare Si is a strong reducing agent, metals more noble than hydrogen ion can be reduced and deposited from a HF etchant following dissolution of the SiO_x protective layer.¹³ This type of electroless process is usually described as galvanic displacement to distinguish it from autocatalytic deposition. This report describes fundamental studies of Au deposition and cluster growth from aqueous HF onto Si(111) using surface second harmonic generation (SHG) and Rutherford backscattering (RBS). The SH signal is strongly enhanced by resonance with the surface plasmon of Au nanoclusters. This should be generally applicable to studies of noble metal nucleation and cluster growth on insulating and semiconducting surfaces as surface plasmon–enhanced SHG.

Experimental

SHG experiments were performed during Au deposition from aqueous HF using the experimental setup shown in Fig. 1. A Continuum Powerlite 6050 Nd:YAG laser operating at 1064 nm, 50 Hz, and 8 ns/pulse was filtered to remove light at harmonic frequencies and reflected from the Si surface at an incident angle of approximately 26° . After filtering out the fundamental and third harmonic frequencies, the SH signal at 532 nm was detected by a gated, inten-

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sified Princeton Instruments LN/1024 CCD. The SH signal was verified to depend quadratically on the laser power, with final experiments performed at a laser power of 5 mJ/pulse. The p-type, 0.01 Ω cm Si(111) sample lay horizontally at the bottom of the virgin Teflon cell. Prior to each experiment, the sample was cleaned by treatment in a 0.50 MHF etchant and SC-1 and SC-2 process solutions. All reagents were of very large-scale integrated (VLSI) grade purity. Following each experiment the sample was replaced. The RBS measurements were performed ex situ by Charles Evans and Associates following sample removal and rinsing.

All the experiments reported here were performed on H-terminated Si(111), which was prepared by immersing a cleaned Si(111) sample into 0.50 M HF, decanting the solution, and rinsing the surface. The perfectly H-terminated Si(111) surface which is formed is known to be stable in air for periods of several hours.¹⁴⁻¹⁸ This surface is probably the most ideal solid-liquid interface which can be prepared, exhibiting the lowest surface recombination velocity ever observed for a semiconductor.¹⁹ Defect densities as low as 0.004% have been reported.²⁰ Preparation of H–Si(111) allows the deposition kinetics to be studied without the complication of an induction period during which HF dissolves the native oxide.

Following preparation of the H-terminated surface, Au was deposited from aqueous solutions containing various concentrations of $KAu(CN)_2$ and HF. These solutions were prepared by mixing concentrated HF with highly purified H₂O, then dissolving $KAu(CN)_2$. They were stable for the duration of the experiments but would deposit a yellowish material, probably AuCN, on the container walls if left overnight. Appreciable formation of HCN was not observed. The pH of these solutions, as determined from equilibrium calculations described later, ranged from about 0.4 to 1.9.



Si(111) in HF + KAu(CN)₂ Solution



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Deposition of Au from aqueous HF onto Si may be described by the following half-reactions

$$Au(CN)_{2}^{-} + e^{-} \rightarrow Au + 2CN^{-}$$
[1]

$$Si + 6F^- \rightarrow SiF_6^{2-} + 4e^-$$
 [2]

with standard reduction potentials of approximately -0.595 and -1.37 V NHE, respectively.²¹ Reaction 2 is often written with HF rather than F⁻ as the reactant. As discussed later, the detailed mechanisms of reactions 1 and 2 are addressed by the present study.

Surface plasmon-enhanced SHG.— Figure 2 shows the sharp increase, which depends on HF concentration, of the SH signal during deposition of Au onto H-Si(111) from solutions containing 10^{-4} M KAu(CN)₂. A temporal maximum is observed for each HF concentration shown in Fig. 2, although this is not always apparent due to the scale chosen. Although the time at which each maximum occurs is reproducible, the intensity of each maximum may vary by as much as two times between repeat measurements. These maxima arise due to resonance between the surface plasmon of Au nanoclusters and the second harmonic photon at 532 nm. Neglecting surface scattering, dynamic depolarization, and radiation damping, the electric field (*E*₀) according to²²

$$E_{i} = \frac{1}{1 + (\epsilon - 1)A} E_{0}$$
[3]

where *A* is a constant describing the spheroid eccentricity. A classical resonance is observed when the denominator vanishes, at which point the surface dipolar charge distribution can absorb maximum electromagnetic radiation, behaving like a resonantly driven cavity. The presence of noble metal hemispheres and hemispheroids and the accompanying strong surface plasmon resonance can produce enormous signal enhancement in surface spectroscopies such as surfaceenhanced Raman spectroscopy (SERS) and SHG.²³⁻²⁷

The surface plasmon resonance occurs in the range 510-540 nm for Au colloids of 2.5-10 nm diam, while the resonance is red-shifted for larger Au colloids.²⁸⁻³⁰ The surface plasmon resonance is difficult to model, depending upon a variety of factors in a complex manner. The peak position and intensity can depend on the cluster size and shape, and the resonance can be as broad as 100 nm.³⁰ In addition, the surface plasmon resonance of embedded Au clusters shifts according to the dielectric function of the surrounding medium,^{31,32} so the Si surface will affect the spectrum in a manner which is difficult to predict. Au nanoclusters lack clear visible absorption features below a diameter of approximately 2 nm, ³²⁻³⁵ so clusters must reach this size before resonant SH enhancement can occur. Sur-



Figure 2. Second harmonic signal as a function of time during Au deposition from 10^{-4} M KAu(CN)₂ at various nominal HF concentrations.

face plasmon-enhanced SHG from Na nanoclusters grown on dielectric substrates in vacuum has been studied as a function of cluster size, and maxima similar to those shown in Fig. 2 have been seen for 100-250 nm diam clusters.³⁶⁻³⁸ Atomic force microscopy (AFM) studies indicate that the maxima in Fig. 2 arise from Au nanoclusters with diameters in the range 70-110 nm, ³⁹ which is the range in which the absorbance of Au nanoclusters reaches a maximum in aqueous solution.40,41 Previous AFM studies have observed the dependence of Au cluster growth rate on HF concentration.⁴² The decline of the SHG signals shown in Fig. 2 back to their original levels was previously believed to arise from interdiffusion between Au and Si.43 We now expect that this decline arises primarily from the onset of radiation damping, which arises due to nonuniformity of the electric field inside larger clusters, but we still expect that interdiffusion may also play a role. The variation in the intensities of the maxima in Fig. 2 arise from random noise in the SHG signal, from differences in nucleation density, and from differences in the cluster aspect ratios.

Mechanism of Au reduction.—Both SHG measurements and AFM studies seem to indicate that Au deposition is kinetically limited by surface reaction. However, a more complex picture is revealed by surface coverage measurements by RBS near the SHG maxima for 0.500 M and 2.50 M HF.⁴³ The measured surface coverages yield average fluxes of 1.5×10^{13} and 1.2×10^{13} atoms/cm² for 0.500 and 2.50 M HF, respectively. These values can be compared to the diffusion flux expected from

$$J = D \frac{C_0}{\delta}$$
[4]

Assuming a diffusion coefficient (D) of 10^{-5} cm²/s and a diffusion layer thickness (δ) of 350 μ m yields a diffusion flux (J) of 1.7×10^{13} atoms/cm² for a Au(I) concentration (C_0) of 10^{-4} M. Given the uncertainty in the assumed values, this agrees well with the observed fluxes. The agreement between the observed fluxes and those expected for diffusion-limited deposition does not alone establish kinetic limitation by diffusion. However, coupled with the strong dependence of the Au cluster growth rate on HF concentration, these results strongly suggest that Au deposition is kinetically limited by diffusion.

This apparent contradiction can be reconciled by proposing that Au deposition is kinetically limited by diffusion of Au(I) species but that growth of Au nanoclusters is kinetically limited by a surface reduction involving fluoride-containing species. This is consistent with initial deposition occurring as the adsorbed intermediate AuCN, as postulated for electrodeposition of Au onto a variety of metal substrates.⁴⁴⁻⁴⁸ The reduction of Au(CN)₂ has been proposed to occur by two parallel processes, direct reduction by reaction 1 at high overpotentials and a two-step reduction process at low potentials⁴⁴⁻⁴⁸

$$Au(CN)_2^- \rightarrow AuCN(ads) + CN^-$$
 [5]

$$AuCN(ads) + e^{-} \rightarrow Au + CN^{-}$$
[6]

Surprisingly, SERS has only identified adsorbed $Au(CN)_2^{-}$, ^{49,50} although evidence for incorporation of nanocrystalline AuCN into Au deposits has been obtained by transmission electron microscopy (TEM) and Auger electron spectroscopy (AES).⁵¹ An alternative explanation to the two-step reduction process described would be initial deposition into a partially discharged species, followed by full reduction and incorporation into a Au nanocluster.

Mechanism of Si oxidation.—Kinetic analysis can be performed on the data in Fig. 2 by noting that rapid attainment of a SH maximum corresponds to rapid growth of Au nanoclusters. The goal is to identify the mechanistically important fluoride-containing species involved in reaction 2. The aqueous chemistry of HF has been thoroughly studied and is complicated by the existence of polymer-type solution phase reactions involving HF.^{52,53} In the present study, only the following two equilibria are considered, since these are known to predominate in moderately concentrated aqueous HF

$$\mathrm{HF} \to \mathrm{H}^+ + \mathrm{F}^-$$
 [7]

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$$HF + F^{-} \to HF_{2}^{-}$$
 [8]

Disagreement exists in the literature regarding the equilibrium constants for these two reactions, in part due to further polymerization at high concentrations of HF.⁵² As the nominal HF concentration is increased, the concentrations of H⁺, F⁻, HF, and HF₂⁻ all increase, so the effects of different species are difficult to isolate. For this reason these two equilibria were manipulated by performing experiments in which HCl and KF were added to aqueous HF. One experiment was performed with 1.71 M HF and 0.780 M HCl and a second with 0.249 M HF and 0.0516 M KF. The results of both are included in Fig. 2.

The data in Fig. 2 are analyzed by taking the time at each maximum to be proportional to the inverse reaction rate. The equilibrium constants for reactions 7 and 8 are taken as 1.30×10^{-3} and 9.62, respectively,⁵⁴ and the concentrations of HF, HF₂⁻, F⁻, and H⁺ in solution are calculated. Logarithmic plots for the reaction rate as a function of the calculated values of [HF] and [HF₂⁻] are shown in Fig. 3 and 4. Similar plots using calculated values of [H⁺] and [F⁻] are nonmonotonic. Comparing Fig. 3 and 4, the two additional measurements with HCl and KF indicate that HF and not HF₂⁻ is involved in the rate-limiting step for Au cluster growth and simultaneous Si dissolution. The slope of the plot in Fig. 3 is 0.54, suggesting that the apparent reaction order with respect to HF is 1/2. Since infrared spectroscopic results indicate that fluorine atoms are found prefer-



Figure 3. Reaction rate in 10^{-4} M KAu(CN)₂ as a function of HF concentration determined from equilibrium calculations.



Figure 4. Reaction rate in 10^{-4} M KAu(CN)₂ as a function of HF₂⁻ concentration determined from equilibrium calculations.

entially at steps,⁵⁵ these are the likely sites of attack by HF, consistent with AFM studies showing preferential deposition at defects.⁴² Figure 5, which shows the reaction rate as a function of ionic strength, was constructed as a test to determine whether colloidal solution phase phenomena might play an important kinetic role. Once again, the cluster growth rate does not vary monotonically with ionic strength. The results reported here are qualitatively unaffected by the particular choice of equilibrium constants.

In order to determine the reaction order with respect to $Au(CN)_2^-$, further SH observations were made during deposition from 0.500 M aqueous HF containing 10^{-4} , 3×10^{-5} , and 10^{-5} M KAu(CN)₂. The temporal maximum was found to be only weakly dependent on the concentration of Au species. A logarithmic plot of the reaction rate as a function of $Au(CN)_2^-$ concentration yields a reaction order with respect to $Au(CN)_2^-$ of approximately 0.10. This suggests that during cluster growth there is an excess of Au(I) species on the surface. Future studies may investigate the kinetics with respect to $Au(CN)_2^-$ by performing experiments at lower concentrations.

Comparison to other results.-The conclusion that HF and not HF_2^- is mechanistically active should be compared to previous studies. At first this might not seem surprising, since reaction 2 is often written with HF as the reactant. However, this conclusion is in disagreement with recent results for Si dissolution into HF, which conclude on the basis of solution phase equilibria that HF_2^- is the active species.56,57 The current system is chemically similar to electrochemical dissolution of Si in aqueous HF to form porous Si, although the chemical reaction mechanism involved in porous Si formation has been less thoroughly studied. Several competing mechanisms have been proposed for porous Si formation, although two are most commonly cited.58 The first proposes complete surface oxidation to Si^{4+} , which is believed to desorb as SiF_4 and react in solution to form SiF_6^{2-} . However, the chemical nature of the attacking fluoride species in this mechanism is unclear. The second mechanism proposes partial oxidation and dissolution of Si(II) as the transient species SiF_2 , which immediately disproportionates to form SiF_6^{2-} and deposit Si on the pore walls.⁵⁸ Although we are aware of no direct evidence for the existence of SiF₂ in solution, its importance in at least a side reaction during porous Si formation is indirectly supported by the observation of amorphous Si deposited on pore walls.58 Again, the nature of the fluoride species involved in this mechanism is unclear. Strong experimental support exists for neither of the mechanisms discussed.

A more thoroughly studied, related system is dissolution of SiO_2 in aqueous HF, which has attracted attention in part to enable prediction of the time at which dissolution is complete. This may allow prevention of metal deposition onto the bare Si surface during aque-



Figure 5. Reaction rate in 10^{-4} M KAu(CN)₂ as a function of calculated ionic strength.

ous processing. Even for the case of SiO₂ dissolution into aqueous HF, where Si does not change oxidation state, Raman spectroscopy of the solution phase products yields twenty observable transitions, suggesting several parallel reaction pathways.⁵⁹ The species H⁺, HF, and HF_2^- have all been proposed to be mechanistically important, so kinetic models containing various combinations of these three species can be found in the literature, 59,67 as summarized in recent reviews.^{68,69} However, the general consensus is that HF_2^- is more active than HF toward SiO2 dissolution.59,60,64,66,68

Conclusions

The current results demonstrate that SHG can be a useful probe of nucleation and cluster growth of metals on insulating and semiconducting substrates. Both the present SHG measurements and past AFM studies indicate that growth of Au nanoclusters deposited from aqueous HF onto Si is kinetically limited by a surface process involving fluoride species. Kinetic analysis of the SHG results indicates that HF rather than HF_2^- is the active species, with an apparent reaction order of 1/2. However, the present RBS measurements suggest that Au(I) deposition is kinetically limited by diffusion. This apparent contradiction can be reconciled by proposing that Au deposition is a two-step process, with initial diffusion-limited deposition of the intermediate species AuCN, followed by surface-limited reduction of this species.

The present results also illustrate the utility of surface SHG for difficult solid-liquid interfacial systems. Due to the aggressive nature of HF, in situ scanning microscopy will be very challenging in this system. On the other hand, due to the rapidity of interdiffusion and the potential formation of metastable structures, ex situ methods may not probe this system effectively. For example, the RBS measurements provide evidence for diffusion of Au up to 1 µm below the surface over an extended time period.

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