Ultra Fine Particles and Coatings

Chikara HAYASHI

Ulvac Japan Ltd. 2500 Hagizono, Chigasaki, Kanagawa 253, Japan

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1. Introductory Review

1.1 First tide

The first high tide in the study behavior of micron/submicron particles in a medium, colloids, was between 1860 and 1910. It is said observation of Brownian motion in 1827 by optical microscope stimulated scientists. In this area Physicists investigated light scattering (L. Rayleigh, J. Tyndall), viscosity (A. Einstein, J. Maxwell), etc. Continued research by chemists and bio-scientists has developed commercialized Sol or Gel products.

1.2 Second tide

The second tide, which was related to electronics, was in author's knowledge, initiated by R. Kubo's theory published in 1962¹⁾ and R. Uyeda and N. Kimoto's visualization of UFPs by electron microscope and electron diffraction systems from the early 1940s²⁾. R. Kubo deduced two conclusions with regard to small clusters;

1) UFP-small clusters tend to be electrically neutral.

2) The density of the electron energy levels is not sufficiently large to verify Fermi-statistics in which there should be a sufficient number of levels in kT , where k is Boltzmann's constant.

The neutrality relates to the work function; the coulomb energy and the thermal energy. The latter relates to the Pauli principle, assuming that the available number of electrons is comparable to the number of atoms in a cluster. Experimental proof of the two required a sufficiently large number of particles with the same size that were isolated from each other for obtaining good sensitivity/noise. For such systems, further theoretical study gave predictions for possible shifts or changes in the material properties, such as the melting point, specific heat magnetization, electronic conductivity and super conductivity. Qualitative agreement between theoretical prediction and experiment on collected particles have often been reported. Most of

those works are published in two collected paper issues, CHOBIRYUSHI (UFP), edited by S. Nagasaki³⁾.

Fig. 1-1 Cohesive Force Against Particle Size.

Fig. 1-2 Accelerated Aging Test 60°C, 90% Relative Humidity.

Typical Composition

a) 95-5 Ni

a)-Hydrogen Reduction

b) 70-30 Co

b)-Sodium Borohydride Reduction

c) 90-10 Ni

c)-Evaporation and Condensation in Inert Gas with Controlled Posy-Oxidation

b') b and 400°C 1 hr in Inert Gas

1.3 First application in the electronics industry and its follow up

Utilization of UFPs of magnetic alloy particles (Fig. 1) for recording tape was the first commercial application in about 1970. The optimum size to obtain the best recording density with the alloys is around 30 nm. Coatings on the substrate tape are applicable both by using UFP dispersed liquid or evaporation and deposition in vacuum. During the course of study of magnetic metal UFPs, A. Tasaki proved that Fe UFPs with very thin surface oxides with few atomic layers can be weather resistant⁴⁾. This fact encouraged possible industrial use of UFPs. The Exploratory Research for Advanced Technology Program for UFPs (ERATO) was inaugurated in 1981. C. Hayashi⁵⁾ brought in researchers from universities, research institutions, and industries from any country to the UFP project. Published reports from the project cover a wide range of topics⁶⁾. The major magnetic recording media as of 1995 is, however, the hard disk which is made of sputter deposited metal alloys of a variety of compositions. The composition of the gases in the sputter discharge zone, the alloy composition, the metallographic structure of the sputtering target materials, and the processing temperature profile are the major controlling factors to obtain

optimum ultra-fine particles, which are the grained structure for the deposited recording media. Observation of the sputter-deposited, fine-grained surface by using a scanning electron probe microscope give images of the surface structure and magnetic flux image microscopy is becoming useful tool⁷⁾. Theoretical aspects of the quantum tunneling of magnetization in small particles was discussed⁸⁾. High resolution transmission electron microscope (HREM) has revealed lattice structures and metallic atom arrangements of UFPs in work done since about 1980. HREM images of Au, Pd, Rd clusters (2 nm ~ 4 nm) attached to a larger UFPs (e.g., about 70 nm) stimulated chemists studying catalysis. Gold clusters on Fe₂O₃ UFPs showed catalytic activity for oxidation, hydrogenation, and other reactions⁹⁾. Gold had long been avoided by chemists as a catalytic substance.

While industrial application of magnetic UFPs had been intentionally investigated in Japan, basic structural/ionization studies on microclusters ($\leq 1,000$ atoms) of metals ions and Van der Waals molecules have been conducted extensively in Europe and USA since the early 1970s by using molecular beams (K. Sattler, W. D. Knight, G. Delacrétaz, A. P. Kaldor et al¹⁰⁾). UFPs larger than clusters have also been investigated both for formation (C. G. Graqvist and R. A. Buhrman¹¹⁾) and shift/change from bulk material properties (W. D. Knight, L. Genzal, et al¹⁰⁾) (S. Sugano¹²⁾).

1.4 The third tide-nanotechnology and the nano world

Around 1985, stimulated by the successful development of the tunneling microscope by Bining and Rohrer, a great number of scientist worldwide started to investigate the nano-world with a variety of microprobe microscopic systems. Then the word nanotechnology came into existence and UFPs are more often called nanoparticles and clusters. Fabrication of quantum dot arrays for quantum wave electro-optic devices or utilization of quantized tunnel electron transport through nanoscale gaps to a small cluster (< 50 Å) against coulomb blockade is already an industrial target.

Electrical charge in a cluster undergoes coulomb blockade when there is an electronic charge outside the cluster. Electrons inside an insulated cluster have an area to exist in that too small compared to their wave length (λf) or mean free path (L), which may result in fluctuation of thermal or magnetic energy especially at the surface. Controlled epitaxial crystal growth on defect free substrates is a common technique for treating semi-conductors when

Fig. 2 New Catalyst Au Cluster on Fe₂O₃ courtesy by M. Haruta.

Fig. 3 Carbon Nanotubes.

preparing quantum wave devices. Carbon balls and nanotubes¹³⁾ appeared in HRTEM pictures (I. Iijima), for example Fig. 3, have been recognized by chemists as new materials for chemistry.

Electronics scientists and technicians are studying ordered array formation and incorporation of atoms other than carbon in the ball or the tube, looking for new semi-conductors. Last, but perhaps one of the most interesting areas, is in biological systems. Artificial synthesis of magnetite chains (10 ~ 50 nm) in magneto tactic bacteria was studied¹⁴⁾. Artificial preparation of the flagella motor of bacteria (Fig. 4) has been tried by using the protein components obtained by biological and gene, technologies¹⁵⁾. Implantation of viruses and other small "particles" by using inorganic nanoparticle as a carrier is opening a successful way to treat plant cells¹⁶⁾.

1.5 Nanostructured materials

The use of clusters or nanoparticles as individual isolated particles is limited because it has been only few years since scientists demonstrated the possibility of handling single clusters with a micro-probe. Condensed phase materials scientists, however, have long been providing data, mostly qualitative but still interesting, for applications. Here the coherency/long range force can play a role. Recent contributions from material scientist (H. Gleiter, M. Multi, R. Siegel, Y. Ishida, and others¹⁷⁾) on the structure and properties of nanostructured materials are stimulating revival in research and industrial applications for new materials.

Fig. 4 Schematic of Bacteria Flagella Motor.

2. Coatings

Deposition of nano-particles for manufacturing electronic components has been developed. The development effort is an outcome from the ERATO UFP project, but was aimed at industrialization/commercialization of UFP technology. Two coating methods, one named the gas deposition (Fig. 5) and the other the UFP paste, have been developed.

2.1 Gas deposition

The principles and evaluation of the gas deposition method have been published⁹⁾. Fig. 5 illustrates the principle. Fig. 6 illustrates a few applications. UFPs entrained in the gas jet are deposited. Existing fluid dynamics theory gives sufficient background for the entrainment but characteristics of the fluid very near (in front of) the target substrate is obtained by experiment. A surprising fact was that almost all UFPs carried by the gas jet can be deposited with very little scattering. The width or diameter of the deposited pattern is the same or can be even smaller than the inner diameters of the nozzle. That is not possible if we start with particles having diameters over a few micrometers. The mean free path L for carrier gas atoms in the gas flow must be larger than the diameter of the UFPs d ($L \geq 5d$). At the same time, the gas atom density must be quite large compared to the density of the UFPs, so that we can have precise deposition. The jet will be injected to a reduced pressure region to

Fig. 5 Schematic Illustration Gas Evaporation-Gas Deposition.

Fig. 6 Typical Application of the GDP.

- a) repair patterns
- b) forming microelectrode
- c) forming a conductive film
- d) bonding and packaging

get rid of stagnation near the target. Under a chosen set of parameters for operation, the entrained UFPs will get the same mass-flow speed as the carrier gas, regardless of specific gravitational density of the UFPs. This means any mesoscopic mixture of different materials in the deposit can be obtained. Metal-metal, ceramic-metal, plastics-metal, etc. composites of homogeneous mixtures, layer by layer or with a gradient composition can be obtained, which leads to a large number of possibilities for applications. Either He or H₂ is advantageous as the carrier because the maximum mass flow speed at the nozzle exit is close to the speed of sound. The largest value of ~ 1 km/sec is obtained for He at room temperature: the higher the speed, the denser the deposit. Typical densities obtained are comparable or even higher than pressed and

Fig. 7 Dependence of deposition rate to evaporation temperature.

presintered samples of the same material. Supersonic speed can be obtained by making Laval expansion for the nozzle, but this results in broader deposit areas.

2.2 Deposition rate

The deposition rate is dependent of the evaporation source temperature when using evaporation. Fig. 7 illustrates some examples. UFPs formed in the evaporation chamber are carried in the transfer tube with converging gas flow. Thus the rate at the deposit is quite high compared to conventional evaporation or sputtering where typical deposition rates are 1 ~ 100 nm/sec.

2.3 Adhesion, electrical conductivity, and hardness

Adhesion strength data for the deposited films were obtained by using a shear force measuring instrument, see Table 1. The adhesion will be diminished by surface adatoms or molecules on the substrate. To avoid water vapor adsorption, the substrate is normally kept at a temperature at 150 ~ 300°C depending on the substrate used. The data are for macroscopically smooth surfaces. The adhesion strength for gas deposited gold is often quite large (up to 2 times) compared to that of wet plated gold. The electrical conductivities are presented in Table 2. Here, a smooth glass substrate is used. Weathering tests at 50°C in 95% rela-

Table 1 Adhesive Strength

	Substrate	Temperature of Substrate (°C)	Adhesive Strength (kgf/mm ²)
Au	Ni	150	2
		200	20
		250	22
Ag	Alimina	30	2
		200	3
		400	4
Cu	Alumina	250	2
Pd	Polyimide	250	4

Table 2 Electrical Resistivity

	Specific Resistance of Gas Deposition Film $\langle A \rangle (\mu\Omega \cdot \text{cm})$	Single Crystal (20°C) $\langle B \rangle (\mu\Omega \cdot \text{cm})$	$\langle A \rangle / \langle B \rangle$
Au	2.6	2.20	1.2
Ag	2.1	1.61	1.3
Cu	2.7	1.70	1.6
Pd	25	10.55	2.4

Fig. 8 Gold Deposit

a) Electro-plated at room temperature, b) Gas Deposition. Deposition rate 7 $\mu\text{m}/\text{min}$ with 0.1 mm ϕ nozzle 30 mm length. c) Electro-plated and 30 min 350°C after annealed. d) Gas Deposition. Gas temperature 600°C.

tive humidity were conducted for deposited Al for up to 1,000 hrs. The specific resistance increased from 3.7 $\mu\Omega\text{cm}$ to 4.0 after 1,000 hrs; this is without the use of a protective layer. Vickers Micro Hardness measurement on a Au deposit prepared on stainless steel at 7 $\mu\text{m}/\text{min}$ with 100 μm diameter nozzle shows about a 80% increase from about 80 kg/mm² to 150 kg/mm² after a post heat treatment at 400°C (Fig. 8). This corresponds to the TiO₂ film formed from UFPs published by R. Siegel¹⁷⁾. The hardness for the deposit made by a carrier gas heated to 600°C was about 35 kg/mm², which is the same as an electroplated film annealed 350°C for 30 min.

2.4 Application

Fig. 9, 10, and 11 present SEM pictures of patterns for micro-components that can be used in the electronics and semiconductor industries. Fig. 12, and 13 illustrate application for metal bonding. Application of this deposition method for PZT (PbO, ZrO, and TiO) or BST (BaO, SrO, and TiO) micro-capacitors is offering competition to sputter deposition. A few micron Ni deposit on a Ti substrate resulted in stronger metal bonding after a lower temperature and short-time bonding than that of conventional brazing using alloy foil as the brazing insert. The low temperature, very thin intermediate zone diffusive bonding is a common advantage for using UFPs. Low temperature processing is preferable to avoid risk of breakage due to fatigue caused by recrystallization.

2.5 UFP paste

Another way to utilize UFPs for coatings has

Fig. 9 Au Spot on Ni Substrate. Height: $13\ \mu\text{m}$, bottom diameter: $16\ \mu\text{m}$, spot to spot: $50\ \mu\text{m}$.

Fig. 10 Scanning electron microscope picture of Au bumps formed by gas deposition process.

Fig. 11 Scanning electron microscope picture of Au connecting lines formed by gas deposition process.

Fig. 12 Ti frames of glasses.

Fig. 13 Breaking force of brazed points by TiCuNi and by Ni-UFP. Ni-UFP makes good joining at lower input power than TiCuNi.

been developed by M. Oda et al. Au, Ag, and Pd UFPs are dispersed in a solvent for paint coating (**Fig. 14(b)**). It has been shown that UFPs stick together or adhere to a substrate at relatively low temperature. With a Au dispersed paste, very smooth coatings $0.25\ \mu\text{m}$ thick are obtained after heating at 300°C for a few minutes to remove solvent (**Fig. 14(a)**). Low temperature processing and the formation of the deposits with very smooth surfaces are two key characteristics of using UFP pastes.

2.6 Remarks for the coatings

Table 3 and **4** present the advantages of the Gas Deposition method which is a thermo-kinetic process. In principle it is applicable even at very low temperature. There is another direction of application that involves using almost the same technique. By

a) Au Film Patterned by Photolithography

b) TEM Picture of Au Dispersed UFP

Fig. 14a)·b) Dispersed UFP (M. Oda)

Table 3 Advantage of Gas Deposition Method

① DIRECT WRITE PROCESSING	MASKLESS
② HIGH SPEED DEPOSITION	SEVERAL $\mu\text{m}/\text{sec}$ 10 ~ 20 μm
③ LOW TEMPERATURE PROCESSING	~ROOM TEMPERATURE
④ UNIFORMLY MIXED UFP FILM	USING MORE THAN TWO ELEMENTS METAL, CERAMICS, ORGANIC MATERIALS

Table 4 Comparison of Existing Coating Technique

DRY COATING	PARTICLE SIZE	MODE	TEMPERATURE	EXAMPLE OR REF
PLASMA SPRAY	μm		HIGH-TEMP	TURBINE
DETONATION	μm	MICRO-JET	HIGH-TEMP	TURBINE
AEROSOL SPRAY	nm		LOW	ORGANIC PAINT COSMETIC
GAS DEPOSITION	nm	MICRO-JET	LOS-MEDIUM	DISCRETE ELECTRON BIO-ENG
IN CLUSTER	nm	VACUUM	IONIC	ELECTRONICS
VAPOR DEPOSITION P.V.D. C.V.D.	Å	mostly VACUUM & OVERALL	MEDIUM to IONIC	L.S.I. FILM, TAPE DISK DISPLAY
ATOM CRAFT	Å	ATOM-PROBE	LOW	STM AFM

using CO_2 and other solidified gas particles, the removal of photoresist films on glass was successfully done. This process can be used to do clean, dry surface-erosion cleaning.

The equipment design concept for the deposition

and the erosion cleaning is quite similar from the applications point of view. The thermo-kinetic process does not damage the metal or ceramic substrate surface. Biological substances will be usable as a target with careful control of the bombarding

particle energy. The smallest size that can be obtained, for example for electronic components, is interesting but has not yet been made clear. The first limitation comes from the physical dimensions of the nozzle, which is around 10 μm as of 1995. The second limitation is the gas flow stability. In consideration of ever increasing environmental problems and the excellent material and energy saving characteristics, the gas deposition method has high potential for the production of industrial coatings in the near future.

References

- 1) Kubo R. (1962) J. Phys. Soc. Jpn., 17, 975.
- 2) Uyeda, Ryozi (1991) Progress in Materials Science 35, Pergamon press plc. Oxford ox 3 OBW, England.
- 3) Nagasaki, S. No. 1 (1975) and No. 2 (1984) CHOBIRYUSHI Agne Technical Center, Tokyo.
- 4) Tasaki, A., Takao, M. and Tokunaga, M. (1974) Jpn. J. Appl. Phys. 13, 271.
- 5) Hayashi, C. (1987) Physics today, December (1987) J. Vac. Sci. Tech., A5(4) part 2 1375. (1993) Materials Science and Engineering A 163, 157-161.
- 6) Hayashi, C., Uyeda, R. and Tasaki, A. (1988) CHOBIRYUSHI, MITA PRESS, Tokyo. Revised and English version is in printing from Noyes Publication, NY.
- 7) Tonomura, A. Report of ERATO Tonomura Project available from Research and Development, corporation of japan (J.R.D.C.) in Tokyo.
- 8) Chudonovsky, F. M. and Gunther, L. (1988) Physical Review Letters 60, No. 8, 661-664.
- 9) Haruta, M., Tsubota, S., Kobayashi, T., Kageyama, H., Gent, M. and Delmon, B. (1993) JOURNAL OF CATALYSIS 144, 175-192. (1995) JOURNAL OF ELECTROCHEMISTRY 381, 167-177.
- 10) Knight, W. D. (1973) J. Vac Sci Tech. 10, 705. Knight, W. D., Clemenger, K., de Heer, W. A. Sanders, W. A., Chou, M. Y. and Choen, M. L. (1984) Phys. Rev. lett 52, 2141. Sattler, K., Muelbach, J. and Recknagel, E. (1980) Phys. rev. Cett 45, 821. Grenzel, L. (1974) Festkörperprobleme 14, 183. Many papers related to clusters and Gases are available in: Belotserkovskii, O. M., Kogan, M. N., Kutateladze, S. S. and Rebrov, A. K. (1985) Rarefied Gas Dynamics 2, 1073-1245. PLENUM PRESS, NY. Delacrétaz, G., Ganière, J. D., Melinon, P., Monot, R., Rechsteiner, R., Wöste, L., van den Bergh, H. and Zellweger, J. M. (1985) RAREFIED GAS DYNAMICS 2, (edited by Belotserkovskii, O. M., Kogan, M. N., Kutateladze, S. S. and Rebrov, A. K.) Excerpts, Abstract of the 3rd Int. Symposium on Small Particles and Inorganic Clusters (ISSPIC), 1984 from free university Berilin, Germany 1173-1185.
- 11) Grangvist, C. G. and Buhrman, R. A. (1976) J. Appl. Phys. 47, 2200.
- 12) Sugano, S. (1991) Micro cluster physics, Springer-Verlag, Berlin Heiderberg Sugano, S., Nishina, Y. and Ohnishi, S. (1986) Micro clusters, Springer-Verlag Berlin Heiderberg.
- 13) Iijima, I. (1991) Nature 354, No. 6348 55-58. Macmillan Magazines Ltd.
- 14) Horikoshi, K. (1989) ERATO Horikoshi Project report, J.R.D.C.
- 15) Aizawa, S. (1988) JUNKATSU (JAPANESE) 33, No. 7, 531-532. Hotani, H. (1991) JRDC Report of Hotani Project.
- 16) Kakuta, H., Seki, T., Matsui, M., Anai, T., Hasegawa, K. and Mizutani, J. (1992) Miami Bio/Technol. Winter Symposium, 21.
- 17) Siegel, R. W. (1991) Annu Rev. Mater. Sci. 559-578. Multani, M. S. (1990) Phase Transitions, 24-26, 3-14, 91-202, 834-. Garden and Breach Science Publishers S.A. United Kingdom. Gleiter, H. (1992) Nanostructured Materials 1, 1-19, Pergamon Press. plc.