Electron Microscope Observation of Ag Clusters Produced by the Ion-Cluster-Beam Method

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Ag metal clusters have been formed on carbon films supported by collodion-coated microgrids with ion-cluster-beam method and observed with a transmission electron microscope. The average size, d , of Ag clusters is about 2 nm and its dispersion, Δd , 1 nm for the deposition time, $t=15$ s, being independent of the deposition conditions. $d=12$ nm and $\Delta d=3$ nm for $t=30$ s, while $d=12$ nm and $\Delta d=7$ nm for $t=60$ s on room temperature substrates. d is larger on a room temperature than on a liquid-nitrogen-cooled substrate and it decreases by ionization and acceleration of the incident beam. The crystallinity is better on room temperature substrates than on liquid-nitrogen-cooled substrates.

(Received April 7, 1993)

Keywords: silver, metallic cluster, transmission electron microscope, nano-structure, ion-cluster-beam deposition

I. Introduction

Nano-scale-controlled-granular materials and nano-crystalline materials become frontier substances in solid state physics and material science⁽¹⁾⁽²⁾, because they yield numerous nonequilibrium structures and anomalous physical and mechanical properties owing to size-, surface- and interface-effects. In traditional metallurgy, such nano-scale particles have been mainly obtained as precipitates from supersaturated solid solutions produced by solid- or liquid-quenching and recently as fragments of metal powders by ball milling. Based upon the development of vacuum technology, however, nano-scale metal clusters and small metallic particles can be easily obtained from vapor states without any serious oxidation and contamination using combination of thermal evaporation and noble gas aggregation, laser ablation and inert-gas-ion sputtering⁽³⁾⁽⁴⁾. Moreover, since several interesting physical properties such as magnetism and superconductivity and metal-insulator transition are dominated by the atomic configurations within nano-scale region of bulk materials, nano-scale-material-tailoring is very important⁽⁵⁾.

Among several vapor-deposition techniques, the ion-cluster-beam (ICB) method is quite unique due to its high productivity of excellent flat composite films, where clusters were generated by homogeneous condensation in the adiabatically cooled supersonic vapor ejected through a crucible nozzle⁽⁶⁾. Before studying nano-scale granular materials, we have tried to produce pure metal clusters which are compositional elements of the granular material. In this study, we choose Ag, which has been a popular standard deposit.

II. Experimental Procedures

An ultrahigh-vacuum-type ion-cluster-beam (ICB) equipment (Mitsubishi D11-type) was used for the present experiment. The background pressure before deposition was 1×10^{-7} Pa and the one during deposition was 1×10^{-4} Pa. Here, the carbon crucible with a cylindrical nozzle of 1 mm in diameter and 1 mm in length was kept at about 1650 K, making the inside pressure of the crucible about 130 Pa. For the observation of transmission electron microscopy clusters formed at the nozzle region were deposited directly onto carbon films supported by collodion-coated microgrids (neutral clusters). Some clusters were deposited onto the same type substrates after electron-impact-ionization and high voltage acceleration of 2.5 kV (ionized clusters). The substrate temperature was kept at about 300 or 100 K without or with liquid nitrogen cooling. The distance between the substrate and the crucible was about 0.5 m. A quartz-crystal-oscillator-type thickness-meter was installed near the substrate holder to monitor the deposition rate, indicating the deposition rate of about 0.06 nm/s. The apparent thickness of the deposited specimens linearly depends on the deposition time, being insensitive to the substrate temperature and the ionization conditions. The deposited specimens were observed by the cold-cathode-field-emission-type transmission electron microscope (Hitachi HF2000-type) within one or two days.

III. Results and Discussion

Figure 1 shows the transmission electron micrographs of Ag deposits produced under several deposition conditions as a function of the deposition time, t . Within the resolution limit of about 0.1 nm, we can roughly estimate

Fig. 1 Transmission electron micrographs of Ag deposits made by the ion-cluster-beam method as a function of deposition time, t . (a) the clusters formed on the room temperature substrate from the neutral beam, (b) on the liquid-nitrogen-cooled substrate from the neutral beam and (c) on the room temperature substrate from the ionized beam.

distribution of the cluster size (the average diameter) of Ag deposits except for the specimen made from the ionized cluster beam for $t=60$ s.

Figure 2 shows the size-distribution of Ag clusters in terms of the cluster diameter, d , estimated from the same two dimensional areas of respective images in Fig. 1. Here, the value of d was visually estimated from these

micrographs. For $t=15$ s, the cluster size is rather insensitive to deposition conditions, showing a sharp distribution peak at around 3 nm. This result indicates that the clusters made by adiabatic expansion of supersonic vapor beam and/or formed on the substrate surface keep the original cluster size probably because of the small probability of incident clusters impinging on the

Fig. 2 Size distributions of Ag clusters formed by ion-cluster-beam method as a function of deposition time, t , estimated from Fig. 1. (a) the clusters formed on the room temperature substrate from the neutral beam, (b) on the liquid-nitrogen-cooled substrate from the neutral beam and (c) on the room temperature substrate from the ionized beam.

substrate, where smaller size deposits such as a monomer and a dimer cannot be distinguished owing to the weak contrast. For $t = 30$ s, the cluster size becomes larger than that for $t = 15$ s, indicating that the clusters coalesce each other and the smaller deposits undistinguished for $t = 15$ s may take part in the cluster growth. The clusters formed from the neutral cluster beam is smaller on the liquid-nitrogen-cooled substrate than on the room temperature substrate, indicating that the cold substrate is effective to reduce the surface migration of deposits. On the room temperature substrate the clusters made from the ionized beam are much smaller than those from the neutral beam. This is ascribable to fragmentation of the clusters by the Coulomb repulsion at the ionization region and by their hard or impactive landing on the substrate⁽⁶⁾. For $t = 60$ s, moreover, the marked growth of clusters can be detected irrespective to these deposition conditions. In particular, the coalescence of clusters is much enhanced in the specimen made from the ionized-cluster-beam (see Fig. 1(c)), because of the migration of energetic clusters over the substrate surface⁽⁶⁾ and the diffusion-enhancement of deposits by ion impinging on the substrate, i.e., an ion assisting effect⁽⁷⁾. Since the coalescence and coagulation of clusters are stochastic processes of the

Fig. 3 Electron diffraction patterns of Ag deposits formed on room temperature substrate from the neutral beam by ion-cluster-beam method as a function of deposition time, t .

incident-cluster-impingement on the substrate and the migration and collision of deposits on the substrate, the cluster-size distribution becomes much broader with increasing t , showing no characteristic distribution peak for $t = 60$ s.

Figure 3 shows the electron diffraction patterns of Ag clusters made from the neutral beam on the room temperature substrate. They show the fcc diffraction rings. In accordance with the growth of crystal size, the very broad diffraction ring for $t = 15$ s becomes sharper for $t = 30$ s and the intensity of diffraction spots increases for $t = 60$ s, indicating the cluster-coalescence and the grain growth. These features are commonly observed for the specimens made from the ionized-cluster-beam.

Figure 4 shows the high resolution images of transmission electron micrographs of Ag clusters deposited under several deposition conditions as a function of t . For $t = 15$ s, the clear lattice image can be detected for the specimens deposited on the room temperature substrates from both the neutral and ionized beams, where many clusters show a single-crystal-like lattice image. On the other hand, the fraction of the clusters with the clear lattice image is small for the specimens deposited on the liquid-nitrogen-cooled substrate. This tendency becomes prominent for the specimens for $t = 30$ s. Here, some clusters formed on the room temperature substrate have a clear lattice image and multiple twins, indicating that their crystalline states are well qualified in comparison with that on the liquid-nitrogen-cooled substrate. The specimen made from the ionized beam displays much larger clusters and linked clusters (see Fig. 1(c)). For $t = 60$ s, many clusters contain the multiple twin structure, being attributable to the enhancement of smaller clusters coalescence.

It is still debated in the ion-cluster-beam-deposition process whether or not the large metallic clusters are relevantly formed by adiabatic expansion of supersonic vapor beam⁽⁷⁾⁽⁸⁾: in the mass-spectroscopy observation of the vaporized atoms a monomer and a dimer are dominant and fractions of large clusters are very small or negligible. On the substrate, however, we can calculate the cluster size distribution in terms of the number of atoms per cluster from the results of Fig. 2. Figure 5 clearly demonstrates that nano-scale-controlled clusters have been realized on the substrate without serious

Fig. 4 High resolution images of transmission electron micrograph of Ag deposits made by ion-cluster-beam method as a function of deposition time, t . (a) the clusters formed on the room temperature substrate from the neutral beam, (b) on the liquid-nitrogen-cooled substrate from the neutral beam and (c) on the room temperature substrate from the ionized beam.

coalescence: the small size clusters of 10^3 atoms can be obtained for $t=15$ s and the large size ones of 10^4 atoms for $t=30$ s. Since coating clusters by other immiscible materials the coalescence can be effectively suppressed (encapsulation⁽⁹⁾ or matrix isolation⁽⁴⁾⁽¹⁰⁾), we can produce several nano-scale-controlled-granular materials by

ion-cluster-beam codeposition: one material constructs clusters and another constructs a matrix, where we have to adjust the relative intensity of these vapor beams.

Acknowledgment

The authors wish to thank Prof. I. Yamada and Prof.

Fig. 5 Distribution of the number of atoms, N , contained in individual clusters made by ion-cluster-beam method as a function of deposition time, t , estimated from Figs. 1 and 2. (a) the clusters formed on the room temperature substrate from the neutral beam, (b) on the liquid-nitrogen-cooled substrates from the neutral beam and (c) on the room temperature substrates from the ionized beam.

G. Takaoka in Kyoto University for their useful comment to the ICB deposition. This work was supported by the New Frontier Program Grant-in-Aid for Scientific Research (No. 04NP0501) given by the Ministry of Education, Science and Culture. One of the authors (G.H.) appreciates Japan Society for Promotion of Science for the financial support.

REFERENCES

- (1) A. E. Berkowitz, J. R. Mitchell, M. J. Carey, A. P. Young, S. Zhang, F. E. Spada, F. T. Parker, A. Hutten and G. Thomas: *Phys. Rev. Lett.*, **68** (1992), 3745.
- (2) H. Gleiter: *Prog. Mat. Sci.*, **33** (1989), 223.
- (3) O. Kajimoto: *Chemistry of Cluster*, Baifukan, Tokyo, (1992), p. 1.
- (4) R. L. Whetten, D. M. Cox, D. J. Trevor and A. Kaldor: *Surf. Sci.*, **156** (1985), 8.
- (5) T. Ikoma: *Bulletin of Japan Applied Physics Society*, **59** (1990), 289.
- (6) T. Takagi, I. Yamada and A. Sasaki: *J. Vac. Sci. Tech.*, **12** (1975), 1128.
- (7) J. G. Pruett, H. Windischmann, M. L. Nicholas and P. S. Lampard: *J. Appl. Phys.*, **64** (1988), 2271.
- (8) W. L. Brown, M. F. Jarrold, R. L. McEachern, M. Sosnowski, G. Takaoka, H. Usui and I. Yamada: *Nuclear Instrum. Methods Phys. Res.*, **B59/60** (1991), 182.
- (9) H. Usui, M. Tanaka, I. Yamada and T. Takagi: *Nuclear Instrum. Methods Phys. Res.*, **B37/38** (1989), 886.
- (10) N. Tanaka, K. Kimoto, F. Yoshizaki and K. Mihama: *Mater. Trans., JIM*, **31** (1990), 588.