Co cluster coalescence behavior observed by electrical conduction and transmission electron microscopy

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We deposited monodispersed Co clusters with mean diameters $d=6$, 8.5, and 13 nm on quartz and microgrid substrates using a plasma-gas-condensation-type cluster beam deposition system. The cluster–cluster coalescence behavior of the Co cluster assemblies was investigated by *in situ* electrical conductivity measurements and *ex situ* transmission electron microscopy (TEM). The electrical conductivity measurement indicates that, below temperature $T\approx 100\,^{\circ}\mathrm{C}$, the Co clusters with $d=8.5$ nm maintain their original size as deposited at room temperature, while the cluster–cluster coalescence takes place at their interface at $T>100\,^{\circ}\mathrm{C}$. The TEM observation indicates that the morphology of the cluster distribution shows no marked change at substrate temperatures $T_s<250\,^{\circ}\mathrm{C}$. Above $T_s=300\,^{\circ}\mathrm{C}$, the interfacial area of coalesced clusters is crystalline, and has its own orientation, different from that of two connected cluster cores. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1354158]

It has often been found that many of the physical properties of nanostructured materials are significantly different from those of their corresponding bulk counterparts. These materials have been traditionally obtained as small crystalline precipitates in matrices via low temperature heat treatments of supersaturated precursors prepared by vapor-, liquid- or solid-quenching methods. The cluster-assembling method,[1,2] in which nanometer-sized clusters are directly deposited onto a substrate, is a promising alternative by which to fabricate nanoscale-controlled materials. Throughout the assembling process, it is desirable to maintain the initial size and structure of the clusters. In practice, however, interaction among the deposited clusters takes place on a substrate, preventing one from achieving this goal. This interaction is known to depend on several factors: deposited materials, cluster size, substrate temperature, and contamination.

Recently, using a plasma-gas-condensation (PGC)-type cluster beam deposition apparatus, we have prepared monodispersed Co clusters with mean sizes of $d=6-13$ nm and standard deviation less than 10% of d.[3] In this size range, Co clusters reveal characteristic percolation behavior during the assembling process.[4] The most striking feature of the Co cluster assemblies is that the coercivity, H_c, rapidly increases at average assembly thickness of $t=2-4$ nm, which is near or below the geometrical and electrical percolation thresholds, and then is almost independent of t up to $t=100$ nm for $d=6-13$ nm. Moreover, a superparamagnetic to ferromagnetic transition is detected for sparsely deposited Co clusters with $d=6$ nm.[5] In addition, we have also succeeded in preparing the core-shell type Co/CoO monodispersed cluster assemblies which exhibited characteristic tunnel-type conductivity and enhanced magnetoresistance, which arises from the uniform Co core size and CoO shell thickness.[6] Enhancement of magnetic coercivity and macroscopic quantum tunneling of magnetization have been observed in the Co/CoO cluster assemblies.[7]

On the basis of the aforementioned studies, and considering the potential of the application of the Co cluster assembly, it is necessary to explore the cluster–cluster coalescence process above room temperature. So far, there are few reports on the experimental study of nanoscale cluster coalescence behavior, while molecular-dynamics simulation studies[8–11] of this problem have been reviewed recently. In this letter, we report the results of the electrical conductivity measurement and transmission electron microscopy (TEM) observation. We describe the relationship between the conductivity change and cluster–cluster coalescence or interfacial structure change.

The samples were prepared by a PGC-type cluster beam deposition apparatus,[3–5] which is based on plasma-glow-discharge vaporization (sputtering) and inert gas-condensation techniques.[12] The apparatus is composed of three main parts: a sputtering chamber, a cluster growth room, and a deposition chamber. The sample substrate can be heated up to 500 °C by a resistive heater and is fixed on the sample holder in the deposition chamber. We used two kinds of substrates for the Co cluster deposition: TEM microgrids for TEM observation and quartz plates with two precoated Au electrodes (4 mm in width and 1 mm separation) for *in situ* electrical resistivity measurements. The effective film thickness, t, of deposited clusters was estimated using a crystal quartz thickness monitor, which corresponds to the weight of the deposited clusters. We carried out *in situ* measurement of electrical conductivity in the deposition

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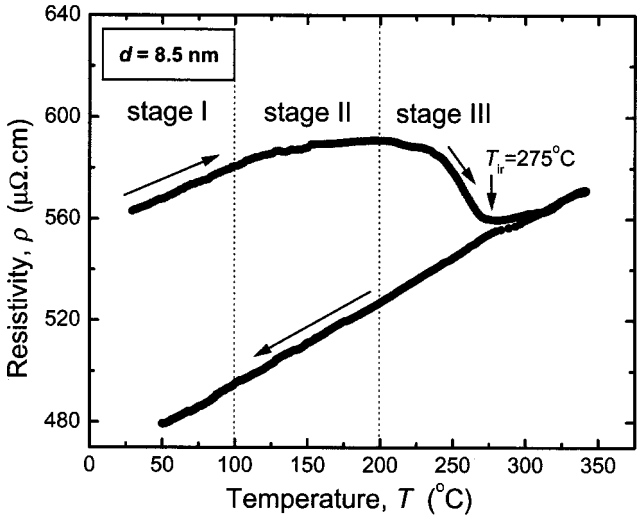

FIG. 1. *In situ* electrical resistivity ρ as a function of temperature T for the Co cluster assembly with $d=8.5$ nm and $t=300$ nm deposited onto a quartz substrate at room temperature, where the heating rate is 10 °C min^{-1}. The arrows indicate the direction of the increase and decrease of the temperature.

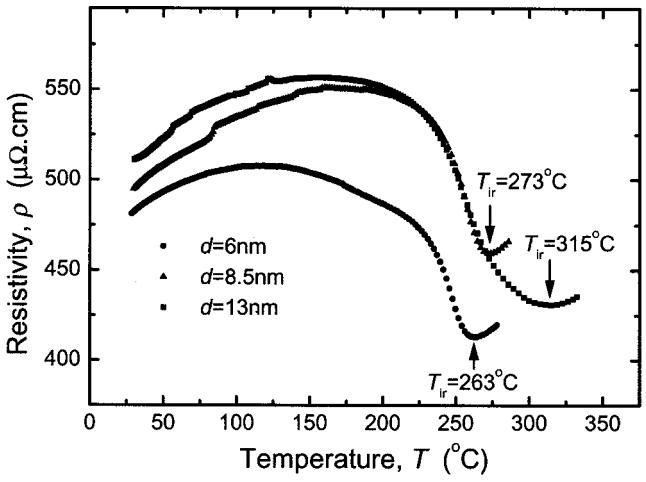

FIG. 2. *In situ* electrical resistivity ρ as a function of temperature T for the Co cluster assemblies with $d=6$, 8.5, and 13 nm and $t=300$ nm deposited onto quartz substrates at room temperature, where the heating rate is 10 °C min^{-1}.

chamber with a vacuum of about 1×10^{-6} Torr. Using a constant current mode, the voltage change between the two electrodes was detected with a digital voltmeter as a function of temperature T.

Figure 1 shows the electrical resistivity ρ vs T for the Co monodispersed cluster assembly with $d=8.5$ nm and $t=300$ nm deposited on the quartz substrate at room temperature, where the heating rate is 10 °C/min. As can be seen from Fig. 1, the temperature dependence of ρ reveals irreversible behavior, being divided into three distinct stages in the temperature-rising curve. Below 100 °C (stage I), ρ linearly increases with increasing T and shows ordinary metallic temperature dependence. This correlates well with the result obtained in the temperature range of 4.2–300 K:[6] it showed the residual resistance at low temperatures and a linear increase with increasing T. At $100<T<200$ °C (stage II), ρ still shows a gradual increase with T, but its rate of increase clearly becomes slower. This observation suggests that the cluster–cluster coalescence starts to take place at their interface in this temperature range. Above 200 °C (stage III), ρ decreases dramatically with increasing T, and then exhibits a minimum at $T_{ir}=275$ °C, which we call the irreversible–reversible transition temperature. When $T\geqslant300$ °C, the resistivity exhibits once again the ordinary metallic temperature dependence and coincides with that in the temperature-lowering curve, resulting in reversible behavior. We show the size dependence of T_{ir} in Fig. 2. This result clearly indicates that T_{ir} depends on the cluster size and is shifted towards the high temperature region with increasing cluster size. Moreover, for the Co cluster assembly with $d=6$ nm, the temperature in which the resistivity started to deviate from linear behavior is lower than that for the assemblies with $d=8.5$ and 13 nm. This observation suggests that small clusters can coalesce more easily than the large ones, probably because of the size-dependent surface melting point of Co clusters. Surface melting of platinum clusters has recently been discussed by Wang *et al.*[13] within the context of the treatment used by Buffat and Borel[14] as follows. The ratio of the melting temperature (T_m) of a Co cluster with a radius r to that of the bulk ($T_0=1493$ °C=1766 K) is given by

$$T_m/T_0=1-(2/\rho_s\lambda)[\gamma_{SL}/(r-\delta)], \tag{1}$$

where the density of the bulk solid, $\rho_s=8.9\times10^3$ kg m^{-3}, is approximately equal to that of the bulk liquid and the heat of fusion, $\lambda=263\times10^3$ kJ kg^{-1}. For the Co clusters with d

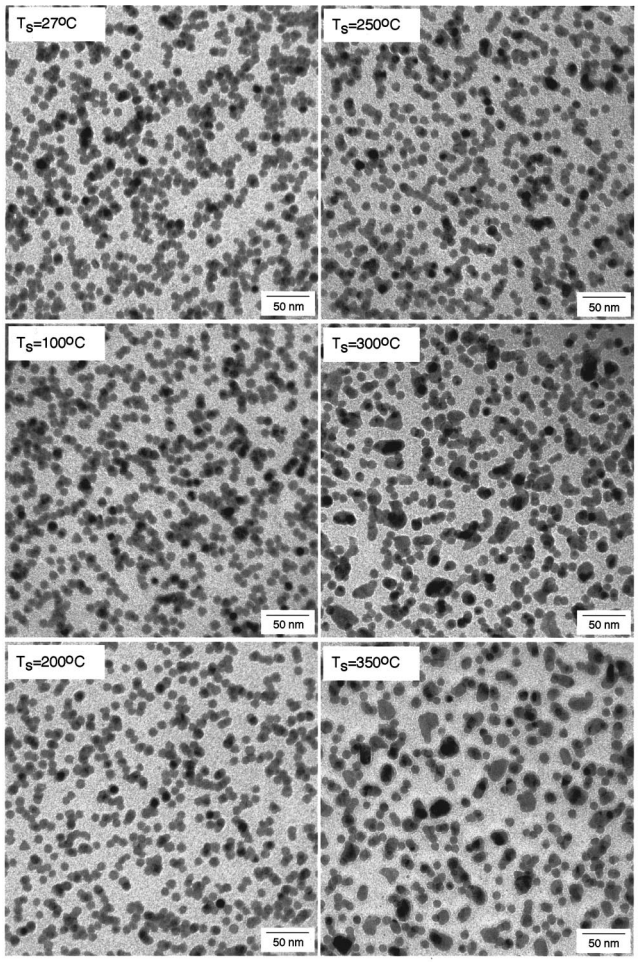

FIG. 3. Bright field TEM images of the Co clusters with $d=8.5$ nm deposited on carbon-film-coated TEM microgrids as a function of the substrate temperatures T_s.

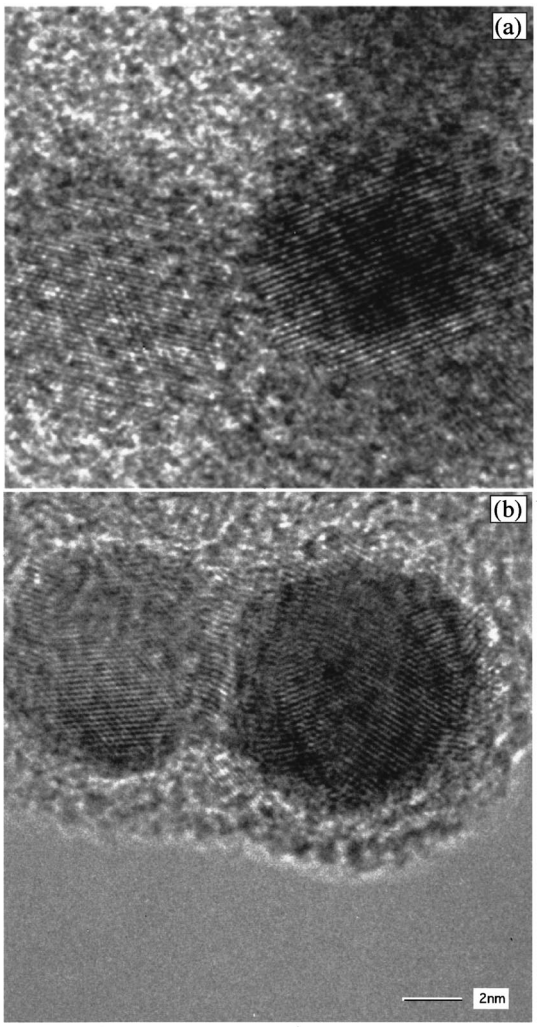

FIG. 4. High resolution TEM images of two clusters contacting each other with $d=8.5$ nm deposited at substrate temperatures of $T_s=$(a) 27 and (b) 300 °C, showing the crystalline structure of the contact area.

$=8.5$ nm ($r=4.25$ nm), if we take a liquid layer thickness, $\delta=0.25r$, then we typically calculate the Co cluster surface melting temperatures of $T_m=545$, 308, and 72 °C for $\gamma_{SL}=2$, 2.5, and 3 Nm^{-1}, respectively. Thus, this model suggests the plausibility of surface melting near 300 °C for Co clusters.

Figure 3 shows bright field TEM images observed at room temperature for the initial deposition stage of Co clusters with $d=8.5$ nm produced at several substrate temperatures, $T_s=27$, 100, 200, 250, 300, and 350 °C. The substrate temperature was only kept during the deposition time (about 2 min) and then was decreased to room temperature. As shown here, at $T_s=27$ °C (room temperature), the clusters are almost monodispersed even though some clusters contact and overlap each other. The morphology of the cluster distribution shows no marked change up to $T_s=250$ °C although the electrical resistivity measurement reveals that the coalescence starts even as low as $T=100$ °C. Using image-analysis software (Image-Pro PLUS: Media Cybernetics), we further estimated the size distributions of the clusters not touching and overlapping each other in the digitized images recorded by a slow scan charge coupled device (CCD) camera in an object area of 350×350 nm^2. The estimated mean cluster sizes are $d=8.54$, 8.56, 8.46, and 8.47 nm with standard deviation of less than 10% of d for $T_s=27$, 100, 200, and 250 °C, respectively, which are insensitive to T_s. When $T_s>250$ °C, the morphology of the cluster distribution is remarkably changed and intercluster coalescence and growth or reconstruction of the combined clusters are detected, in agreement with the behavior of the rapid decrease of the resistivity in this temperature range (Fig. 1, stage III).

As described above, the TEM observation and the electrical resistivity measurement of the coalescence process of the clusters are different from each other in the temperature range of $T=100-250$ °C. This indicates the higher sensitivity of the resistivity measurement for the change of interface structure in comparison with the TEM observation. On the other hand, the fact that the morphology of the cluster distribution shows no marked change up to $T_s=250$ °C also suggests that cluster–cluster coalescence mainly takes place in the interfacial area or contacting part within such a short deposition time. In order to further examine the microstructure of the interfacial regions of the combined clusters, high resolution TEM observation seems to be an effective method. However, it is difficult to obtain good images containing information on the interfacial structure. Figure 4 gives typical images of two Co clusters which contact each other prepared at $T_s=27$ and 300 °C. For $T_s=27$ °C [Fig. 4(a)], we do not detect the tendency to coalesce between the two clusters touching each other, while for $T_s=300$ °C [Fig. 4(b)], the two clusters are connected and form a so-called neck structure. Moreover, we can see that the interface region of the two clusters possesses its own crystal orientation, different from that of the two cluster cores. This indicates that the interfacial area of the clusters contacting each other is crystalline at $T_s=300$ °C: they not only ''touch'' but also partially coalesce in the interface area.

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