

Composite deposition of Co and Si clusters by rf/dc plasma-gas-codensation

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A double-glow discharge cluster source system has been made by modification of a conventional co-sputter-deposition apparatus. Using this equipment, we tried to produce Co clusters generated by a dc glow discharge mode, Si clusters by an rf glow discharge mode, and deposit them simultaneously on a substrate. Putting a separate plate between these two glow discharge rooms, we have obtained a mixture of Co and Si clusters. Here, the Co clusters are distributed rather at random, while the Si clusters are aggregated to form a larger group. Taking off the separate plate, we have obtained core-shell clusters, in which small Si clusters surround Co core clusters. These features are quite different from the instantaneous alloying and/or very rapid atom diffusion that has been expected at contact interfaces between nanometer-sized small Co and Si clusters. They suggest that this double-cluster source system is useful to fabricate various sorts of cluster composites that cannot be prepared by thermodynamical methods, such as co-evaporation and precipitation.

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Cluster-assembling is a candidate process for fabricating nanoscale structure-controlled materials.¹ For this purpose, we have to make clusters regular in size to utilize the size-dependent characteristics, to prevent clusters from oxidation and surface coalescence, and to keep their independence on a substrate. Using a plasma-gas-condensation (PGC)-type cluster deposition apparatus, we have prepared monodispersed transition metal clusters with the mean diameter d between 6 and 15 nm and a standard deviation less than 10% of d .² When we deposit such clusters on a substrate and increase the deposition time, the number of clusters increases, while their intact sizes are maintained in this size range. For Co clusters, we have observed a geometrical and electrical percolation³ and a change from superparamagnet to ferromagnet at a certain critical deposition time.⁴ We have tried to oxidize the surfaces of transition-metal clusters uniformly,⁵ to stabilize cluster surfaces, and to protect coalescence of nanometer-sized clusters because the melting point of their oxides is so high. Moreover, we may add a character to simple metal clusters by surface oxidation. The core-shell-type monodispersed Co/CoO cluster assemblies thus obtained reveal tunneling-type conduction properties⁵ and a macroscopic tunneling-type magnetic relaxation,⁶ which can well be separated from the thermal hopping and classical relaxation regimes at high temperatures.

When we deposit vapor atoms and clusters on substrates, extremely fast migration of atoms and microclusters has been observed even at ambient temperature.^{1,7} This feature is attributed to surface diffusion of atoms, surface melting of clusters and/or defect-induced diffusion of clusters. One of the spectacle features in metallurgy is the spontaneous alloying for island-like metal clusters prepared on transmission electron microscope grids by thermal evaporation:⁸ the initially formed metal clusters are alloyed with metal atoms

supplied by the post-evaporation. In this context, it is very interesting to study what happened by simultaneous deposition of two different kinds of clusters, while it also increases variety of cluster-assembled materials.

We made a two-source PGC cluster deposition system by modifying our previous co-sputter-deposition apparatus, which has a couple of facing target-type sputtering rooms used for preparing alloy films.⁹ Figure 1 schematically shows the experimental setup. Here, one cluster source system is operated with dc glow discharge mode for preparing metal clusters and another in rf glow discharge mode for preparing nonmetallic materials. For preparing clusters, we reduced the distance between the target-shield space to prohibit arc-discharge in high Ar gas atmosphere (from 0.1 to 1 kPa).¹⁰ We rebuilt an air-tight wall between sputter chamber and deposition chamber to differentiate the vacuum conditions of these two regions. A removable separation plate can be placed between chambers 1a and 1b, where the vacuum con-

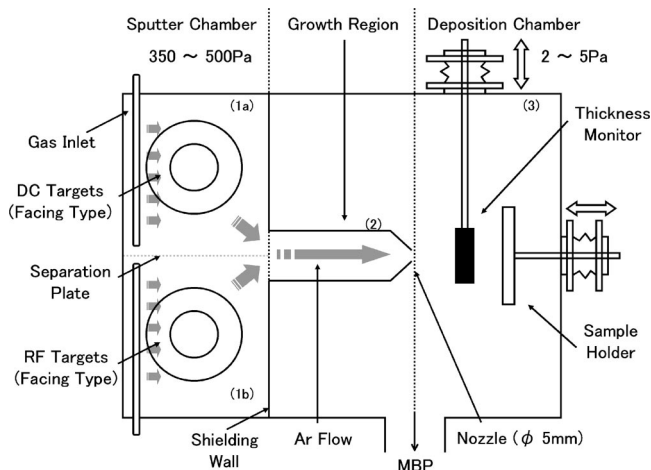


FIG. 1. Schematic set-up of the two-source PGC apparatus.

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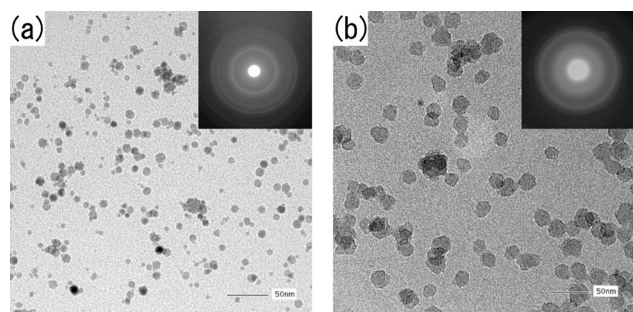


FIG. 2. Bright-field transmission electron microscope (TEM) image and electron diffraction (ED) pattern of (a) Co clusters deposited on a carbon microgrid by a single dc glow discharge mode and (b) Si clusters deposited on a carbon microgrid by a single rf glow discharge mode.

ditions of both chambers are almost the same. A large amount of Ar gas, whose flow rate was 200 to 400 sccm, was introduced into the sputtering chamber from a gas inlet, and evacuated by powerful mechanical booster pump (500 m³/h) through a small nozzle. The clusters formed in the growth region were ejected together with Ar gas through this small nozzle.

Even in a simple Si cluster deposition, it was rather difficult to stabilize rf discharge in such high Ar gas atmosphere, because the rf plasma could not be confined near the targets, although the dc plasma could easily be so confined. Figures 2(a) and 2(b) show typical transmission electron microscope images of elemental clusters obtained by a simple discharge mode: (a) Co clusters obtained by the dc glow discharge mode and (b) Si clusters obtained by the rf glow discharge mode. The sizes of these clusters are not so monodispersed as those prepared by using our previous single-cluster source PGC cluster deposition system. In the present experiments, since the cluster nucleation and growth could not be confined in a small space, there was a wide variety of cluster sizes. In the previous experiment,² on the other hand, several differentially pumped rooms were connected to carry clusters into better vacuum condition and to minimize their aggregation. Moreover, such a long transportation path also serves to exclude smaller clusters before deposition. These factors lead to a size selection of larger clusters. In Fig. 2, the average size of Si clusters is much larger than that of Co clusters. A careful observation indicated that Si clusters seemed to be secondarily grown particles composed of much smaller primary particles. The electron diffraction experiment indicates that the structure of Co clusters is fcc and that of Si ones is amorphous.

When both dc and rf glow discharges were simultaneously operated and the electric power of the rf discharge was rather high, the rf and dc discharges interfered each other. Since the glow discharges were unstable, we could apply rather small rf powers in comparison with flexible dc powers. Thus, the vaporization ratio of Co and Si could not be well controlled in double-discharge experiments, as opposed to a rather smooth control in the single dc glow discharge experiments. Figure 3(a) shows the Co and Si cluster assembly prepared with placing the separation plate between chambers 1a and 1b and under the following conditions: the Ar gas flow rate is 300 sccm, the dc input power is 170 W, and the rf input power is 150 W. Here, separated clusters of

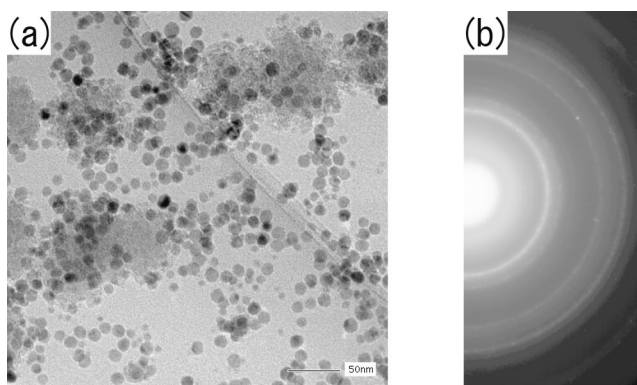


FIG. 3. Bright-field TEM image (a) and ED pattern (b) of Co and Si clusters deposited on a carbon microgrid by the dc and rf double-discharge mode, placing the separate plate between the two discharge regions: the dc glow discharge for Co and the rf glow discharge for Si. The average chemical composition of the cluster assembly is about 42 at. % Co.

about 10 nm in diameter are Co-rich clusters, while larger, cloudy ones are probably Si-rich clusters, because the latter morphology is similar to the one observed in Fig. 2(b). The average chemical composition of these clusters is about 42 at. % Co. As shown in Fig. 3(b), the diffraction pattern consists of fcc rings and broad halo rings, being attributed to Co and Si clusters, respectively.

Figure 4(a) shows Co and Si cluster assembly prepared without placing the separation plate and under the following conditions: the Ar gas flow rate is 300 sccm, the dc input power is 250 W, and the rf input power is 150 W. As seen in this figure, the dark contrast regions were usually surrounded by the gray contrast regions, a so-called core-shell structure. This feature is different from that in Fig. 3(a), while the diffraction pattern shown in Fig. 4(b) consists of diffused fcc rings and broad halo rings, similar to those in Fig. 3(b). The chemical composition of this assembly is about 37 at. % Co. However, we were able to measure the chemical composition of the core-shell-type cluster that was prepared with the similar operational condition, but had different chemical composition. As shown in Fig. 5, the chemical composition of the dark core region is about 56 at. % Co and that of the gray shell region is about 19 at. % Co, whereas the average one is about 28 at. % Co.

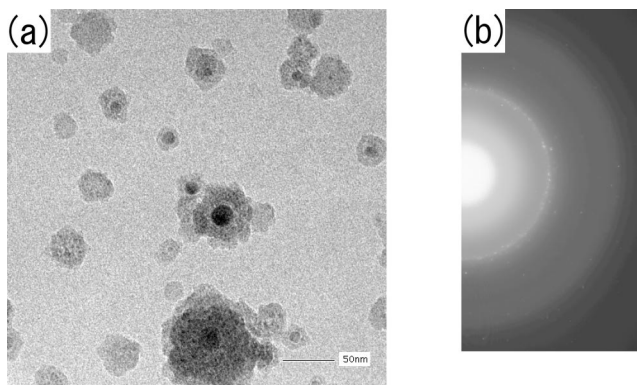


FIG. 4. Bright-field TEM image (a) and ED pattern (b) of Co and Si clusters deposited on a carbon microgrid by the dc and rf double discharge mode without placing the separate plate between the two discharge regions: the dc glow discharge for Co and the rf glow discharge for Si. The average chemical composition of the cluster assembly is about 37 at. % Co.

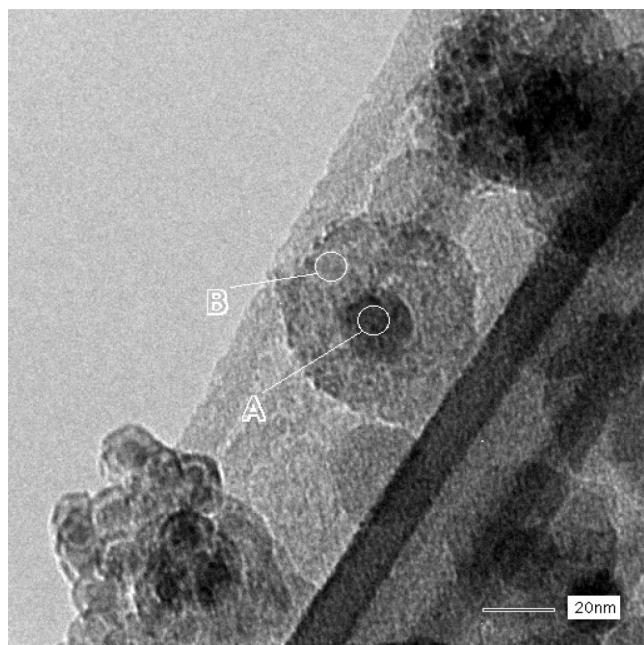


FIG. 5. Bright-field TEM image and energy-dispersive x-ray analyses of Co and Si clusters deposited on a carbon microgrid by the dc and rf double-discharge mode without placing the separate plate between the two discharge regions: the dc glow discharge for Co and the rf glow discharge for Si. The average chemical composition of the cluster assembly is about 28 at. % Co.

These immiscible characters are quite different from the previous experiment, in which we oppositely placed two different metal targets and used the single-glow discharge mode in homogeneously alloyed clusters.¹¹ In the equilibrium phase diagram, moreover, Co and Si form very stable intermetallic compounds, CoSi, Co₂Si, and CoSi₂,¹² indicating their formation enthalpies are negative and their absolute values are so large that Co–Si alloy clusters have been expected, in contrast to the present results. Indeed, there have been many reports on the instantaneous alloying between nanoscale island-like clusters on substrates with post-deposited atoms at ambient temperature⁸ and rather easy silicide formation when island-like grown films are deposited on a silicon substrate and annealed above 400 °C.¹³

When we carefully check the equilibrium phase diagram of Co–Si system,¹² Co forms the primary solid solution up to 12 at. % Si at about 750 °C, while Si forms almost no primary solid solution up to 1400 °C. Since the vaporized atoms and clusters are very quickly thermalized in such a high Ar gas atmosphere, Co clusters and Si clusters do not reach their equilibrium states when they are formed separately, mixed later in the growth region, and simultaneously deposited on the substrate, as shown in Figs. 3 and 4. There are many defects and irregularities on the cluster surfaces that are much less stable in the Si clusters, whose chemical bonds

are covalent and anisotropic, in comparison with the Co clusters, whose chemical bonds are metallic and isotropic. The strong covalent bonds enhance the secondary aggregation of primary Si clusters, as shown in Figs. 2 and 3. If the cluster nuclei are mixed before they enter the growth duct, the Co clusters act as nuclei of Si primary clusters to form the core–shell clusters. Even then, we cannot explain why and how intercluster atom diffusion is suppressed and Co and Si clusters do not coalesce to form alloy clusters at their contact and/or collision events. In the present experiment, we have to take into account of the vacuum condition (0.1 Pa) of the cluster deposition chamber being more than three orders of magnitude worse than in the previous experiment.^{2,14} If very active Si cluster surfaces are oxidized by O₂ impurity included in Ar gas, the alloying of Si with Co are severely suppressed. At present, we cannot clearly explain the immiscibility between nanometer-sized Co and Si clusters. However, these unique results suggest forming ability of various sorts of Co and Si nanocomposite materials.

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