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Nanoparticle Research from a view point of Industrial Use

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Nanometer size particles (nanoparticles) attract much attention because of their high potential as breakthrough technology in conventional industrial fields. However, they have several drawbacks to overcome in order to realize such expectations. The difficulty of mass-production of the particles, their size control, very high reactive characteristics, etc., are barriers for the attainment of the effective utilization of the nanoparticle's characteristics. In this paper, the former efforts used to apply nanoparticles for industrial purposes, examples of the problems with nanoparticle industrialization and what kinds of applications are considered for nanoparticles are discussed.

Key words: nanoparticle, gas deposition, industrial use, breakthrough technology, laser, differential mobility analyzer

1. INTRODUCTION

New technological R&D is strongly expected to activate the present economical state because almost all manufacturing technologies supported key industries such as the semiconductor industries, automobile industries, etc., are reaching maturity. In such a situation, nanotechnology is expected as a key technology for the breakthrough of the present status of industrial technologies. Nanotechnology itself is a general term for the technology dealing with micro-substances so that the essence of it is very wide and not clear. However, it is very clear that new materials such as fullerenes, nanotubes, and nanoparticles attract much attention for the development of nanotechnology.

The expected uses of nanoparticle applications are electric cells, memories, semiconductor devices, catalysts, cosmetics, medical treatments and so on. In these fields, people have already some idea as to what kind of performance is expected when the particles are applied although the efforts for the realization of these ideas have not yet been undertaken.

Nanoparticles have been studied since 1970 by many researchers because they might have new physical and chemical characteristics through a size effect on their regular characteristics, the mixing effects of different types of nanoparticles, etc. Such research activities have often been very much scientific and basic so that they were not easily transferred into industrial expectations. Consequently, the researches were far from the development of new applications.

In order to use nanoparticles in an industrial application, we should know what is required for the nanoparticles for each use and the market size for the nanoparticles. If the market is very small, no industrial sector will want to use them. At the same time, we must demonstrate their advantages by utilizing the characteristics of the nanoparticles and eliminate their drawbacks from an application point of view. Therefore, the drawbacks such as the agglomeration of particles, their oxidation, high production cost, etc., should be improved. The advantages must be fully demonstrated.

Another important matter is to get precise information from users. This was not easy for nanoparticle researchers. Consequently, the main efforts for the industrialization of nanoparticles by R&D people were to study the characteristics of the particles and/or show what nanoparticles could do. R&D people tried to make users consider their application.

Vacuum Metallurgical Co., Ltd., (VMC) has continued to supply the nanopowders of metals such as Ag, Fe, Ni, Cu, etc. for 30 years and has tried to present information concerning utilization of nanoparticles such as thin film formation and its characteristics, bump formation and wiring made of nanoparticles. At the same time, VMC has tried to develop and sell instruments for nanoparticle synthesis and thin film formation. However, VMC could not get a high return from current markets. Therefore, before describing the applications of particles, we had to better understand VMC's experiences in order to successfully realize the industrial use of nanoparticles.

2. THE EFFORTS OF VMC FOR NANOPARTICLE DEVELOPMENT

VMC is the first company in the world to have produced nanoparticles by mass-production using an evaporation-condensation method that was proposed by Prof. Uyeda [1].

In 1980, Dr. Hayashi, who was a representative of VMC, led a national project of nanoparticles and issued important scientific and technological results [2]. In the mean time, VMC was trying to sell several kinds of nanopowders and instruments for nanoparticle manufacturing.

The most important initial product was Fe-Co magnetic nanopowder expected to be used for the manufacturing of videotapes because the application of a Fe-Co nanopowder could realize a higher density recording [3]. However, this trial did not succeed due to the high production cost and the improved efforts of conventional production methods so that nanoparticle lost one of the most important big markets that needed mass-production and mass-consumption. On the other hand, VMC's Ag nanopowder has become very popular in the world since it showed very good thermal conductivity at the extremely low temperature [4]. People called it Japanese powder. This Japanese powder still has a worldwide demand. However, the market size is very small, therefore, it could not be the product that sustained VMC.

VMC used a high frequency electric furnace to produce nanopowders. This method was not the best for mass-production and could not make nanoparticles from high melting temperature metals and reactive metals so that the kinds of powder were limited although the quality of the powder was very good and satisfied all users. The use of an induction furnace for nanoparticle production might have been a drawback in terms of its high cost and limited use of certain materials.

As VMC's method was not a mass production method, VMC tried to devote efforts to the use of all the nanoparticles produced without any loss of nanoparticles. A direct nanoparticle printing system (called the Jet Printing System; JPS) was developed to realize such a concept [5]. JPS is composed of a nanoparticle production chamber and thin film synthesis chamber where the nanoparticles are directly drawn onto a substrate through a nozzle to make a thin film, wiring, etc. VMC tried to show what kind of materials JPS could conduct. Wiring for electric circuits, the formation of thin films, bump formation, etc. were good examples.

Tables I and II show the experimental efforts done by VMC in order to show the potential of JPS [6]. That is, the conductivity of the thin film produced by JPS and the adhesion strength between a substrate and nanopowder films. The electric resistance of a thin film of Au nanoparticles is 20% higher than the bulk resistance,

Table I Specific resistance of the thin film produced by JPS [6].

	Specific Resistance of JPS Film <A> (μΩ · cm)	Single Crystal (20 °C) <B> (μΩ · cm)	<A> / <B>
Au	2.6	2.20	1.2
Ag	2.1	1.61	1.3
Al	3.6	2.66	1.4
Cu	2.7	1.70	1.6
Ni	16	7.04	2.3
Pd	25	10.55	2.4

Table II Adhesion strength between the substrates and the films produced by JPS [6].

Film	Substrate	Temperature of Substrate (°C)	Adhesion Strength (kgf/mm²)
Au	Si wafer coated with Ni film	150	2
		200	20
		250	22
Ag	Alumina	30	2
		200	3
		400	4
Cu	Alumina	250	2
Pd	Polyimide	250	4
Ni	Palladium	300	8
	Alumina	300	6
	Polyimide	300	2
Al	Nickel	250	2
	Silicon	250	2
	Polyimide	250	2
	Glass	250	2
	Alumina	250	2

which is still high, and the adhesion strength is at a level that satisfied customers. VMC showed more information concerning the deposition rate for thin film formation, the nature of wiring, the structure of the thin films, the bump formation for electrodes and so on. These kinds of efforts are still continuing. Also, VMC presently has started to supply nanopartilce pastes for screen-printing and the repairing of wiring defect sites in semiconductor industries to enhance the nanoparticle business.

3. THE KEY FACTORS FOR THE INDUSTRIAL USE OF NANOPARTICLES

VMC suffered from finding a big market that could consume a large amount of nanoparticles. Few application fields was the cause of not being able to find any practical uses. There were other causes such as the difficulty to supply nanopowders with the same diameter, no agglomeration and no oxidation, the difficulty of its handling and its mass-production without degradation of the particles. Few application fields might be able to overcome these concerns.

3.1 The quality of nanoparticles (nanopowder)

Nanopowders are requested to be of high purity, suitable size distribution and shape with good information on crystal structure and so on. Especially, the precise control of the particle size and size distribution is very important for generating new particle characteristics depending on the size effects such as their chemical reactive characteristic, sintering characteristic and quantum effects. We cannot say that researchers have presented the experimental data for specimens prepared by using nanoparticles with a precisely controlled size until now. We did not have a suitable tool or method to obtain a large amount of mono-dispersed nanoparticles. Therefore, it was not easy to confirm the new characteristics depending on the size effect. Concerning the mono-dispersed nanoparticles, a differential mobility analyzer (DMA) has been used to classify the as-obtained nanoparticles. This method enables us to obtain mono-dispersed nanoparticles with same diameter. If we can make thin films composed of particles with the same diameter and composite matter made of different nanoparticle mixing, we may have more useful characteristics that we have not yet discovered.

3.2 Handling of nanoparticles

The handling of nanoparticles includes their stabilization, suppressing the agglomeration and oxidation and utilization methods like JPS. The stabilization of nanoparticles is important to maintain the constant nature as a powder and for easily handling because nanoparticles are chemically very active and easily change their nature. The slight oxidation of nanoparticles by keeping them in an inert gas atmosphere is a method for their stabilization until now. This method cannot be used for the request to avoid oxidation.

It is not easy to control the agglomeration of particles. Once agglomeration occurs, we cannot separate them. The separation of the agglomerates from the powder is the only way. DMA [7-9] is available for this. However, since DMA cannot deal with the amount of powder needed for industrial applications, we need another reliable method or tool for agglomeration treatment.

The concept of JPS might be one of the good approaches for nanoparticle handling, because in this system, nanoparticles are utilized before degradation of the particles occurs.

The drawback of JPS was its speed to make products like thin films and wiring, therefore, JPS is limited for non-mass-production applications. In general, it is not available for mass-production systems.

The development of a mass-production method for nanoparticles should be conducted. In the USA and Europe, methods using plasma seem to be mainly used for nanoparticle production. In general, plasma methods are considered to have difficulty in controlling the size distribution of nanoparticles compared to gas-evaporation and condensation methods although they have the advantage of mass-production. The improvement of the plasma method should be conducted in order to obtain high quality nanopowders. Based on communications with researchers in the USA, they are trying to improve the technique.

3.3 The approaches related to practical use

Nanoparticle researchers have examined the characteristics of nanoparticles and its products like a film and composites mainly for scientific interest. VMC's approach like JPS was a special approach. We think it is important to show what nanoparticles can present as did VMC. However, even this approach is not sufficient to make particles for industrial applications. More directly linked approaches to the customers are truly necessary.

If one considers applying nanoparticles of dielectric materials in the field of memory, one should make the memory directly with the particles in order to confirm whether the idea is feasible. Such trials have been very limited.

We are now in a kind of boom for nanotechnology. We would like to positively utilize this opportunity for nanoparticle industrialization.

4. SUCCESS STORIES FOR NANOPARTICLE APPLICATION

We can see that there are several success stories for nanoparticle application in terms of mass-production use.

Nanophase Technologies Co. (USA) has succeeded in supplying zinc oxide nanoparticles for health care products like a sun protection cream. QinetiQ (England) has provided a huge amount of aluminum nanopowders for ignition systems. Exxon Mobil Co. (USA) has used zeolite nanoparticles as a catalyst to crack gasoline. Kawatetukougyo Co. (Japan) has succeeded in supplying submicron size nickel powder for capacitor electrode. If carbon black and molybdenum disulfide particles can be included in the category of nanoparticles, carbon black is used in tires and in the toner of copy machines while molybdenum disulfide is used as an engine oil additive.

In these examples, plasma seems to be used as the heat source for the mass-production and the fine control of the size and size distribution of the particles are not severely restricted. The performance and cost are needed here.

If we can introduce large amount of nanoparticles with a controlled size into an industrial market at a low price, nanoparticles will find new markets and can become an industrial material. The hopeful markets are shown in the first section. That is, people have already noticed where nanoparticles are expected for their utilization even if their confirmation is not very clear. Therefore, what we should do is to conduct experiments to attain hopeful results in application fields by solving the problems for mass-production and obtaining high quality nanoparticles. In this sense, a new mass-production method that can synthesize high quality nanoparticles should be developed as soon as possible.

5. OUR STUDY IN THE NATIONAL PROJECT: ADVANCED PHOTON PROCESSING AND MEASUREMENT TECHNOLOGIES SUPPORTED BY METI AND NEDO

The advanced Photon Processing and Measurement Technologies Project started in 1997 as a 5-year project [10-11]. VMC has participated in this project along with the collaboration with the Mechanical Engineering Lab. (MEL) of AIST and the Matsushita Electric Industry to establish a new processing technology using the laser ablation technique. The objective of VMC in this project is to develop a fabricating technology for a micro-composite electrical circuit using high quality nanoparticles. To obtain the objective, we investigated two subjects that included the manufacturing of nanoparticles of almost all materials and the establishment of the technology for the perfect control of the diameter of nanoparticles. VMC then tried to produce nanoparticles from high melting temperature metals like tungsten, molybdenum, ceramics, etc. in order to increase the kinds of materials that we can use. Concerning the control of the nanoparticle diameter, the Photon Project set a goal that the geometric deviation value of the particle diameter should be controlled to less than 1.2 in the diameter range of about 1 nm to 50 nm. VMC also had another objectives to draw wiring with less than a several μm width by spraying nanoparticles on a substrate and to synthesize nanometer size functional composites by *in-situ* mixing of two different kinds of nanoparticles.

The objective to make nanoparticles of high melting temperature metals was achieved. Tungsten [12-14], molybdenum [13], tantalum [13], etc., were demonstrated as nanoparticles. The nanoparticles of alloy and/or composite like the NiCr alloy and (Ba, Sr) TiO_3, etc., were also produced. Consequently, we have been able to prepare nanoparticles of almost all materials.

The size control of particles was also successfully achieved. The size control was not realized by the control of the operating conditions such as laser power, ambient pressure, target size, etc. The objective was achieved by the sintering of the as-grown nanoparticles and their classification by DMA. Figure 1 shows the experimental apparatus. The Q-switched pulse Nd: YAG laser (Spectra-Physics, INDI-50, CA, USA) was used as the

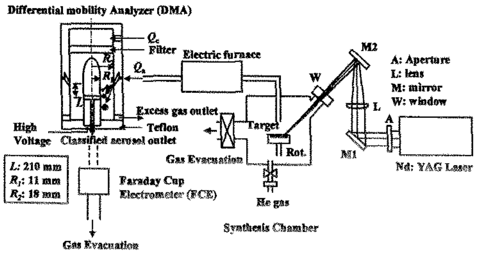

Fig. 1 Schematic diagram of the apparatus.

light source. The full-width at half-maximum of the pulse width was 4.5-5.5 ns. The generated particles are transported to the DMA through a carrying tube by He gas and classified to the expected size by the DMA. The electric furnace is placed before the DMA in order to obtain spherical nanoparticles by thermal annealing. We could control the shape of the nanoparticles by changing the temperature of the electric furnace, and the reshaping temperature of the nanoparticles was in good accord with the expected values. Figure 2 shows the TEM images of classified tungsten [13] and gold nanoparticles [15] of 10nm and 40nm size. Each particle had a geometric standard deviation of $\sigma_g \leqq 1.2$.

We have obtained a good tool that can control particle size so

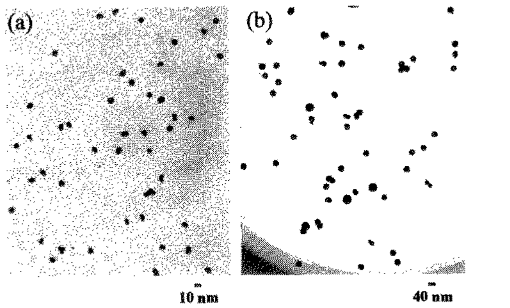

Fig. 2 TEM images of classified tungsten and gold nanoparticles. (a) W nanoparticles (10 nm classified), sintering temperature: 1273 K [13], (b) Au nanoparticles (40 nm classified), sintering temperature: 1273 K.

that we can realize our anticipations of size depending on the characteristics of the particles. We have to clarify the true effect of diameter size on the particle characteristics and bulk materials made of nanoparticles including thin films and wiring.

Concerning the synthesis of functional composites, we succeeded in synthesizing composites with a nanometer-sized structure by the *in-situ* mixing of two kinds of nanoparticles. That is, the NiCr alloy film and (Sr, Ba) TiO_3 film were produced from two different sources and their characteristics examined.

The electrical resistance of a thin film composed of nanoparticles could be controlled by the change in the synthesis conditions. Figure 3 shows the relation between the electric resistance and ambient pressure for a thin gold film that was used for capacitor electrodes [16].

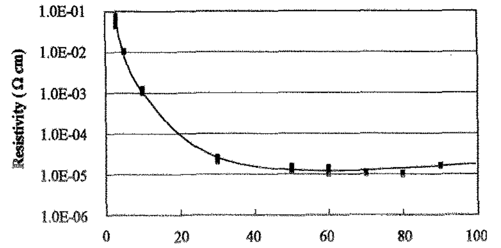

Fig. 3 Pressure dependence of the electrical resistance in gold films [16].

Finally, we demonstrated a capacitor made of a BTO nanoparticle thin film sandwiched between gold nanoparticle thin films, which is shown in Fig. 4. Figure 5 shows its capacitance versus frequency.

Figure 6 shows what we made using the laser type JPS.

In VMC's study, there was a new discovery. Nanoparticles with a several hundreds nm size automatically arranged in the area around the laser irradiated mark on the tungsten target [17]. Figure 7 shows the AFM image. The height of the particles was about 180 nm [18]. We could make a square arrangement and triangular one from them [17]. Such a new phenomenon might

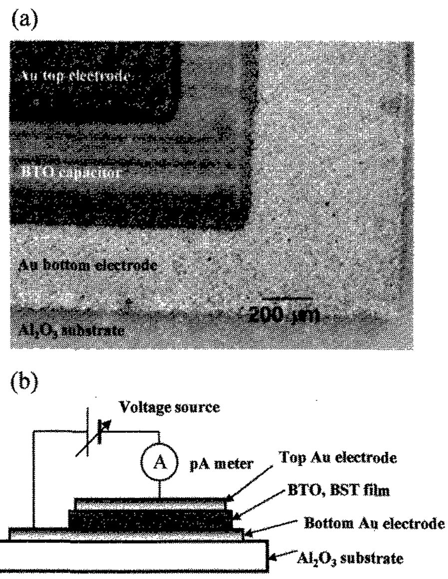

Fig.4 Capacitor of BTO nanoparticle thin film sandwiched with gold nanoparticles electrodes produced by the laser type JPS.

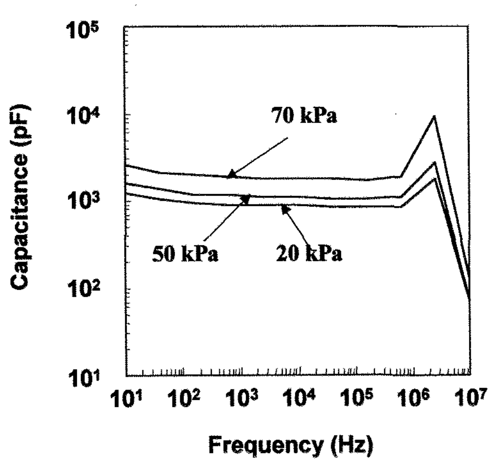

Fig.5 Capacitance versus frequency for the capacitor.

lead to new applications. As nanotechnology has not been actively cultivated, another phenomena might exist.

Matsushita Electric Co. tried to make a quantum dot device of silicon nanoparticles [19-20] by the *in-situ* mixing of silicon and indium oxide nanoparticles. The objective of their study is also to clarify the size effect of particles on optical characteristics and use the size-controlled silicon nanoparticles in an optical device by controlling the color of the emitting light through a controlled band gap.

As mentioned above, the Photon Project has been able to prepare nanoparticles with nearly the same diameter and synthesize thin films containing finely controlled nanoparticles.

6. CONCLUSION

In January of last year, President Clinton of the USA

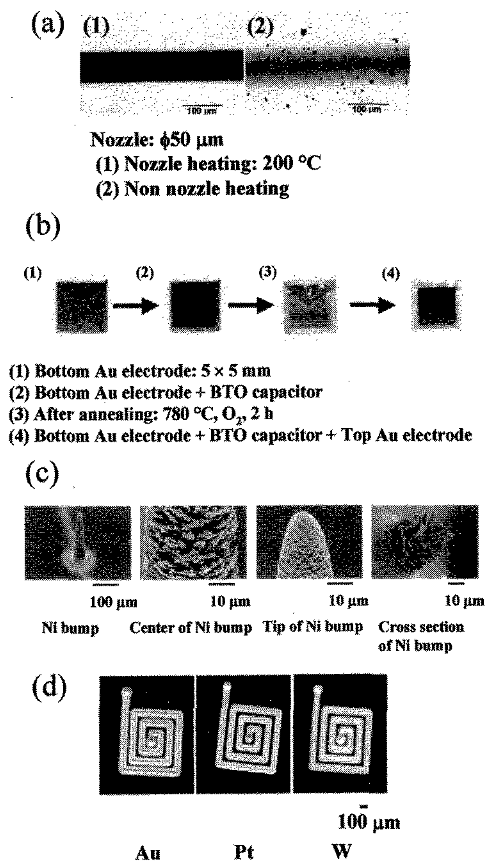

Fig.6 Micro electrical parts directly drawn using laser type JPS. (a) micro wiring, (b) multi-layer films, (c) micro bump, (d) micro electric coil.

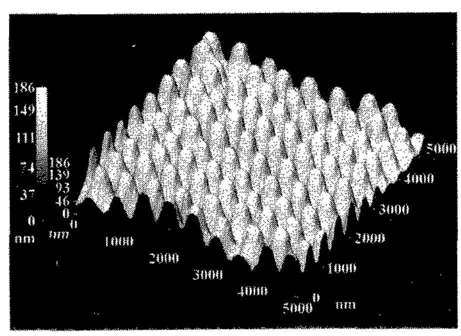

Fig.7 AFM trace of self arranged nanoparticles on a W substrate [18].

described how nanotechnology was important for the development of technology and the economy and prepared a budget for technology development. We researchers have well known the importance of this field even if President Clinton did not point it out.

This movement in the USA had a strong impact on the Japanese government and industries. National laboratories have been reorganized to strengthen their research activities in this field so that more than two nanoparticle related laboratories were created and many researchers were added to this field. Also, a huge budget might be given to this area.

In the industrial sector, the Mitsubishi Corporation and Mitsui & Co., Ltd., famous trading companies in Japan, have taken part in the nanotechnology business and constructed new companies for fullerene and carbon nanotube development. Such changes are very welcome to all people engaged in material engineering and research. Therefore, we need to clarify the market and solve the problems that are the barriers for its practical use as soon as possible. The subjects to solve are as follows.

1) The development of a size control technique for any size in the submicron size range, which can be used for mass-production.
2) To clarify the size effect that is applicable to big markets like the electrical industries, biotechnology, medical industries, environmental technology, etc.
3) The development of new mass production methods without the degradation of the quality of nanoparticles in order to decrease production costs.
4) The technique of nanoparticle handling including a classification method, stocking method, carrying method, mixing method, stabilizing method, etc., should be improved for use in industrial applications.
5) The development that relates directly to needs is requested.

7. ACKNOWLEDGEMENTS

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