

Alloy Formation of Supported Gold Nanoparticles at Their Transition from Clusters to Solids: Does Size Matter?

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Gold nanoclusters of a size approaching the molecular limit (< 3 nm) were prepared on Si substrates in order to study alloy formation on the nanometer scale. For this purpose, indium atoms are deposited on top of the gold particles at room temperature and the formation of AuIn_2 is studied by x-ray photoelectron spectroscopy *in situ*. It is observed that the alloy formation takes place independent of whether the particles electronically are in an insulating molecular or in a metallic state. Most important, however, closed packed full-shell clusters containing 55 Au atoms are found to exhibit an outstanding stability against alloying despite a large negative heat of formation of the bulk Au-In system. Thus, Au_{55} clusters may play a significant role in the design of nanoscaled devices where chemical inertness is of crucial importance.

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Isolated metal nanoclusters offering the prospect of being used as building blocks in the rapidly developing field of nanotechnology recently have attracted much interest. Presently, however, size-selected clusters are mostly elemental and restricted in diameter to below 2 nm if prepared with atomic precision [1,2]. Naturally, one would like to extend this class of materials to include compounds and alloys for free [3] as well as supported [4] clusters. In the latter case, a prominent recent example is FePt nanoparticles [5], which are candidates with a potential for ultrahigh density data storage applications due to their ferromagnetic behavior at room temperature as opposed to pure Fe clusters of the same size which are strongly fluctuating superparamagnets. Of similar importance are semiconductor quantum dots like CdSe nanocrystals offering attractive optical properties [6,7] or bimetallic core-shell particles leading to extraordinary catalytic behavior different from that of the pure shell metal [8].

Although alloy clusters are very attractive objects due to the extended variety of their properties, understanding the process of alloying for feature sizes approaching the molecular limit, central for the development of multicomponent nanoscaled devices, still remains a challenging task. On one hand, alloy formation has been predicted theoretically [9] and found experimentally [10] even for metals known to be immiscible in the bulk phase after reducing their particle size (critical size: 2–3 nm [9]). On the other hand, surface-segregated, core-shell nanoparticles could be produced in systems like Pd-Ag [8] which are known to be fully miscible in the bulk phase.

In the special case of Au nanoparticles (size > 3 nm) rapid alloying was found experimentally [11,12] and ex-

plained theoretically [13–15] as being due to surface melting even at room temperature in bimetallic systems with a large negative heat of mixing like Cu or Sn after vapor deposition onto Au nanoparticles kept at ambient temperature. In addition, alloying within a surface layer of 3–4 nm has been reported during the deposition of In atoms on top of Au films even at cryogenic temperatures [16,17]. Assuming a similar reaction depth for Au nanoparticles as for Au films, one expects a complete intermixing and alloy formation for particle sizes below 3 nm.

Such an expectation, however, neglects all changes in the electronic density of states induced by the electron confinement. In the size range studied here (0.8–2.9 nm), quantum size effects lead to a transition from a “bulklike” (metallic) to a “molecular” (insulating) behavior [18] when starting with larger clusters and progressing towards smaller ones. The diameter range where this transition is expected can be experimentally narrowed down to particle sizes between 1.4 nm (clusters containing 55 atoms) and about 1.2 nm (clusters containing 33 atoms), the former being electronically in a metallic state [19] while the latter were found in an insulating molecular state [20].

Here, we demonstrate that supported gold nanoparticles spanning the above critical diameter range can be transformed into AuIn_2 at room temperature by additional indium deposition independent of whether the particles electronically are in an insulating molecular or in a metallic state. Most important, however, closed packed full-shell clusters containing 55 Au atoms (Au_{55}) are found to exhibit an outstanding stability against alloying despite a large negative heat of formation in the bulk Au-In system.

In order to clarify the influence of electronic and/or geometrical effects, two types of Au nanoparticles were prepared on top of silicon substrates covered by a thin layer of natural silicon oxide. The first method is based on the self-assembly of the diblock copolymer poly(styrene)-block-poly(2-vinyl-pyridine) [21] forming reverse micelles within an apolar solvent like toluene. After loading the core of these micelles with HAuCl_4 , a monomeric layer can be obtained on top of the substrate by an optimized dip coating. In a subsequent step, the polymer matrix is removed by exposure to an oxygen plasma resulting in gold oxide particles, which then are reduced by a hydrogen plasma to elemental Au. The final result is an array of well-separated naked Au nanoparticles of rather uniform size and spherical shape showing a high degree of hexagonal order (for more details, see Refs. [22,23]).

An example of the quality of the nanoparticle ensemble prepared along the micellar route is given in Fig. 1 which displays a scanning electron microscopy (SEM) image of the final arrangement of naked 2.9 nm Au particles. Although not perfectly ordered, the particle array exhibits a high degree of hexagonal short range order. From non-contact atomic force microscopy (AFM) and transmission electron microscopy (TEM) images, Gaussian size distributions could be extracted with averages of 2.9 ± 0.5 nm, 1.6 ± 0.3 nm, and 1.3 ± 0.3 nm for the different micellar solutions used in the present study. In case of the very smallest Au particles (0.8 nm according to the quantity of Au salt added to the micellar solution), neither AFM nor TEM were able to allow a precise measurement of the particle diameter. In this case the particle size can be estimated from x-ray photoelectron spectroscopy (XPS) data (using a FISONS ESCALAB-210 electron spectrometer and monochromatized Al-K_α radiation) taking advantage of a final state effect induced by the photoemission process itself [24,25].

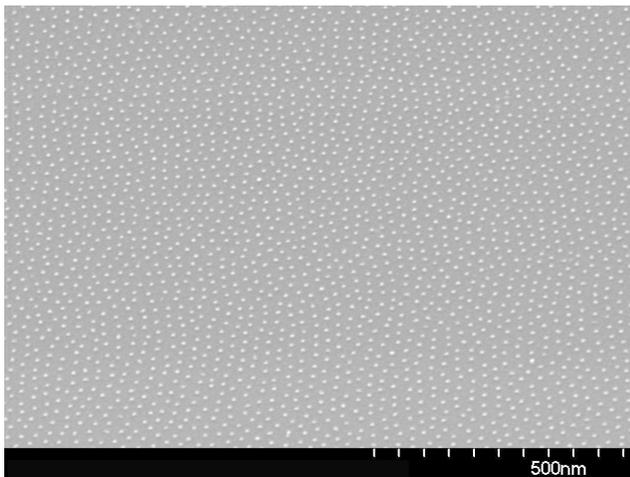


FIG. 1. SEM image (tilted view) of hexagonally arranged, well-separated Au nanoparticles prepared by a micellar method described in the text. Analysis of the size distribution by means of AFM and TEM yields an average diameter of 2.9 ± 0.5 nm.

In Fig. 2 the corresponding Au-4f spectra are presented as acquired for the different particles after their preparation right before the vapor deposition of In. Obviously, as compared to the position of bulk Au (dashed vertical line) there exists an increasing shift towards higher binding energies (corresponding to a decreasing kinetic energy of the outgoing photoelectrons) as the size of the nanoparticles is reduced. This loss in kinetic energy is a consequence of a temporal charging of the nanoparticle due to the photoionization process [24,25].

This phenomenon becomes more evident in Fig. 3 where the energy shifts as determined from Fig. 2 are summarized together with results reported in the literature for size-selected clusters [20,26]. Obviously, a $1/d$ behavior can be recognized as indicated by the solid curve justifying the modeling of the nanoparticles as extremely small spherical capacitors (see inset of Fig. 3). These capacitors are positively charged with one elemental charge during the escape of the photoelectron, thereby reducing its kinetic energy due to Coulomb interactions. Consequently, this model enables one to estimate their diameters from the corre-

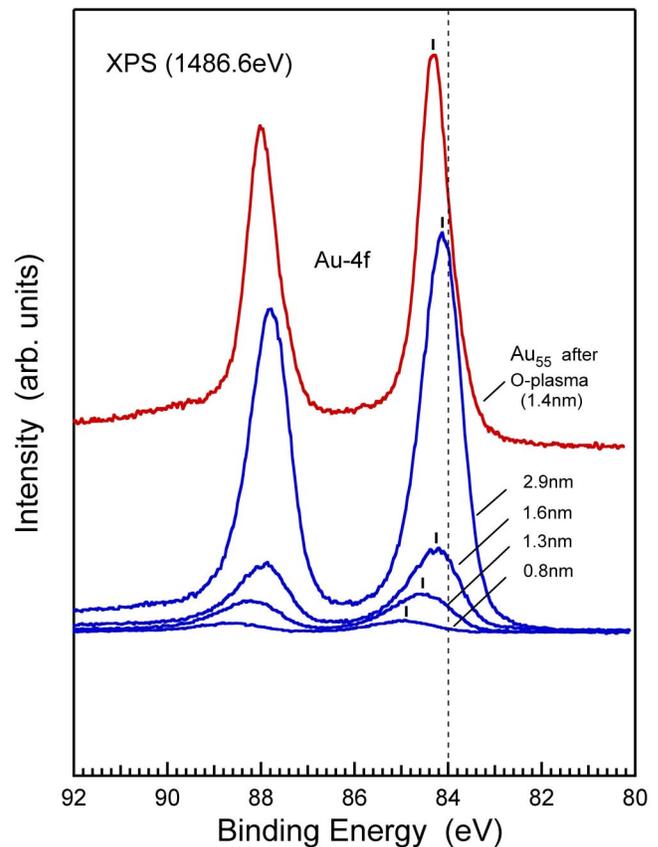


FIG. 2 (color online). Au-4f photoelectron spectra measured on atomically clean Au nanoparticles of different sizes prepared by a micellar technique. For comparison, results obtained from *in situ* cleaned Au_{55} clusters acquired after exposing the sample to an oxygen plasma in order to remove the organic ligands are added. The dashed vertical line indicates the corresponding line position of a bulk Au reference sample.

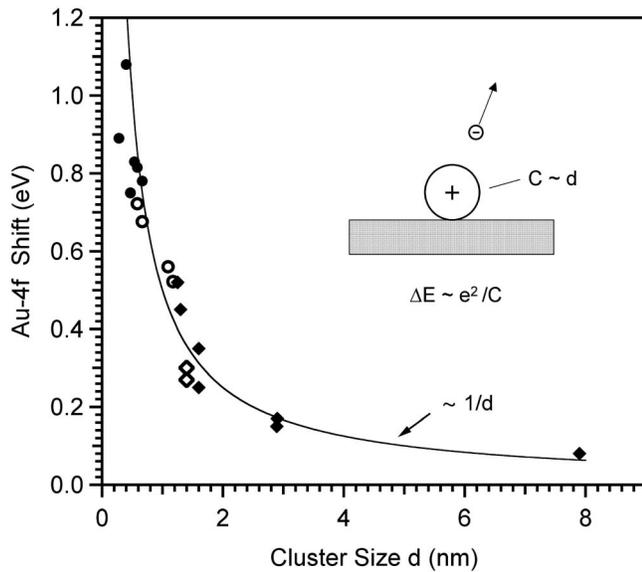


FIG. 3. Au-4*f* binding energy shift as measured on ensembles of isolated gold nanoparticles or clusters prepared by different techniques. Full squares: micellar method, Si/SiO₂ substrates; open squares: ligand-free Au₅₅ clusters on Si/SiO₂; open circles: size-selected clusters on amorphous carbon [20]; full circles: size-selected clusters on Si/SiO₂ [26]. The line represents a 1/*d* behavior serving as guide to the eye.

sponding energy shifts of the Au-4*f* spectra relative to the bulk value. In this way, from a shift of 0.85 eV as observed for the smallest Au particles studied in this work, a diameter of about 0.7–0.8 nm (corresponding to less than 10 Au atoms) can be extracted, confirming the size expected from the specific loading of the micellar cores with metal salt.

The Au dots prepared by the micellar technique were complemented by an ensemble of monodisperse Au₅₅ clusters (diameter 1.4 nm), each originally stabilized by a triphenyl-phosphane ligand shell [27]. Again, exposing a monolayer of these clusters to an oxygen plasma allowed one to completely remove all organic ligands. Thus, for the present study on possible size effects of alloy formation, well-defined Au nanoparticles were at hand with diameters ranging from 0.8 to 2.9 nm clearly extending previous work [11,12] to a size regime where quantum size effects in the electronic structure become dominant.

An answer as to the influence of the electronic state of the nanoparticles on alloy formation can be given by our main results presented in Fig. 4. Here, the measured Au-4*f* core-level spectra are displayed after evaporating 4 monolayers (ML) of In on top of the as-prepared isolated Au nanoparticles. Taking the Au-4*f*_{7/2} binding energy position of a gold film as a reference (cf. bottom reference spectrum and vertical solid line), it is immediately recognized that all Au nanoparticles independent of their size exhibit a common chemical shift upon reaction with In atoms by 0.9 eV towards higher binding energies (dashed vertical line) with the only exception being the Au₅₅ clusters. In their case, the line position is conserved despite the

coverage with In atoms (here a small amount of the chemically shifted component is neglected). Using the measured binding energy shift of 0.9 eV as a fingerprint for the resulting Au-In phase, all nanoparticles with the exception of Au₅₅ can then be identified as consisting of the intermetallic compound AuIn₂ (see topmost curve) with no traces of still nonreacted elemental Au.

This interpretation of the experimental results critically depends on the assumption that the Au-4*f* binding energy shifts measured after In deposition are no longer affected by final state charging effects but are solely due to a chemical shift reflecting a new ground state induced by alloying. This can be expected in case of a metallic coupling of the nanoparticles to the evaporated In film (which, in part, is consumed during alloying), thereby significantly increasing the capacitance leading to a vanishing charging related energy loss during photoemission. Such a behavior can directly be seen in case of the nonreacting Au₅₅ clusters which, prior to In evaporation, exhibit a final state shift of 0.25–0.3 eV, which, however, is completely reduced

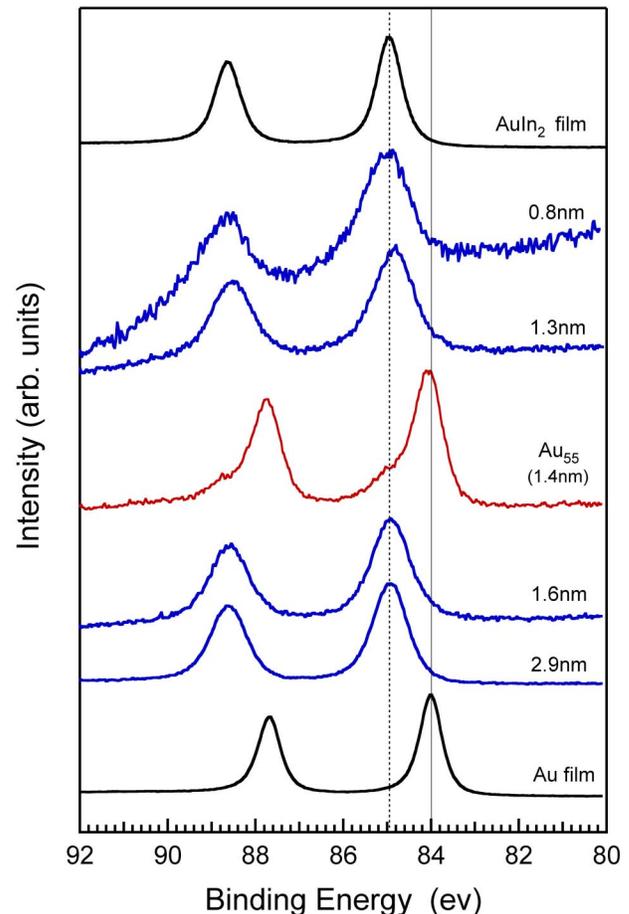


FIG. 4 (color online). Au-4*f* photoelectron spectra as obtained after vapor deposition of 4 ML indium under UHV conditions at ambient temperature on top of Au nanoparticles of different size. Clear evidence is provided for the formation of the intermetallic compound AuIn₂ for all particle sizes with the only exception of Au₅₅ (1.4 nm).

after In deposition. Similarly, a reduced final state shift towards the bulk Au position is expected for all nanoparticles when covering them with an additional 4 ML of In, thereby increasing exclusively their size without forming an alloy. In contrast to this assumption, however, experimentally energy shifts are observed only towards higher binding energies (even in the case of the smallest nanoparticles a shift from 0.85 eV towards 0.90 eV is found). Thus, we can safely assume that the room temperature deposition of In leads to a chemical shift due to an alloy formation, while final state charging effects are suppressed by an electrical contact between the small capacitors and the evaporated film. This metallic contact, on the other hand, prevents one from estimating the size of the alloyed nanoparticles (by means of XPS) which is obviously an important parameter for various nanoparticle applications. Therefore, further work will be necessary to clarify this point.

Based on these arguments, one concludes that alloying into AuIn₂ is obtained for all particle ensembles except for Au₅₅. The extraordinary stability of the latter is further corroborated by the observation that coalescence between Au₅₅ clusters obtained by using multilayers rather than a monolayer prior to the plasma-induced removal of the ligands, immediately results in a significant contribution of the chemically shifted component at 84.9 eV in the spectrum.

Thus, one concludes that the size dependent electronic properties of the Au nanoparticles are not decisive of whether the alloy formation into AuIn₂ does occur: Despite the 0.8 nm Au clusters behaving molecularly prior to the indium deposition rather than metallicly as the particles above 1.6 nm do, they all react completely into AuIn₂; i.e., the quantum size effects in the electronic structure of the nanoclusters obviously do not play an important role. For applications in nanoscience this is promising news, since it opens the prospect of an *a posteriori* manipulation and tailoring of metallic nano-objects by their subsequent alloying. On the other hand, the present results underline the striking stability of the “magic-number” Au₅₅ clusters against alloy formation despite the existence of a large negative heat of mixing in the Au-In system acting as a strong driving force. Considering the above stated independence of the alloy formation to the detailed electronic properties of the reacting Au nanoparticles, this extraordinary stability must be exclusively related to the structural closing of the packing shell of these nano-objects. This, in turn, makes Au₅₅ clusters attractive as chemically inert building blocks for new nanoscaled devices. Thus, the present results concerning the alloy formation in metallic nanoparticles offer a new design tool for tailoring properties of nano-objects.

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