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► **To cite this version:**

K. Mihama, N. Tanaka, A. Ichimiya. ELECTRON MICROSCOPIC OBSERVATIONS OF SMALL GOLD CLUSTERS. *Journal de Physique Colloques*, 1977, 38 (C2), pp.C2-197-C2-201. 10.1051/jphyscol:1977242 . jpa-00217082

HAL Id: jpa-00217082

<https://hal.science/jpa-00217082>

Submitted on 4 Feb 2008

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ELECTRON MICROSCOPIC OBSERVATIONS OF SMALL GOLD CLUSTERS

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Résumé. — Des particules d'or de 5 à 10 Å de diamètre, difficilement observables sur des supports de carbone, peuvent être nettement observées sur des supports en oxyde de béryllium. Une structure interne formée de quelques points peut être détectée sur l'image de ces petites particules. Chacun de ces points semble correspondre à l'image d'un unique atome d'or.

Abstract. — Gold particles of 5 ~ 10 Å in diameter, which are scarcely observed with carbon films, can clearly be observed with the beryllium oxide films. An internal structure consisting of a few dots can be detected in the image of such fine particles. Each of the dots corresponds possibly to the image of a single gold atom.

1. Introduction. — Observations of fine particles by using electron microscope have been carried out for a long time. One of the present authors (K. M.) [1] has studied the nucleation stage for the growth of films deposited in vacuum, in which the observation of particles less than 10 Å in diameter is required since the size of the critical nucleus is less than 10 Å. For particles larger than 10 Å in diameter, there is no essential difficulty to observe the particles with electron microscope by an ordinary technique. However, on the observation of particles less than 10 Å in diameter some problems arise to detect the particles in electron micrographs: A granular image composed of dots of a few Å in size observed as the noise of carbon supporting films disturbs the fine details of the particle images. Since the noise is characteristic of the amorphous structure, crystalline supporting media [2-4] have been tried, besides amorphous films of extremely thin thickness. Furthermore, tight fixation of particles on the supporting films turns out to be important for decreasing the effect of electron irradiation.

In the present paper, the development of the observation of extremely fine gold particles in our laboratory by using electron microscope is described. First, the results obtained by using carbon films as amorphous supporting films are mentioned. Next, the observation of gold particles by using molybdenite flakes [5] as crystalline supporting media is mentioned. Finally, the results obtained by using newly developed beryllium oxide films [6] as low noise specimen supporting films are described in some detail.

2. Experimentals. — Gold particles were prepared by the vacuum evaporation technique on cleaved surfaces of sodium chloride, the pressure being 10^{-5}

to 10^{-8} torr. Backing the particles by carbon films was carried out in an ordinary manner.

Molybdenite flakes used as crystalline supporting media were prepared by repeated cleaving by the aid of adhesive tape. For obtaining clean flakes, thermal etching of molybdenite flakes was carried out by keeping the flakes at around 500 °C in an atmosphere of 10 torr oxygen for a few minutes.

Beryllium oxide films used as the backing for the particles were prepared by the evaporation of ceramic beryllium oxide by an electron heating in an ultra high vacuum. Furthermore, the preparation of gold particles by simultaneous deposition of gold and beryllium oxide was also used.

The films with gold particles were separated from the substrates in distilled water and mounted on microgrids for electron microscopy. Microscopic observations were carried out by JEM 100B and JEM 100C electron microscopes operated at 100 kV. In the latter microscope, a specially designed objective pole piece [7] with $C_s = 0.7$ mm was used. In the present experiment, only bright field images were used.

3. Experimental results and discussion. — Figure 1 shows an electron micrograph of gold particles grown on cleaved surfaces of sodium chloride backed by a carbon film of about 30 Å thick. Even with the small thickness, particles less than 10 Å in diameter are hardly detected because of the granular image which appears as the noise of the carbon film. Since the noise image, whose details vary with the amount of defocus, is characteristic of the amorphous structure, the noise problem may not be solved as long as amorphous supporting films are used in transmission electron microscope.

Several attempts have been made to use crystal-

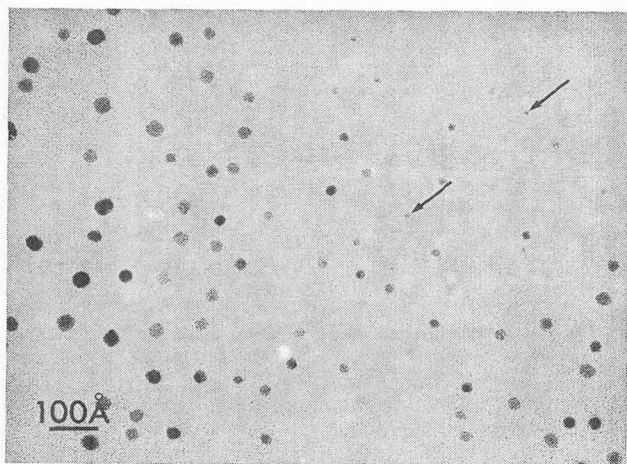


FIG. 1. — Gold particles backed by a carbon film of 30 Å thick.

line supporting media, such as beryllium plates [2] or graphite flakes [3, 4]. Molybdenite flakes prepared by repeated cleaving by the aid of adhesive tape were tried, but with this medium the noise due to the contamination on the surface could not be eliminated completely. However, thermal etching of molybdenite flakes brought about contamination free regions partly [5]. Figure 2 shows an electron

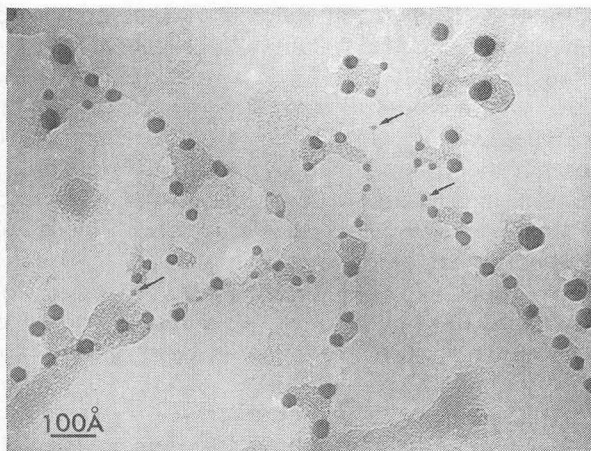


FIG. 2. — Gold particles grown on thermally etched molybdenite flakes.

micrograph of gold particles grown on molybdenite flakes thus treated. Gold particles of about 10 Å in diameter can be detected, but all gold particles are found only on the area or along the boundaries of the contamination. The result is interpreted as that the growth of particles is prohibited in the contamination free regions probably due to a low activation energy for surface diffusion of gold atoms. Furthermore, a migration of particles or a coalescence among particles can also be detected during the microscopic observation, the electron current being about 1.5 A/cm² (Fig. 3). This means that tight fixation of particles on supporting media is important for high resolution electron microscopy.

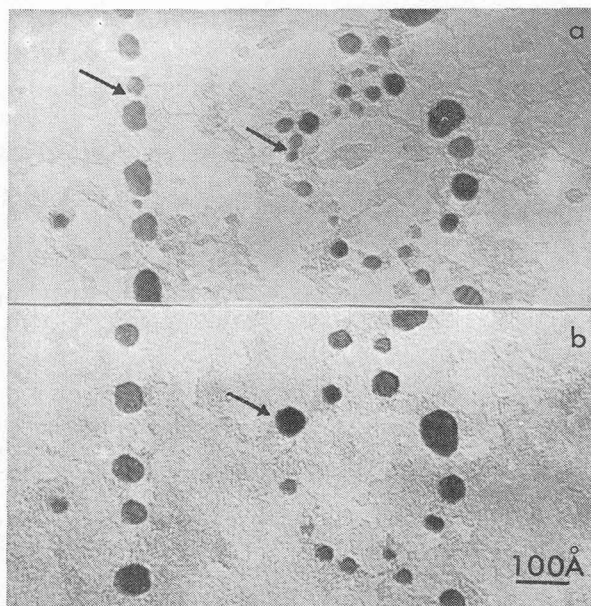


FIG. 3. — Coalescence among particles during the microscopic observation. (a) Just after the observation ; (b) After 25 minutes of the observation.

In these circumstances, the present authors have developed beryllium oxide films [6] as low noise specimen supporting films for a few years. Figure 4 shows an electron micrograph of gold particles

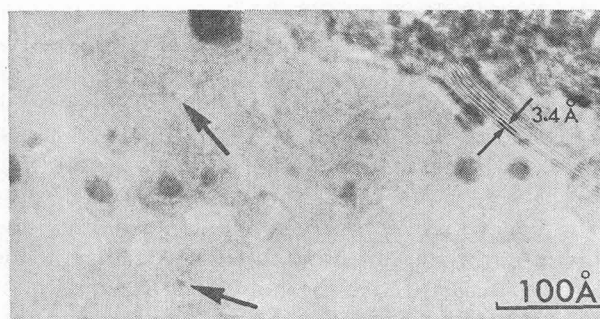


FIG. 4. — Gold particles backed by a beryllium oxide film. Particles less than 10 Å in diameter are indicated by arrows.

grown on sodium chloride surfaces backed by a beryllium oxide films. The film is composed of crystal grains, whose mean size is about 100 Å in diameter. The grain boundaries of the film are visible with some contrast. However, the area in each grain is uniform in contrast. It can be recognized at a glance that the noise in each grain is much lower than that of the carbon film of about 30 Å thick (Fig. 1). Quantitative data on the noise and the average contrast measured by the microdensitometer are shown in table I for various amounts of defocus. The data for the carbon film of about 30 Å thick are also shown for reference. It is very clear that the noise and the average contrast of the beryllium oxide film are less than one half of those of the carbon film. In the micrograph, most

TABLE I

Noise and average contrast of beryllium oxide films of about 50 Å thick and carbon films of about 30 Å thick for various amounts of defocus. The noise of a hole means that of photographic emulsion (FG film, FUJI PHOTO CO., LTD) and it serves to measure the contrast of the film.

Amount of defocus Δf (Å)	Noise (%)		Hole	Contrast (%)	
	BeO film (~ 50 Å)	Carbon film (~ 30 Å)		BeO film	Carbon film
—	—	—	—	—	—
+ 1 400	4.0	14.3	2.3	0.7	7.9
+ 700	5.1	13.2	2.3	1.4	9.6
~ 0	3.3	4.7	2.0	1.7	9.8
- 700	3.1	8.4	2.1	3.7	8.3

of the gold particles grow along the surface steps of sodium chloride and those less than 10 Å in diameter can be clearly observed as indicated by arrows. Lattice fringes observed in the right of the micrograph are of graphitized carbon powder dispersed previously on sodium chloride surfaces and they serve the calibration of the microscopic magnification. In the imaging of these extremely fine objects, the phase contrast, which strongly depends on the amount of defocus, is mainly concerned. Consequently, the interpretation of the image must be carried out by using through focus

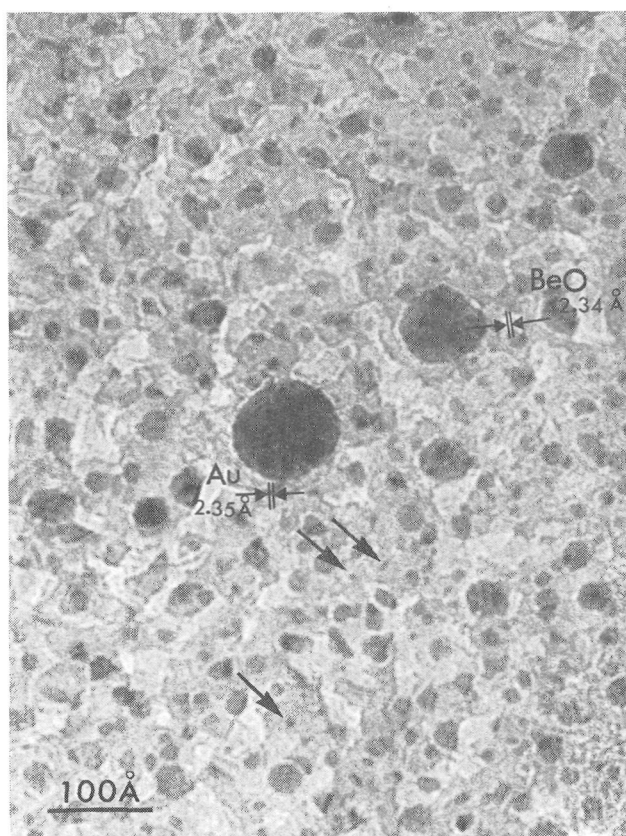


FIG. 5. — General aspect of gold particles prepared by the simultaneous deposition technique.

images. This point will be discussed in some detail in the following paragraph.

For preparing smaller particles, the simultaneous deposition of gold and beryllium oxide onto cleaved surfaces of sodium chloride is attempted. In this case, most of gold particles are embedded in the film and consequently the growth is no longer epitaxial. Figure 5 shows a general aspect of gold particles thus prepared. The size distribution of the gold particles is not sharp. Lattice fringes are observed in relatively large gold particles or in some grains of beryllium oxide films. In the image of most of gold particles less than 10 Å in diameter, an internal structure composed of a few dots can be observed as indicated by arrows, the size of each dot being around 3 Å. The relative spacing and the relative arrangement of these dots vary with the amount of defocus as shown in figure 6, for example. The measured spacings of dots for various amounts of defocus fit approximately with Thon's curve [8, 9] which shows the relation between the spatial frequency of the image and the amount of defocus. This means that the internal structure is ascribed to a selective imaging of the projected potential distribution of the particle.

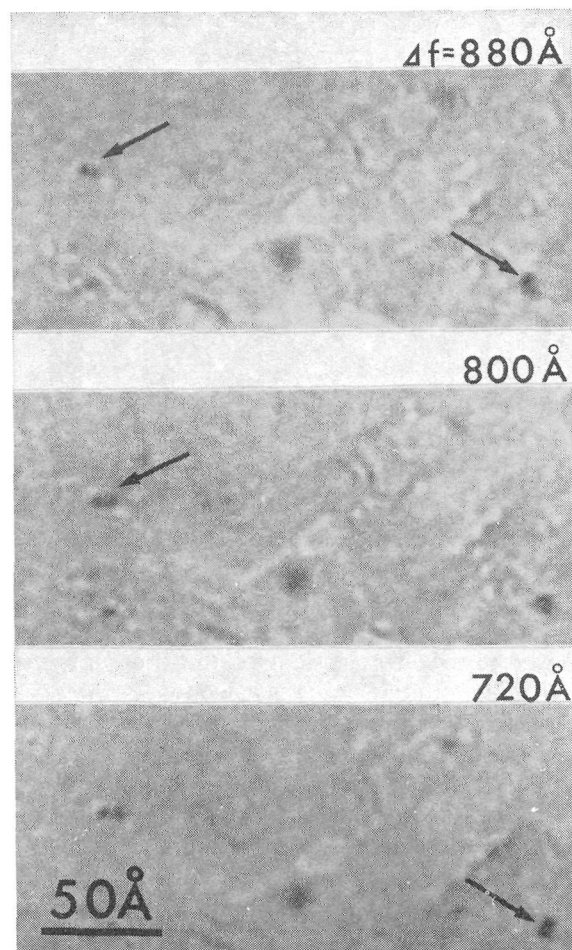


FIG. 6. — Variation of internal structures with the amount of defocus.

Consequently, the image by selective imaging represents only a reflection of the particle structure. However, the selective imaging may be connected with the imaging of individual single atoms, if a particle be composed of a few atoms with suitable orientation such as monolayer arrangement. For imaging of these individual atoms, the optimum focusing condition must be chosen. In practice, through focus series are taken with fine focal step and the best image is selected. Then, the amount of defocus for each micrograph is determined by an appropriate method, for example the optical diffraction method [10]. Image interpretation is then carried out by examining variations of image details as well as the contrast with the aid of calculated values. Figure 7 shows electron micrographs of gold particles prepared by the simultaneous deposition technique. For the particle indicated by an arrow in figure 7(a), an image consisting

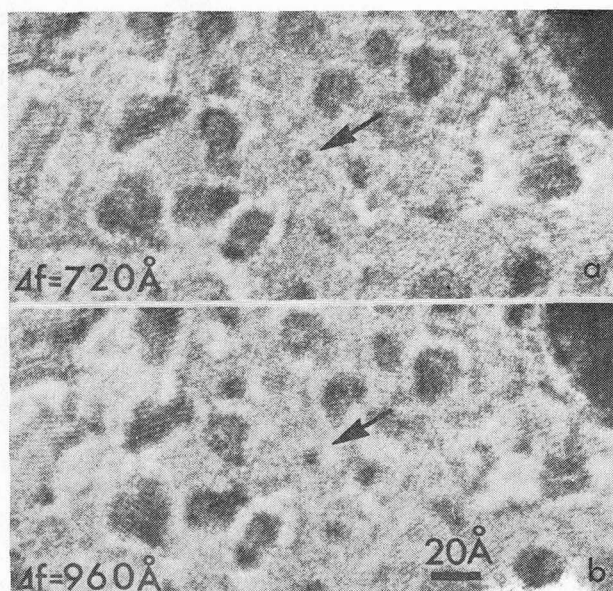


FIG. 7. — Internal structure composed of rectangular arranged four dots, whose spacing is about 2.8 Å.

four dots arranged in square can be observed. The contrast of each dot is as large as 20% and the relative spacing of dots is about 2.8 Å which is the nearest neighbour distance of crystalline gold. However, the arrangement of the four dots varies with the amount of defocus as shown in figure 7(b). Therefore, the image can be interpreted in terms of the selective imaging of the projected potential distribution as described above. In this case, the particle may be composed of a few gold atoms stacked rather three dimensionally and the projected potential is not simple. In the contrary, for the particles indicated by A and B in figure 8(a), constituent dots having rectangular or hexagonal arrangement, respectively, with the spacing of about 2.8 Å are recognized. The micrograph was

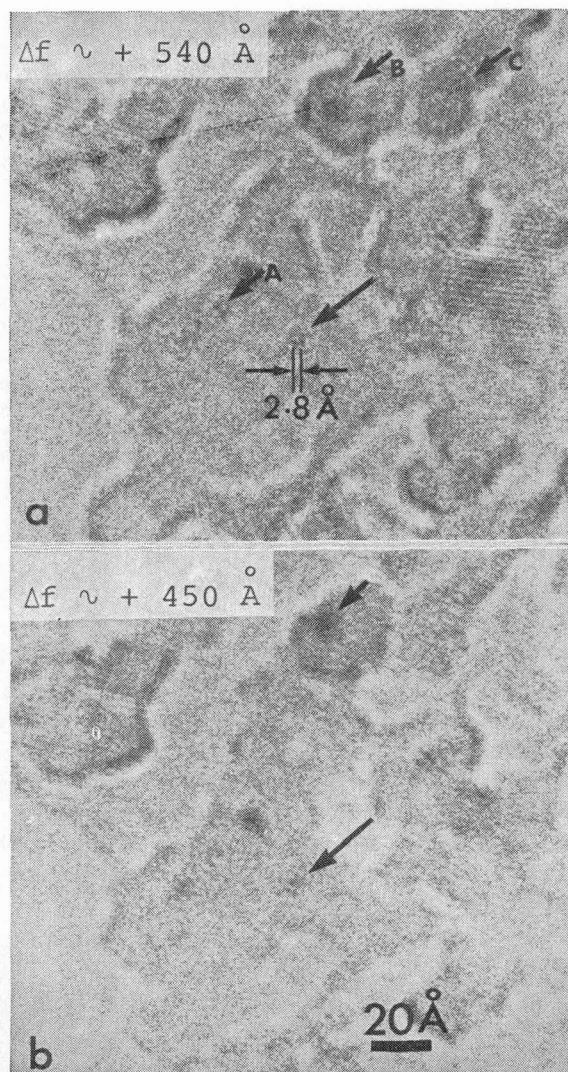


FIG. 8. — Gold clusters composed of rectangular and hexagonal arranged dots. Each dot corresponds possibly to a single gold atom.

taken at the defocus, $\Delta f \sim 500$ Å, which is close to Scherzer's optimum defocus [11], $\Delta f = \sqrt{C_s \lambda}$. Each dot has the contrast less than 15% which agrees approximately with the calculated ones [3, 12] for single heavy atoms. When the amount of defocus deviates slightly from the optimal one the images become weak and obscure as shown in figure 8(b).

According to the following reasons, that is, the spacing and arrangement of constituent dots, the contrast and the behaviour of the image with the amount of defocus, it is concluded that each dot observed in figure 8(a) corresponds possibly to a single gold atom [9].

4. Summaries. — For the observation of fine particles, low noise specimen supporting films must be used. Beryllium oxide films have really the characters adequate for the present purpose. The particles with tight fixation on the supporting films are also necessary for resisting heavy electron

irradiation. The interpretation of microscopic images must be carried out by using through focus series and measuring the contrasts, because a large portion of the contrast is due to the phase contrast mechanism for extremely fine particles. The image of individual gold atoms of small clusters can be obtained for the specimen prepared by the simultaneous deposition technique. Growth of particles with monolayer arrangement as shown in figure 8 is rather accidental and beyond control in the present experiment. For particles with three dimensional atomic arrangement, the image interpretation turns

out to be not easy, even when the size is less than 10 Å, because the projected potential distribution is no longer simple because of overlapping of atoms.

Acknowledgments. — The authors wish to express their sincere thanks to Pr. R. Uyeda for his valuable discussion throughout the work. Thanks are also due to Mr. A. Horata and Mr. S. Shima for their assistance of the present work. The authors also wish to thank Pr. S. Shima of Fujita-gakuen University for a general guidance of treating harmful Be-materials.

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