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## Communications

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### Size-Induced Metal to Semiconductor Transition in a Stabilized Gold Cluster Ensemble

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Organic ligand stabilized metal clusters are a unique composite system possessing nanometer scale domains in which a metal core is encapsulated by an insulating organic monolayer. The confinement of a group of neutral metal atoms in such a small domain confers electronic properties that may be intermediate between continuous metals and quantized molecular species depending on the actual size of the domain. The insulating monolayer encapsulant is a conductivity barrier through which facile electron tunneling and/or hopping occurs. As a composite, both domains can exert strong influences on the macroscopic electrical conductivity. The strengths of these influences depend on their intrinsic nature and dimensions of each domain. Such materials are postulated to have exciting prospects for applications in microelectronics and possibly molecular electronics.<sup>1</sup> Our interest is in the development of these materials as the responsive component in a microelectronic chemical vapor sensor. In preparing and characterizing several series of these materials with variable core sizes and ligand shell thicknesses, we have ob-

served a transition from a positive to a negative temperature coefficient of electrical conductivity for thin films of a homologous series of alkanethiol-stabilized gold clusters as described below and illustrated in Figures 1 and 2.

As a model system, alkanethiol-stabilized gold clusters have a chemistry that is very amenable to systematic variation in both size of the gold core and thickness of the ligand shell. They are easily dispersed to concentrations as high as 10 wt % in nonpolar organic solvents and can be manipulated and characterized as soluble organic compounds. Recently, a synthesis of elegant simplicity was reported for this system where a nanometer scale gold cluster derivatized with a monolayer of dodecanethiol is described.<sup>2</sup> In this two-phase system, gold chloride is dispersed by a phase-transfer agent in a toluene solution of the alkanethiol and is subsequently reduced by contact via rapid stirring with an aqueous sodium borohydride solution. As neutral gold particles nucleate and begin to grow, they are sequestered by a monolayer of the alkanethiol in a kinetically controlled fashion. Simple variation of the gold:alkanethiol stoichiometry generates a series of stabilized clusters with a large range in core size.<sup>3</sup> We have prepared such a series of dodecanethiol-stabilized gold clusters (see Table 1). As an abbreviated nomenclature for the normal alkanethiol-stabilized gold cluster we use the following general form: Au:C<sub>n</sub>(X:Y), where the subscript *n* denotes the number of carbon atoms in the alkane chain and (X:Y) denotes the gold:alkanethiol stoichiometric ratio used in the synthesis. As practical limits to desirable variations, a lower limit occurs where the electrical conductivity becomes very low and difficult to measure (e.g., X:Y = 1:3 for the dodecanethiol system)

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Table 1. Characterization of the Au:C<sub>12</sub>(X:Y) Cluster Series

(X:Y) <sup>a</sup>	(1:3)	(1:1)	(3:1)	(4:1)	(5:1)	(8:1)
$W_{Au}$ <sup>b</sup>	0.7195	0.7549	0.7957	0.8427	0.8709	0.8947
$R_{Core}$ (nm) <sup>c</sup>	0.86	1.14	1.56	2.29	2.97	3.61
Au atoms/core <sup>d</sup>	155	360	922	2920	6370	11 400
$\sigma_{200C}$ ( $\Omega$ cm) <sup>-1 e</sup>	$2 \times 10^{-9}$	$1 \times 10^{-8}$	$5 \times 10^{-8}$	$2 \times 10^{-7}$	$1 \times 10^{-6}$	$3 \times 10^{-6}$

<sup>a</sup> Gold:thiol stoichiometry employed in cluster synthesis. <sup>b</sup> Weight fraction of gold in cluster from TGA measurement. <sup>c</sup> Radius of gold core in cluster calculated from  $W_{Au}$  using eq 7 of ref 4. This represents an average with a dispersity ranging from 10 to 50% as indicated by measurements of refs 2, 3, 4, and 14 on the Au:C<sub>12</sub>(1:1) cluster. <sup>d</sup> Number of gold atoms in the cluster core calculated from  $R_{Core}$  and the 58.0 atoms/nm<sup>3</sup> atom density of bulk gold. <sup>e</sup> dc electrical conductivity of the cluster film from the interdigital microelectrode measurement.

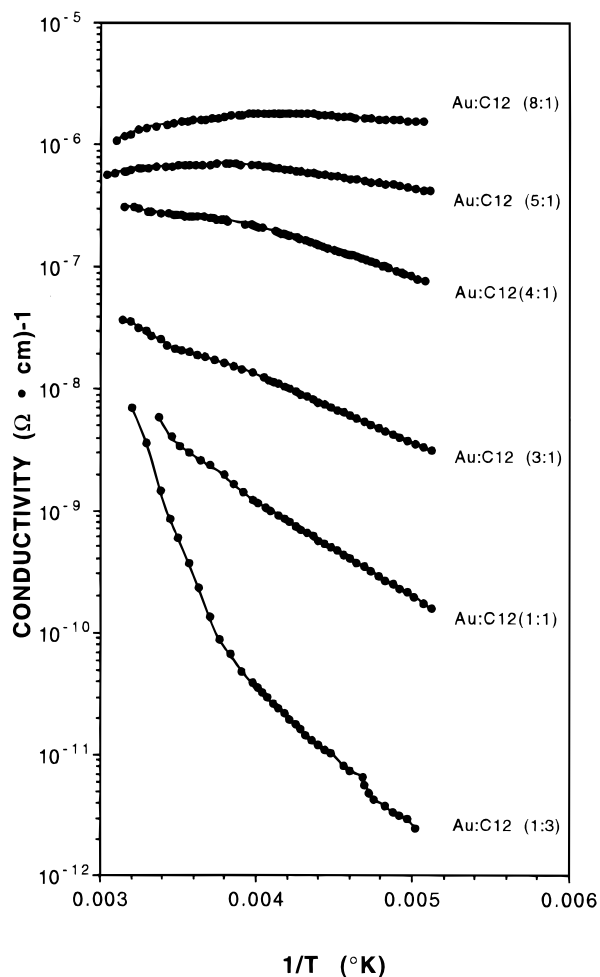


Figure 1. Arrhenius plot of the Au:C<sub>12</sub>(X:Y) thin films' conductivity dependence on temperature.

and an upper limit occurs where the core approaches a size too large for the shell to solubilize (e.g., X:Y = 8:1 for the dodecanethiol system).

Thorough characterization of the Au:C<sub>12</sub>(1:1) cluster size has been reported along with a very useful spherical model relating the core size to the alkanethiol coverage.<sup>4</sup> For this particular cluster, the core has a radius of 1.1 nm, and two of three gold surface atoms (assuming a hexagonal closest packed arrangement) are functionalized with a chemically bonded alkylthiolate. We have employed this model with our thermogravimetric analysis (TGA) measurements to calculate the core radii for the other members of the Au:C<sub>12</sub>(X:Y) series. The results are presented in Table 1.

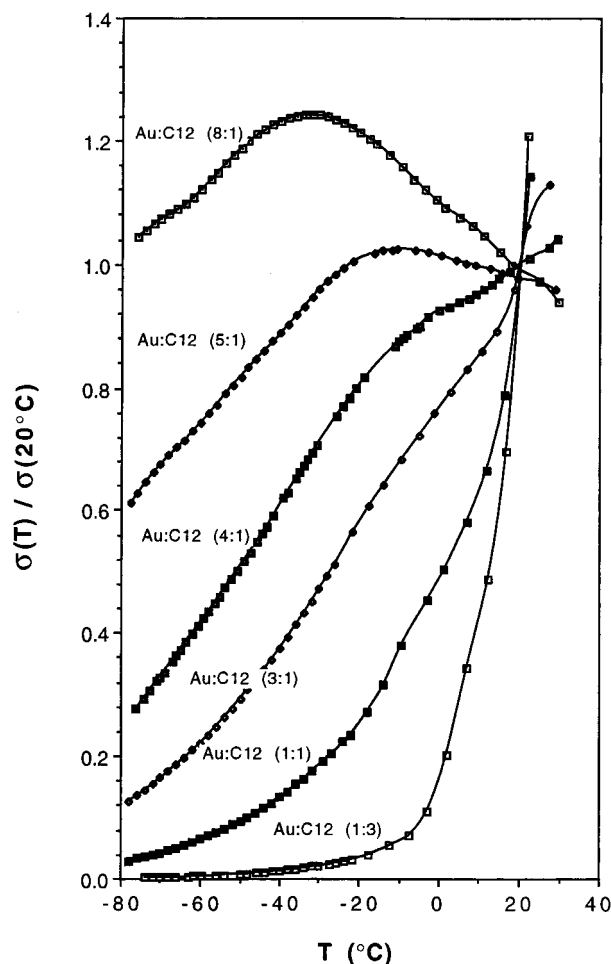


Figure 2. Linear scale conductivity-temperature plot of the Au:C<sub>12</sub>(X:Y) thin films where each individual cluster is normalized to its value at 20 °C.

Direct current conductivity measurements were made on films approximately 0.4 μm thick deposited on an interdigital microelectrode<sup>5</sup> (see Table 1). There is a regular increase in the conductivity with increasing gold core size. The conductivity dependence on deposition thickness is nearly linear over a 0.03–0.7 μm range, and Ohm's Law is followed over a ±2 V range. The temperature dependence of the conductivity is presented in Figures 1 and 2. The Arrhenius plot shows the magnitudes to which the gold core size and temperature variation affect the level of conductivity. The data for

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(5) The interdigital electrode (MSI P/N 302 device, Microsensor Systems Inc.) is an electrode array consisting of 50 finger pairs ( $n$ ) with the following dimensions: spacing ( $d$ ), 15 μm; finger width, 15 μm; overlap length ( $L$ ), 4800 μm; electrode thickness, 1500 Å. For an electrode of this geometry the conductivity of a film deposited on it is related to the film thickness ( $h$ ), current ( $I$ ), and voltage ( $V$ ) as follows:<sup>6, 7</sup>  $\sigma = [d/((2n - 1)L)][I/h][V/I]$ . This electrode geometry is designed

the Au:C<sub>12</sub>(1:1) member of the series are very close to being linear in this plot, and its slope yields an activation energy of 15.8 kJ/mol, which is in good agreement with the 16 kJ/mol reported for this cluster.<sup>4</sup> However, for the cluster series the nature of the conductivity temperature dependence is not well represented by the Arrhenius plot.

Figure 2 presents a simple linear scale conductivity vs temperature plot where the conductivity of each cluster deposition is normalized to its value at 20 °C. This causes a common crossover point at 20 °C and, as a practical point, illustrates susceptibility to thermal fluctuations at room temperature. If it is assumed that the dodecanethiol ligand shell thickness does not vary from member to member of this series, then the systematic variation in gold core size displays a most interesting effect on the temperature dependence of the electrical conductivity. At temperatures from 0 to 20 °C this effect progresses from a thermally activated semiconductor type dependence to a thermally deactivated metallic type dependence as the core size increases. Looking at the entire temperature range of these data, it is apparent that this transition emerges as a maximum at progressively lower temperatures for clusters with larger core sizes.

As mentioned above, there is a distinct dependence of the dc conductivity on the metal core size in the gold cluster film. Further, there appear to be at least two processes, one thermally activating the other thermally deactivating, influencing the conductivity of this series of composite ensembles. Two mechanisms are conceivable as relating to the core size effect. First is a "size-induced metal-insulator transition" which relates to the effect on core conductivity as the core size shrinks to the domain of the de Broglie wavelength, the decrease in conductivity being approximately in proportion to the third power of the particle diameter.<sup>9</sup> While we do not observe a slope corresponding to the third-power dependence in a log-log plot of the core radius-conductivity data in Table 1, the trend of a decreasing conductivity with core size is certainly there. The

for measurement on thin films the thickness of which should not greatly exceed that of the electrode (i.e., not greater than a factor of 10) since the electric field rapidly diminishes at distances greater than this factor above the plane of the electrode. This analysis will be presented in detail in a future publication.<sup>8</sup>

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second mechanism has to do with the effect of the core size on the charging energy barrier to tunneling. It has been shown by low frequency ac measurements that an increase in gold cluster radius (0.72–10 nm) strongly diminishes this barrier (0.3–0.01 eV).<sup>10</sup> Thus, with increasing core size, the conductivity of the core becomes more metallic in nature while the tunneling through the ligand shell becomes more facile. These mechanisms would appear to be qualitatively consistent with the data in Table 1.

The conductivity temperature dependence (i.e., its departure from Arrhenius behavior) is quite unique in that previous studies of other gold cluster systems<sup>11–14</sup> have not displayed the behavior illustrated in Figure 2. At present the mechanism of this behavior is unclear, but we have reproduced this behavior when octanethiol and hexanethiol are substituted for dodecanethiol in the cluster synthesis. In addition to the metal core, the organic ligand shells could be the origin of this thermal effect. The ligand shell thickness manifests a very strong effect on electrical conductivity as a resistance barrier between contacting metal clusters. The effect of this barrier has been reported for ligand shell thicknesses corresponding to normal alkanethiol carbon chain lengths of 8, 12, and 16 where a dramatic conductivity decrease of two orders in magnitude for each tetramethylene increment in thiol chain length was observed.<sup>4</sup> We have found that these ligand shell thickness effects superimpose on the cluster core size effect described above, and we are currently completing a two-dimensional (i.e., core size and ligand shell thickness) property map with gold core radii ranging from 0.6 to 3.6 nm and alkanethiol chain lengths ranging from 4 to 16. This will be reported in detail soon.<sup>8</sup>

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