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Sintering of Alkanethiol-Capped Gold and Platinum Nanoclusters

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One of the unusual properties of metal nanoclusters is the size dependence of the melting temperature. Studies show that the melting temperature is a decreasing function of the cluster diameter, although the actual dependence is not known, due to the difficulties associated with the experimental measurements. We have synthesized narrow dispersity alkanethiol-functionalized Au and Pt nanoclusters in inverse micellar solutions and have measured the sintering temperatures of these films using a capacitance technique to determine the onset of film conductivity. Cluster sintering is accompanied by pronounced optical changes and a thermal signature that can be observed in differential thermal analysis. The large optical absorbance of nanocluster films makes laser sintering a practical method for the formation of metallization layers.

Introduction

It is known that metal nanoclusters exhibit size-dependent melting temperatures that are far below that of the bulk metal. The earliest measurements of the reduced melting temperature of metal nanoclusters were reported by Takagi¹ in 1954, using transmission electron microscopy (TEM). Later measurements of the melting temperature used selected area diffraction (SAD) from Au nanoclusters deposited on a holey carbon grid on a heated stage in an electron microscope.² They found that the melting temperature was reduced as much as 300 °C from bulk and depended on cluster size, with the smallest clusters melting at the lowest temperature. Experimental measurements for 1.0-20.0 nm diameter Au nanoclusters grown in an inert gas beam were later made using field emission from a single nanocluster, where a significant change in cluster shape was noted just below the melting transition.³ Several characteristics of the field emission, including the emission current, were used to follow the melting transition. These authors conclude that the melting point depression is largely due to the large internal stress from the large specific surface area and melting transitions as low as 40% of bulk were found for 2.0 nm nanoclusters. Interestingly, for nanoclusters smaller than 2.0 nm, the melting temperature did not decrease. Elegant experiments on 2.2 nm Na139 nanoclusters⁴ used the temperature dependence of the photofragmentation mass spectrum to determine that the melting temperature of these clusters is 28% lower than bulk sodium and the latent heat of fusion is reduced 46%. Finally, using a novel scanning nanocalorimetric study of Sn islands on a silicon nitride substrate, the melting temperature and enthalpy of the islands were determined as functions of island size.⁵ Melting point depressions of 31% were found for islands of 10 nm in diameter.

In this paper, we investigate the related phenomena of alkanethiol-coated metal nanocluster sintering. Sintering is accompanied by the onset of film conductivity, as well as changes in the optical absorbance and film mass. The nanoclusters we synthesize are capped with alkanethiols, and by changing the alkanethiol chain length, we demonstrate that cluster sintering is not driven by loss of the capping agent but instead can lead to the loss of the capping agent. Sintering temperatures near 200 °C are observed for both Au and Pt nanoclusters.

Experimental Section

Synthesis and Purification. The nanoclusters were synthesized in inverse micelles by directly dissolving the metal salt (hydrogen tetrachloroaurate(III) hydrate, hydrogen hexachloroplatinate(IV) hydrate, or sodium hexachloroplatinate(IV) hydrate) into an anhydrous solution of surfactant in a hydrocarbon solvent.^{6,7} Dissolution occured overnight with vigorous stirring in a light-shielded container. When appropriate, reduction was carried out under argon in a Vacuum Atmospheres glovebox. The molar ratio of reducing agent to metal salt was typically 4. The reacted solution was removed from the glovebox, and the clusters were stabilized by capping with an alkanethiol or other suitable agent at least 1 h after chemical reduction. The stabilized clusters were then purified by surfactant extraction or precipitation. Under appropriate conditions, essentially monodisperse clusters formed.

We used both nonionic and cationic surfactants to form inverse micelles. The nonionic surfactants had a polyether headgroup attached to a linear hydrocarbon tail. These surfactants were designated by the nomenclature C_iE_j where *i* was the number of CH_x units in the alkyl chain and *j* equaled the number of ether groups; e.g., $C_{12}E_5$ denotes penta(ethyleneglycol) mono-*n*-dodecyl ether. In the samples prepared for these studies, the surfactant concentration was 10.0 wt %, *i* = 12, and *j* was in the range of 4–8. The metal salt concentration was 0.01 M, and the reducing agent was lithium triethylborohydride (Super-Hydride). The ultrapure nonionic surfactants we used were obtained from Nikko Chemicals, Japan. The hydrocarbon solvent we used was usually pentane, chosen for its volatility, and after cluster synthesis and capping with dodecanethiol, the nonionic surfactant was extracted from these nano-

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Figure 1. TEM of 6.0 nm Au nanoclusters synthesized in nonionic inverse micelles.

cluster solutions with *n*-methylformamide (NMF), which effectively extracted the surfactant without emulsifying. After three NMF extractions to remove the surfactant and salts, a small amount of oil-solubilized NMF was extracted from the organic phase with deionized water, followed by an extraction with 0.1 mM NaOH to remove any excess thiol. This procedure resulted in highly purified nanocluster solutions. For example, thermal gravimetric analysis (TGA) of a Pt nanocluster solution after evaporation of the pentane solvent showed a weight loss of 12%, this probably solely due to the alkanethiol ligand. Figure 1 shows 6.0 nm Au nanoclusters prepared in this manner.

Synthesis and purification in cationic surfactants was carried out differently and was a variation of the method developed by Brust⁸ and further refined by Whetten.⁹ The cationic surfactant tetraoctylammonium bromide (TOAB) was dissolved in toluene to form a 0.24 M solution. The metal salt was dissolved directly into this solution to a concentration of 0.1 M. The alkanethiol was then added to the solution to a concentration of 0.1 M, and reduction was done on a lab bench with sodium borohydride in water. The nanocluster solutions were then purified by methanol precipitation. After methanol addition, the nanoclusters were centrifuged at 200 g for 30 min to form a pellet, the supernatant was decanted, and the pellet was resuspended in pentane. Au nanoclusters formed by this technique were ~2.0 nm diameter, as measured by high-resolution TEM (Figure 2).

Film Formation. A reasonably uniform film of alkanethiolcoated nanoclusters can be formed by spraying a nanocluster solution onto a heated glass slide with an airbrush powered by filtered nitrogen. Heating the slide to ~ 100 °C ensures that the solvent in the atomized droplets volatilizes quickly, creating a film free of ring-like drying instabilities. It is interesting that the color of a Au nanocluster film is purple, although the nanocluster dispersion is orange or red (depending on the cluster size). This color change is characteristic of cluster aggregation, but we find that the film can be easily redissolved with pentane to form an orange or red sol. A Pt film is brown in color and can also be readily redissolved. An optical micrograph of a film is shown in Figure 3.

Results and Discussion

Sintering Temperatures. The sintering temperatures of the nanocluster films were determined using a simple capacitance



Figure 2. HRTEM of 2.0 nm Au nanoclusters synthesized in cationic inverse micelles, with the alkanethiol capping agent present during reduction. Lattice fringes indicate single crystalline domain particles.



Figure 3. Optical micrograph of a sprayed Au nanocluster film at a magnification of $250 \times$.



Figure 4. Schematic of the capacitance technique used to measure the onset of film conductivity.

technique, that avoids having to make electrical contact to the film, to detect the onset of the film conductivity (Figure 4). The principal of this technique is simple: before sintering, the film conductivity is low, so the capacitance of the copper electrodes is low, due to the electric shielding employed (not shown). As the film sinters, the conducting layer creates a large capacitance by essentially "folding" the copper electrodes together. The capacitance measurements were made at 1.0 MHz, a thermocouple was placed between the glass slides to monitor the temperature, and a glass cover ensured a reasonably isothermal environment.

In these conductance studies, \sim 6.0 nm Au nanoclusters were used, synthesized in nonionic inverse micelles, and purified by extraction. Pt nanoclusters were \sim 4.0 nm in diameter and synthesized by the same technique.



Figure 5. Example of a sintered Au thin film at $250 \times$ magnification.

The sintering of Au nanocluster films is visually striking. After the films are gradually heated, the dull purple color of the nanocluster film suddenly changes to bright gold, with a concomitant change in the conductivity (the capacitance changes by several orders of magnitude). Experiments on Au nanoclusters prepared in nonionic surfactants indicate a sintering temperature close to 210 °C, which is much lower than the bulk melting temperature of 1064 °C. We find the formation of conducting films at such a low temperature remarkable, even though surface atom diffusion, not melting, drives sintering. Excessive heating of the film after sintering causes cracking and a significant loss of conductivity. An optical micrograph of a sintered Au film is shown in Figure 5.

Experiments on Pt nanoclusters coated with dodecanethiol give a sintering temperature of 190 °C, significantly lower than the bulk Pt melting temperature of 1772 °C. The sintering of the Pt nanocluster film is equally dramatic as the gold, with a sudden change from dull brown to metallic silver. At this point, it is not clear whether sintering is driven by alkanethiol desorption or vice versa.

Optical Properties. The above studies show that the optical signature of sintering is coincident with the onset of film conductivity, permitting the use of optical absorbance to monitor sintering. Sintering is a kinetic process, so the observed sintering temperature depends on the heating rate, calling into question the utility of the term "sintering temperature". Accordingly, we next conducted an optical absorbance study of the sintering of 6.0 nm Au nanoclusters at temperatures up to 180 °C, to determine how strongly the sintering rate depends on temperature.

The study of the optical properties of nanoclusters dates back to Faraday,¹⁰ who first observed the curious wine red color of a gold sol. This was later understood in a celebrated paper by Mie.¹¹ In fact, the color of a Au sol depends on the cluster size and the absorption resonance blue-shifting and broadening with decreasing size, causing a color shift from red to orange.¹² In contrast, a dried Au nanocluster film is purple, due to complex electromagnetic interactions in particle arrays¹² causing a red shift of the absorbance peak (Figure 6). Kreibig shows that the purple color is due to Au clusters being in close proximity, yet not touching. If the Au surfaces of the clusters come into contact, the optical absorbance spectrum changes dramatically.

An Au nanocluster film was annealed at temperatures from 100 to 180 °C. Appreciable sintering did not occur until annealing at 180 °C for 18 h, causing the large change in absorbance shown in Figure 6. The resultant gold film does not dissolve in pentane. Decreasing the temperature from 210 to 180 °C thus increases the sintering time by at least five orders of magnitude.



Figure 6. Changes in the optical absorbance during thin film formation and sintering. The optical absorbance of the Au solution is shown for comparison.



Figure 7. Example of laser sintering of an Au film. Magnification is $62.5 \times$.

The optical absorbance of the nanocluster films facilitates laser sintering at ambient temperatures. To demonstrate this, we exposed an Au film to an argon ion laser operating at a wavelength of 488 nm, which quickly sintered the clusters and created a Au wire. Dissolving the unexposed film with pentane leaves a conducting wire, such as in Figure 7. This wire is irregular because the glass substrate was merely held by hand, but this concept of direct writing wires is nonetheless demonstrated.

Thermal Analysis. TGA and single differential thermal analysis (SDTA) studies were conducted on the nanocluster films both to assess film alkanethiol content and to determine whether volatilization of the alkanethiol drives sintering. In the latter case, Au nanoclusters were capped with thiols of differing chain lengths, and thus differing volatilities, to determine if this results in significant shifts in the sintering temperature, and whether the loss of thiol is coincident with sintering.

To assess the alkanethiol content of the nanocluster solutions, we added consecutive aliquots to 70 μ L alumina crucibles, letting the solvent evaporate between additions until at least 5 mg of dried sample had accumulated. For the 2.0 nm Au samples purified by MeOH precipitation, the sample weight loss depended on the thiol used, ranging from 20.8% for octanethiol, 24.4% for decanethiol, 27.7% for dodecanethiol, to a maximum of 49.6% for tetradecanethiol. For the 4.0 nm Pt samples purified by extraction, weight losses as low as 12.8% were observed over the same temperature range.



Figure 8. TGA and SDTA measurements of 2.0 nm Au nanoclusters capped with octanethiol (top) and tetradecanethiol (bottom) show that sintering is not driven by volatilization of the capping agent. In the case of octanethiol, the reverse is true; the loss of surface area due to sintering causes the thiol to volatilize because its boiling temperature is below the sintering temperature.

A second issue is whether the loss of the organic capping layer drives cluster sintering, so that the observed sintering temperature is unrelated to the rate of surface atom diffusion on the nanoclusters. The TGA data and the SDTA data indicate that this is not the case. The SDTA data show the difference between the oven temperature and the sample temperature, and a peak is observed when the clusters sinter. In Figure 8, data are shown for Au nanoclusters capped with octanethiol and tetradecanethiol at a heating rate of 5 °C per minute. TGA data for the octanethiol sample show a very rapid weight loss that is associated with the 211.6 °C SDTA peak for this sample. Because this temperature is greater than the 199 °C boiling point of octanethiol, the sintering of the clusters must rapidly reduce the surface area for thiol binding, causing the unbound thiol to immediately volatilize. At the other extreme is the sintering behavior of Au nanoclusters capped with tetradecanethiol. The SDTA peak is at a slightly higher temperature, 221.4 °C, at which point the weight loss of thiol is very small, $\sim 3.0\%$. The sintering of the nanoclusters again reduces the available surface area for thiol binding, but the boiling point of tetradecane is very high, ~ 300 °C, so the liquid layer of thiol on the sintered Au surface volatilizes at higher temperature. Samples prepared with decanethiol and dodecanethiol show an intermediate behavior. We conclude that although the thiol capping agent can have a measurable impact on the sintering temperature, the volatilization of the capping agent does not drive sintering. Instead, sintering can drive the volatilization of the capping agent, due to the loss of Au surface area.



Figure 9. TGA and SDTA measurements of 6.0 nm Au nanoclusters capped with dodecanethiol show a weak thermal signature at 210 °C, due to the low specific surface area of these clusters.

The thermal signature we observe is the difference between the sample temperature and the reference temperature of the oven. During this sintering transition, this difference actually increases, which is contrary to what is normally expected in a melting transition. In fact, it is hard to understand how cluster melting could contribute to this thermal signature, unless the clusters could melt without sintering, and we have already observed sintering. Even if the individual clusters did melt, due to an anomalously low size-dependent melting temperature, the heat absorbed would be released again as the clusters coalesced to form larger clusters, which would solidify and release heat, due to the expected increase in melting temperature with cluster size. In fact, the contributions to this thermal signal are more complex nonequilibrium effects, involving the irreversible loss of surface area during sintering: Cluster superlattices simply are not at a thermodynamic ground state. The Au atoms near and at the surface are probably higher in energy than the interior atoms, so decreasing the surface area should reduce the average energy of an Au atom, liberating heat. There is a concomitant loss of binding sites for the alkanethiol, which should be an opposing thermal effect, but the clusters would simply not sinter if this binding energy was dominant. It is expected that this exotherm would be much smaller for the larger, 6.0 nm Au nanoclusters, which have only one-third of the specific surface area.

TGA and SDTA data taken at a heating rate of 5 °C/min are shown in Figure 9 for the 6.0 nm Au nanoclusters coated with dodecanethiol. The thermal signature is indeed much smaller and can be difficult to resolve. Although it is probably meaningless to attempt to quantify a weak signal with a poorly defined baseline, the temperature change is roughly one-sixth the magnitude of the signal for the 2.0 nm nanoclusters. It is expected that the surface atoms on the 2.0 nm clusters are on average higher in energy than those on the 6.0 nm clusters, due to the high percentage of edge sites on the former.

It is also noteworthy that for the 6.0 nm clusters the sintering peak occurs at 210 °C, which is indistinguishable from that of the 2.0 nm clusters. It seems to us strange that sintering does not exhibit a significant size dependence, but perhaps this suggests that it is the lability and surface mobility of the bound alkanethiol that determines the sintering temperature. Otherwise, the thiol is too strongly bound to permit the nanoclusters to contact each other on the time scale of the experiment. One could argue that a size dependence should occur, due to cluster surface curvature affecting the thiol binding energy, but this is not evident in these data.

Evidence for increased mobility of nanoclusters at elevated temperatures has been provided by Korgel et al.,13,14 who used low-angle X-ray diffraction to study the structure of superlattice films of dodecanethiol-stabilized 3.5 nm Ag clusters. A broadening and eventual loss of the superlattice peaks was observed near a correspondingly broad DSC transition at 180 °C. The loss of diffraction was attributed to melting of the superlattice with a premelting transition between 75 and 140 °C attributed to thiol desorption. It was not reported if this transition was reversible. In our experience, alkanethiols do not adhere as strongly to Ag nanoclusters as to Au or Pt, perhaps due to the formation of a surface oxide even under reasonably anaerobic conditions, so the relation of these observations to our experiments is uncertain. Under high vacuum, we have found that Ag superlattices are not stable to alkanethiol desorption even at ambient temperature, and this can lead to fusion or sintering of adjacent clusters, as observed by TEM. However, the results of Korgel et al. are at least consistent with the idea that at elevated temperature alkanethiol lability leads to cluster mobility that permits sintering. It is possible that the Ag nanocluster superlattices produced by Korgel et al. were free of surface oxide and had alkanethiol binding energies comparable to that of Au or Pt.

Conclusions

We have developed pure Au and Pt nanocluster films and have made measurements of the sintering temperature of these films by measuring the onset of film conductivity capacitively, through optical absorbance measurements, and through thermal analysis. These Au and Pt metal nanocluster films sinter at temperatures far below the bulk melting temperature of these metals and show pronounced optical changes. Laser annealing is also shown to be an effective method of sintering and could be a practical method of making interconnections on flexible polymeric media. Finally, it is shown that sintering is not driven by volatilization of the alkanethiol, since it is possible to sinter the films with little loss of thiol. Instead, thiol desorption can be driven by sintering.

Acknowledgment. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL8500. This work is supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (DOE).

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