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# Electron microscopy and optical properties of small gold and silver particles in glass

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Transmission electron micrographs of small gold and silver particles grown in glass show uniform particle size in a particular sample. The silhouettes of the particles are those expected for pure particles of f c c metals. From the particle sizes measured from the micrographs and the kinetics of particle growth, the diffusion coefficient of gold in the glass is calculated. This calculation allows particle sizes early in the growth process to be estimated. The optical absorption spectrum for particles containing about 100 atoms is shown.

## 1. Introduction

Theories of the electronic structure of metal atoms and of bulk metals are widely accepted and supported by many experimental results. However, the transition between these two states is less understood. The electronic structure of metal clusters containing less than about 100 atoms is important in catalysis and surface physics. Catalysts used in refining petroleum, the synthesis of chemicals, and control of automobile exhaust consist of small metal or alloy particles supported on alumina or silica matrices.

Theoretically, it is generally assumed that individual electronic energy levels of atoms move closer and closer together as the atoms agglomerate, merging into an electronic conduction band for bulk metals. There have been several different methods used to calculate the energy levels of small metallic particles [1–7].

Experimentally, it is difficult to prepare small metallic agglomerates that are of uniform size. Metal vapours and condensates containing pairs, triplets, and larger aggregates have been studied, but in the resulting spectra only a few lines resulting from atomic pairs have been positively identified. In most preparations of metallic particles the size distribution is so complex that it is difficult to assign spectral features to particles of a certain size.

Metallic particles of very uniform size can be grown in glass [8, 9]. The glass must contain a photosensitive nucleating agent such as cerium oxide; nucleation sites are formed by irradiating the glass with ultraviolet light or X-rays. Then the glass is heated to 400 to 600° C to grow the particles. No appreciable growth occurs during nucleation, and the number of particles remains constant during growth.

In previous work the sizes of small gold and silver particles were calculated from the rates of growth and the shift of the plasma absorption band, respectively [9, 10]. These calculations were somewhat uncertain, so in this study the particles were observed by transmission electron microscopy [11] to provide more accurate sizes. The calculated sizes of the silver particles in the earlier study were about right, but the gold particles were somewhat larger than estimated before. The more accurate sizes allow a better correlation between size and optical properties of the small particles.

The equilibrium shapes of small crystalline particles give information on the relative surface energies of their different crystal faces (lattice planes) [12]. Impurities and temperature of formation can influence these shapes strongly; again glass provides

an inert medium for protected growth of metallic particles.

## 2. Experimental methods

Gold and silver particles were grown in an glass of composition 71.5 wt% $SiO_2$, 23.5% $Na_2O$, 4% $Al_2O_3$, 1% ZnO, 0.02% $CeO_2$ and 0.01% gold or 0.002% silver. The glass was melted at 1400° C and then cooled rapidly to room temperature. Particles were nucleated by irradiation of the glass with ultraviolet light or a $^{60}Co$ $\gamma$-ray source, and grown by heating the glass at a constant temperature in the range 400 to 630° C. More experimental details are given in [9, 10].

Thin splinters of glass for observation in the electron microscope were stripped from freshly broken surfaces of the glass with cellulose acetate tape [11]. A thin carbon film was evaporated normally onto the tape, which was then cut into small pieces and mounted on the electron microscope grids. The cellulose acetate was washed away with acetone, and the glass fragments on the carbon film could then be examined in the microscope.

## 3. Experimental results

Transmission electron micrographs of particles of gold and silver grown in a glass containing gold or silver are shown in Figs. 1 to 8. The measured particle sizes and heat-treatments are given in Table I. The samples were heated for times long enough to precipitate completely the gold or silver in the glass; subsequent heating resulted in no further change in particle size. The heating temperature was changed during growth in samples G3 and G4, as noted in Table I. The samples received different radiation doses, which is the reason for different number densities of particles and, therefore, different particle sizes after growth was finished. In any one sample the particle size was very uniform; in most cases variations were hardly detectable on different micrographs. The final gold concentration was the same in all the gold samples, as judged from the optical absorption at 436 nm. At this wavelength there is no effect of particles size on optical absorption [9], at least for the sizes given in Table I, because the absorption results from band-to-band transitions, not from free-electron absorption. From chemical analysis, the total gold concentration in the glass was $1.4 \times 10^{-4}$ gm $cm^{-3}$; apparently all the gold precipitated in the particles, because use of this concentration value in the formula for optical absorption of particles gave optical constants in reasonable agreement with measured values for bulk gold [9, 10].

TABLE I Size of gold and silver particles and heat-treatment of glasses to grow them

| Sample | Growth temperature (° C) | Growth time (min) | Measured particle dimensions (Å) |
|---|---|---|---|
| Gold | | | |
| G1 | 530 | 2624 | 160 × 200 |
| G2 | 530 | 5341 | 500 × 580 |
| | | | 300 × 510 |
| G3 | 530 | 822 | 330, 440 |
| | plus 630 | 203 | |
| G4 | 430 | 1601 | 38 |
| | plus 480 | 1763 | |
| Silver | | | |
| S1 | 580 | 1269 | 160 |

The silhouettes of the particles in Figs. 1 to 5 agree well with those of Sundquist for particles of gold and other fcc metals [12]. From a pairwise-interaction model Sundquist deduced that fcc metals should have (1 1 1) and (1 0 0) facets with rounded edges. Although the particles are equiaxed, the silhouettes usually have different dimensions in different directions because of the faceting. Sundquist described theoretical and experimental evidence that impurities in the particles can sharpen the edges and corners; thus the shapes of the particles in Figs. 1 to 5 indicate that these particles are quite pure.

The gold particle in Fig. 6 has a different shape from the others and that predicted by Sundquist. The reason for this difference is uncertain.

From the final particle size, the concentration of gold precipated, and the kinetics of precipitation the diffusion coefficient of gold in the glass can be calculated, since the rate of precipitation is controlled by diffusion of gold [8, 13]. The equation for the diffusion-controlled growth of competing particles is:

$$\frac{3C\,Dt}{R_f^2\rho} = \frac{1}{2}\ln\frac{(W^{2/3}+W^{1/3}+1)}{(1-W^{1/3})^2} - \sqrt{3}\tan^{-1}\left(\frac{\sqrt{3}\,W^{1/3}}{2+W^{1/3}}\right) \quad (1)$$

where $C$ is the concentration of gold in the glass, $D$ is its diffusion coefficient, $W$ is the fraction of total precipitation at time $t$, $R_f$ is the final particle radius, and $\rho$ is the density of gold. For sample G1 the precipitation was half over after 258 min at 530° C. Then from Equation 1 and the gold con-

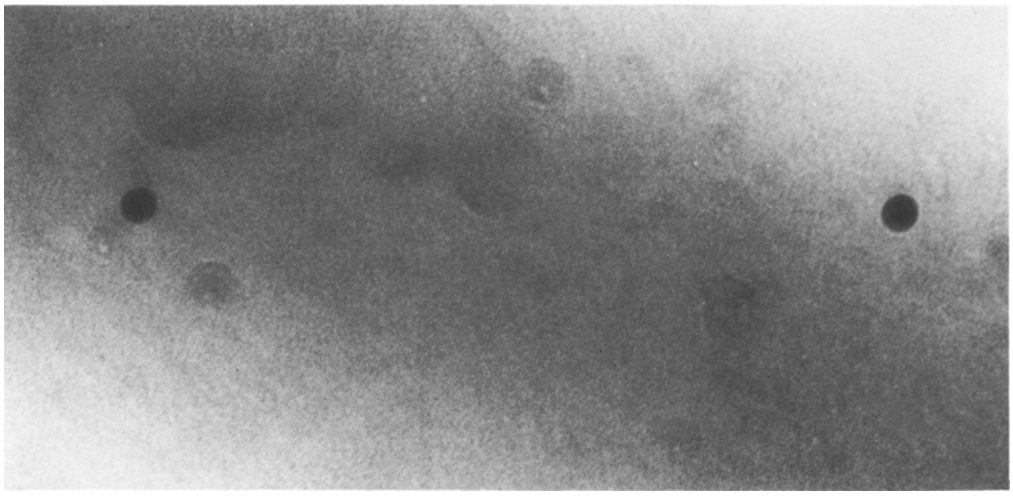

*Figure 1* TEM of gold particles in glass, treatment G1, × 255 000.

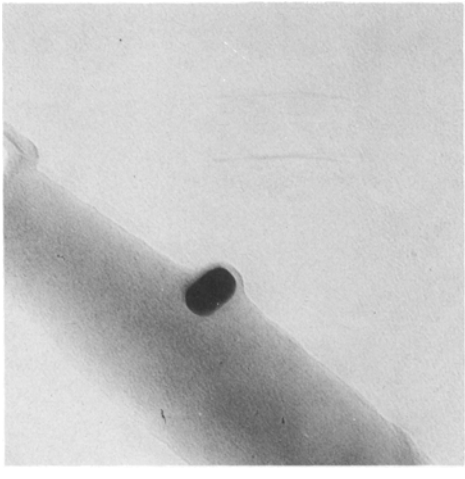

*Figure 4* TEM of gold particles in glass, treatment G2, ×138 000.

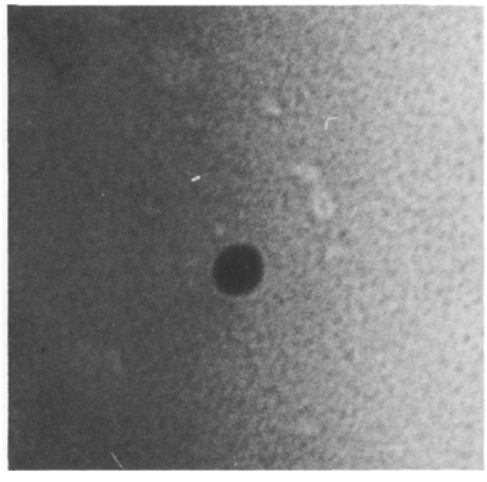

*Figure 2* TEM of a gold particle in glass, treatment G1, × 360 400.

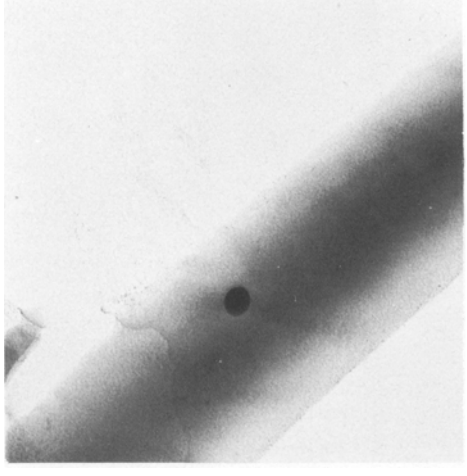

*Figure 3* TEM of a gold particle in glass, treatment G2, × 60 000.

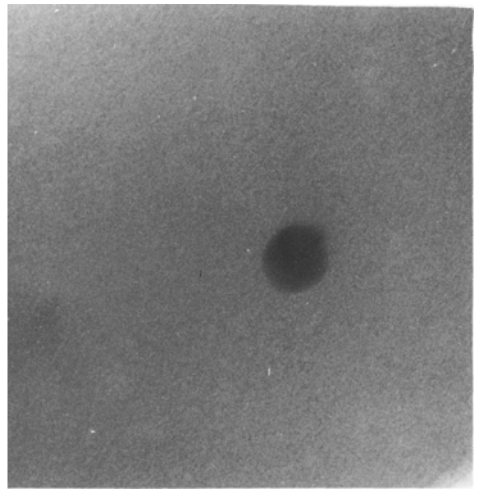

*Figure 5* TEM of a gold particle in glass, treatment G3, × 260 000.

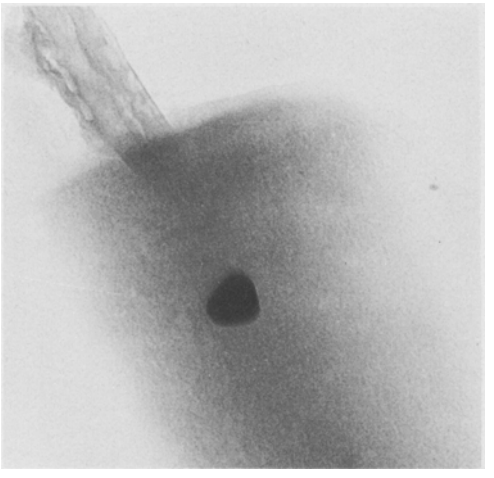

*Figure 6* TEM of a gold particle in glass, treatment G3, ×160 000.

centration given above, $D \approx 2.9 \times 10^{-12}$ cm$^2$ sec$^{-1}$. This result compares with that of $6.8 \times 10^{-13}$ cm$^2$ sec$^{-1}$ found by Maurer for a similar glass at the same temperature. Since Maurer's result was used to calculate particle radii in [9, 10] these radii are too small by about a factor of two as compared to the present measured results. For example, the data in Fig. 8 of [9] were claimed to show that the optical absorption at 436 nm was constant down to a particle containing only five atoms. In the light of the present results, this limit must be about forty atoms.

The silver particles in Fig. 8 are from sample B of Fig. 3, [10]. It was estimated that the particle radius at 80% of the final radius was about 50 Å; from the oresent results this value should be about 64 Å. The band width calculated from this latter

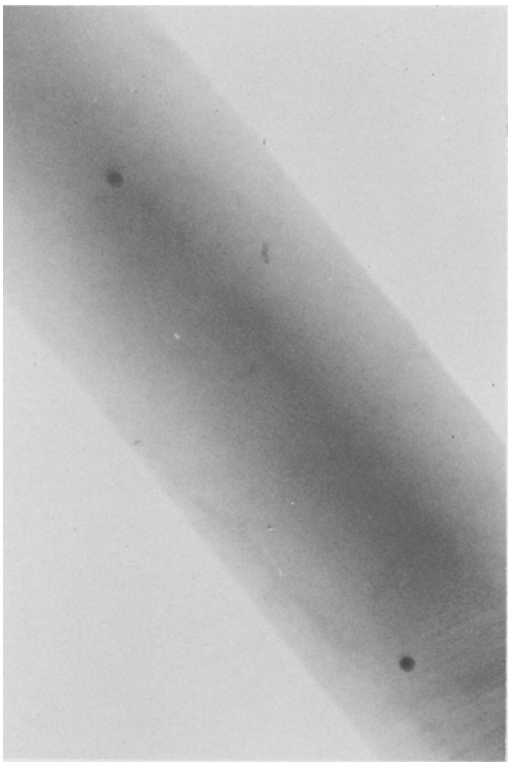

*Figure 8* TEM of silver particles in glass, treatment S1, ×112 500.

value is 176 Å, in good agreement with the experimental value of 187 Å.

Some additional work was done on very small particles to examine the optical spectrum as a function of particle size. A glass sample containing gold was heavily irradiated with ultraviolet light and the absorption of the sample measured as a function of annealing time at 430° C. During ir-

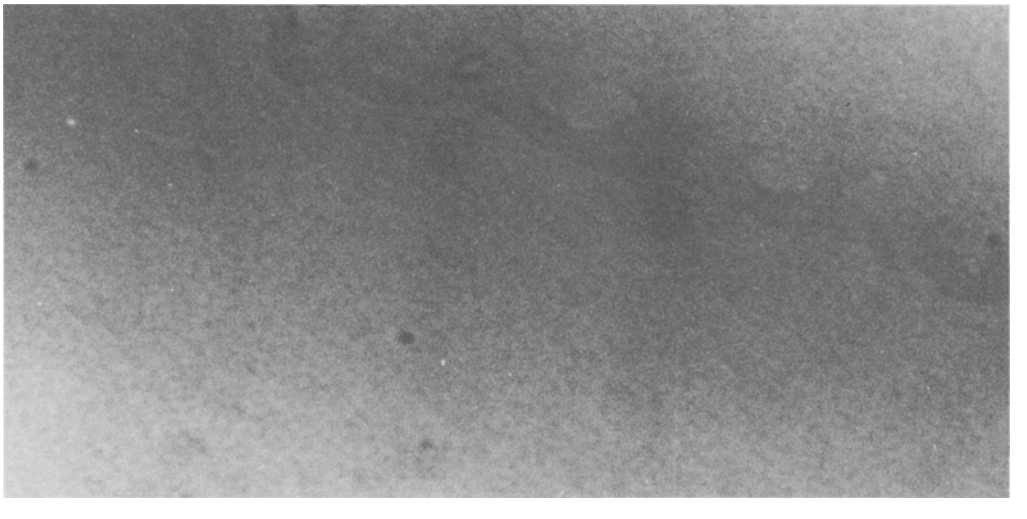

*Figure 7* TEM of gold particles in glass, treatment G4, × 458 000.

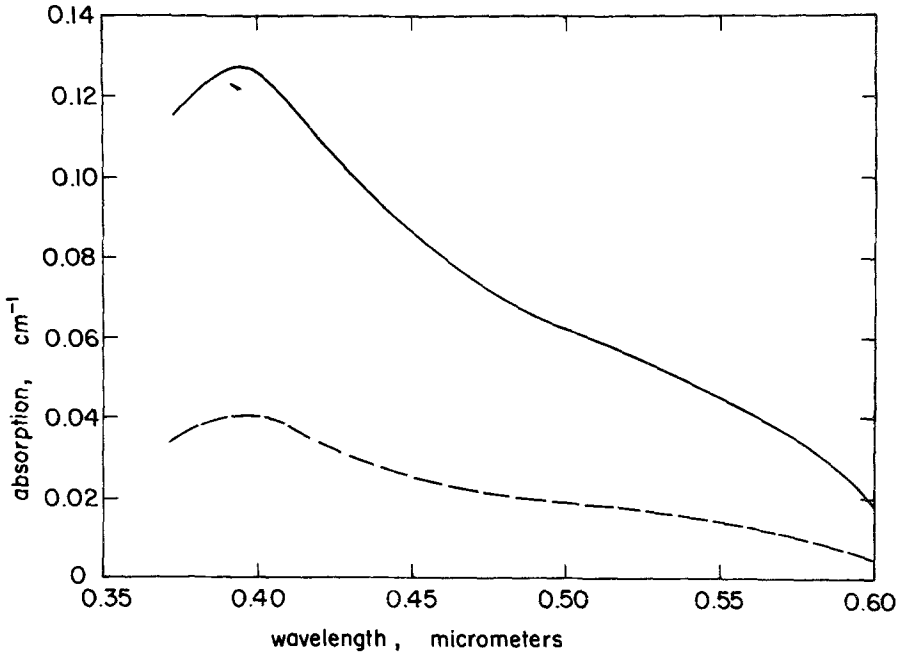


*Figure 9* Difference between spectrum of irradiated gold-containing glass 2.06 cm thick aged 10 min and after ageing 20 min (dashed line) and 32 min (solid line).

radiation the sample became hot enough to grow the clusters by a small amount, so it was difficult to estimate their size; from comparison with other samples aged at this temperature, it was estimated that the clusters contained between 50 and 100 atoms. The spectrum after ageing 10 min was taken as a background to eliminate reflection losses, changes during irradiation, and short-time annealing of damage. The difference between the spectrum at 10 min and those at 20 and 32 min of total ageing time are shown in Fig. 9. These spectra are believed to be characteristic of particles containing from 50 to 100 atoms. They show no lines or bands, and the absorption decreases at wavelengths longer than the normal absorption edge (about 0.48 $\mu$m) in the free-electron region, in contrast to the absorption band at 0.525 $\mu$m for larger particles.

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