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Low energy alkali ion scattering investigation of Au nanoclusters grown on silicon oxide surfaces

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ABSTRACT

The atomic and electronic structures of Au nanostructures grown by deposition onto various silicon oxide surfaces were probed with low energy alkali ion scattering. Charge state-resolved time-of-flight spectra of scattered 2 keV $^{39}K^+$ ions were collected from Au deposited onto an untreated Si wafer with a native oxide, a thermally grown oxide surface, and atomically-clean Si(111). It is shown that nanoclusters form on both oxides, but not on the clean Si. A quantitative analysis of the ion scattering spectra indicates that the nanoclusters are initially flat, two-dimensional structures that start to develop a second layer at about 0.5 Å of deposited Au and then form three-dimensional islands. The neutral fraction of scattered 2 keV $^{39}K^+$ ions decreases with deposition indicating changes in the quantum state occupancy with cluster size. The shapes of the clusters differ on the native and thermal oxides, leading to shape-dependent neutralization.

1. Introduction

It is well known that the behavior of gold (Au) at the nanoscale is distinct from its normal properties as a noble metal. Most significant is that while gold metal is chemically inert, certain size Au nanoparticles resident on an oxide support show very large catalytic activity [1]. The activity of the nanoparticles depends on their size and the particular material employed as a support.

One of the most common methods for the growth of nanoclusters on surfaces is via direct deposition of a metal onto a dissimilar substrate, such as an oxide [2]. If the surface energy of the metal (plus the interface) is greater than that of the oxide, clusters will form when the metal atoms are deposited. It has been observed that the clusters often nucleate at defect sites on the surface, such as point defects (oxygen vacancies) or line defects (antiphase domain boundaries) [3–7], such that the size and shape distribution of the clusters depends on the initial defect density of the substrate. Although much is known about this growth process, there are still open questions concerning the evolution of cluster size and shape, the role of the substrate oxide, the formation of states that display quantum size behavior and the relationship between these.

In this paper, we probe the growth of Au nanoclusters formed by deposition onto silicon oxide substrates, as well as Au deposited onto clean Si. Low energy ion scattering (LEIS), employing potassium (K) alkali ions as the projectiles, is used to monitor the atomic and electronic structures of the clusters as they form. In an earlier paper, we concentrated on the differences between Li^+ and K^+ ion scattering from Au clusters grown onto a single type of silicon oxide surface [8]. Although the present paper uses only K^+ ion scattering, it complements the earlier work by including additional materials and by using numerical simulations to aid in the data interpretation, thereby eliciting a more detailed understanding. Here, Au is deposited onto a native silicon oxide, a thermally grown SiO_2 overlayer and clean Si. The shape of the scattered ion spectra is sensitive to the atomic structure of the Au nanoclusters, while charge exchange during scattering provides a measure of the quantum size behavior of the nanomaterial [9–12]. The clusters evolve from single layer to multilayer structures during growth, they are negatively charged while adsorbed atop the oxide layer, and they display quantum effects as their size changes.

2. Experimental procedure and simulations

The sample preparation and subsequent measurements were carried out in an ultra-high vacuum (UHV) chamber with a base pressure of 5×10^{-11} Torr. This system has a load lock so that new samples can be inserted without breaking vacuum in the main analysis chamber. Prior to Au deposition, Si(111) substrates were prepared *in situ* in three different ways. First, a surface covered with a native oxide, which is denoted here as SiO_x, was prepared by heating the wafers at 475 K for 20–30 min to desorb water and hydrocarbons. This outgassing step does not remove the native oxide layer, but instead leaves the surface covered with suboxides. Following outgassing, the surface was exposed to 1×10^{-6} Torr of water vapor for 32 s (32 L) to hydrogenate the wafer in a controlled fashion. Second, a

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thermally grown SiO_2 overlayer was prepared by annealing a Si(111) wafer at 973 K with an e-beam heater under 1×10^{-5} Torr of dry O_2. Annealing times of 10 and 25 min yield oxide thicknesses of 3.7 Å and 9.3 Å, respectively [13]. Third, a clean Si(111)-7×7 wafer was prepared by heating in vacuum to remove the native oxide via the following recipe from the literature [14]. The samples were first heated to 900–950 K overnight to outgas, and then annealed at 1420–1450 K for 30–60 s to remove the native oxide, cooled quickly to 1000–1100 K, held at that temperature for 120 s, and finally cooled down to 300 K at a rate of ~2 K/s.

Au was deposited from an evaporator that consisted of Au wire (Johnson Matthey, 99.998%) wrapped around a W filament (Mathis). The Au was deposited at a rate of ~4 Å/min, as calibrated with a quartz crystal microbalance. The presence of Au and the absence of other contaminants were verified with Auger electron spectroscopy using a cylindrical mirror analyzer (CMA).

Time-of-flight (TOF) was used to collect charge state-resolved energy spectra for scattered 2 keV $^{39}K^+$ ions [15]. K ions were produced from a thermionic emitter source (Kimball Physics). The ion beam was deflected across a 1 mm^2 aperture to produce 120 ns pulses at a rate of 80 kHz. The incident beam was incident at 45° from the surface normal, while the sample normal was aimed directly towards a microchannel-plate (MCP) detector mounted at the end of a 0.635-m-long flight tube, yielding a scattering angle of 135° with respect to incident trajectory. For some measurements, the sample was rotated away from this orientation, but the scattering angle remains fixed. Ions and neutrals scattered at 135° were collected after traveling through the flight tube, which contains a pair of stainless steel deflection plates. The deflection plates were grounded to collect 'total yield' spectra, while 300 V was placed between the plates to remove the scattered ions and collect the 'neutrals only' spectra.

Ion scattering simulations were performed using the Kalypso software package [16]. All the simulations were of 2.0 keV ^{39}K scattering either from isolated groups of Au atoms or from layers of Au atoms that are arranged in the form of a Au(111) single crystal. The targets were considered to be at 300 K with suitable lattice vibrations included in the simulations. The scattering parameters matched our experimental setup: incoming projectiles were incident at 45° from the surface normal and scattered projectiles were collected within an acceptance angle of ±5° from the normal. To simulate the random nature of the polycrystalline Au clusters, the impact points were randomly assigned in the 0–60° range between two extreme projectile azimuthal angles of the Au(111) target, which includes all unique incident angles. To increase the calculation speed, interactions between target Au atoms were ignored so that the simulation only computed K–Au interactions.

3. Results and discussion

3.1. Atomic structure

Fig. 1 shows characteristic TOF 'total yield' spectra for 2 keV $^{39}K^+$ scattered from two different coverages of Au grown on SiO_x. The sharp, intense peak dominating each of the spectra is due to quasi-single scattering (SS), which refers to a $^{39}K^+$ particle that suffered a single binary collision with a surface Au atom. The spectra are displayed with respect to the scattered kinetic energies, which were converted from the flight time by assuming that the energy losses leading to SS were purely elastic. A large scattering angle insures that a large fraction of the backscattered projectiles have singly scattered [17]. The SS peak is the only feature present in the low deposition (0.17 Å) spectrum. The shoulders in the 2.74 Å spectrum are due to impinging ions that suffered multiple scattering (MS) and plural scattering (PS) from Au atoms. In PS, as suggested by the name, the ion experiences two or more in-plane collisions, which results in a higher scattered energy then with SS. In MS, the ion loses additional energy as it scatters from two or more atoms along a path that is out of plane. The PS and MS trajectories require that there be a collection of Au atoms in proximity to each other. Note that all of the K^+ scattering spectra are free of any features that are not related to scattering from Au. Since K is heavier then the substrate material (Si and O), any projectiles that interact with the substrate atoms would be scattered in the forward direction and become embedded in the material. In this manner, the substrate can be considered to be invisible to the scattered ion beam.

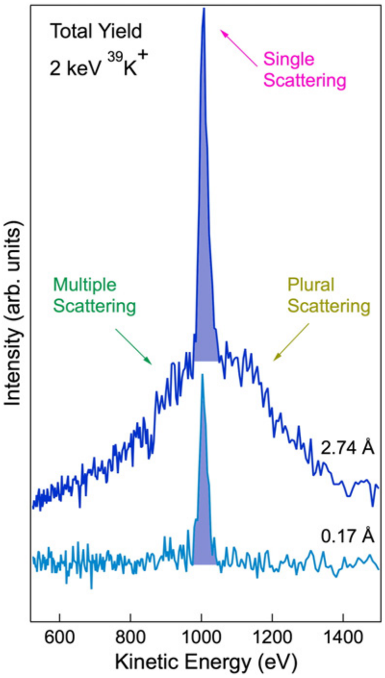

Fig. 1. Time-of-flight spectra of the 'total yield' collected at a 135° scattering angle for normally incident 2 keV $^{39}K^+$ scattered from 0.17 Å and 2.74 Å of Au deposited on SiO_x. Note that the measured flight times were converted to kinetic energy for the abscissa.

To illustrate how the spectra evolve with Au coverage on SiO_x, Fig. 2 shows 'total yield' TOF spectra collected following a range of depositions. The emergence of the MS and PS features is clearly seen as more Au is deposited. The MS and PS features begin to appear at around 0.49 Å of Au, as indicated in the figure with an arrow. After a deposition of 0.87 Å is reached, the intensities of the MS and PS features relative to the SS feature have saturated.

Au grown onto SiO_2 is likely to deposit in a different manner, as the details of the growth depend on the structure at the surface. Fig. 3 shows 'total yield' spectra for 2.0 keV $^{39}K^+$ scattered from various Au depositions on a thermally grown oxide of 9.3 Å thickness. It is seen that the SS peak dominates the spectra collected following small depositions, while MS and PS features appear when the deposition exceeds 2 Å.

Deposition of Au onto Si(111)-7×7 should be very different from growth on oxides, as nanoclusters are not expected to form. Fig. 4 shows 'total yield' spectra of 2.0 keV $^{39}K^+$ scattered from Au deposited onto clean Si. Small depositions yield a SS peak, while depositions above ~0.4 Å show only a small intensity in the MS region. Note that PS features do not appear for deposition onto clean Si.

To perform quantitative analysis of these data, a background is first subtracted and the peaks are then integrated. The SS peaks in Fig. 1 are shaded to indicate how a typical background would be established and how the contributions from SS would be determined via integration. In monitoring the SS peak intensity as a function of growth, the 'total yield' spectra are employed, as these have better statistics than the 'neutrals only' spectra, and the integrals are normalized by the collection time and beam current. To determine a