Structures and Physical Properties of Metal-MgO Single Crystalline Composite Films

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Metal-MgO single crystalline composite films including nm-sized metal crystallites (Au, Pd, Fe, Co, Ni) and atom clusters were prepared by a simultaneous vacuum-deposition. The atomic structures and their influences on the electric resistivity and magnetic properties were studied for Au-MgO and Fe-MgO composite films. The resistivity of the Au-MgO films is affected by gold clusters embedded in MgO films. The magnetic properties of the Fe-MgO films show a spin glass-like nature that may be due to aggregates of iron crystallites. Growth of nm-sized γ -iron crystallites is also found in as-grown Fe-MgO composite films prepared at 350°C.

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I. Introduction

Composite films including nm-sized metal crystallites and atom clusters are currently of great interest in studying the quantum size effect and also in developing new functional materials. In the 1970's, metal-SiO₂ cermet films⁽¹⁾ as one of the composite films were extensively studied for search of new physical properties, especially the transport properties, optical properties and magnetic properties⁽²⁾.

The composite films (cermet films) were usually composed of an amorphous matrix and randomly oriented metal crystallites of a few nm in size, because they were prepared by sputtering. Electron microscope observations of the films gave information about the size and separation distance of the crystallites. Detailed studies about the atomic structures related to the properties have not been performed due to the insufficient image resolution.

In our previous studies of gold crystallites and clusters in vacuum-deposited films by high-resolution electron microscopy, we concluded that single crystalline matrices or supporting films were more suitable than amorphous ones for observations of small clusters⁽³⁾. Epitaxially oriented nm-sized metal crystallites in/on single crystalline films are helpful to study origins of the physical properties with anisotropy.

On the basis of these results, we have recently developed single crystalline composite films of metals and magnesium oxide (MgO), where nm-sized metal crystallites and atom clusters are embedded in single crystals of MgO⁽⁴⁾⁻⁽⁷⁾. The single crystalline nature and high transparency for electrons are useful for observations of atom clusters of lighter elements such as 3d tran-

sition metals.

In the present paper, we describe recent results of structures and physical properties of the metals (Au, Pd, Fe, Co, Ni)-MgO composite films, especially the electric resistivity and magnetic property.

II. Experimental

Metal-MgO composite films including nm-sized metal crystallites and atom clusters were prepared by a simultaneous vacuum-deposition of metal and MgO. The metal and MgO were deposited simultaneously on (001) cleaved and (011) polished surfaces of sodium chloride. The substrate temperature was set to be 300 to 350°C for epitaxy. Thickness of the composite films was measured to be 2 to 30 nm by a quartz oscillator. Deposition rates of the metal and MgO were 0.05 to 0.3 nm/s and 0.3 to 1.0 nm/s, respectively. Volume fraction of the metal was controlled to be 5 to 40%. In order to ensure embedding of metal crystallites, MgO of 10 nm in thickness was deposited both sides of the composite films. Total thickness of the specimens is thus 22 to 50 nm. Atomic absorption spectroscopy was also used to measure metal content in MgO. The composite films thus prepared were separated from the substrate in water and mounted on a microscopic grid for observations with high-resolution electron microscopes (H-1250ST, JEM-4000EX and JEM-2010).

Annealing of as-grown composite films was performed in situ after deposition in a temperature range of 100 to 500°C, and also performed in another chamber in a range from 500 to 900°C by mounting on the microscopic grid.

Measurement of the electric resistivity was performed by the DC four-probe method in a vacuum chamber with electrodes of gold on the substrate. The magnetic property was measured with a SQUID magnetometer (Hokusan, HSM-200). The specimens were also accom-

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panied with the substrate. The thermo-magnetic curves (M-T curves) were recorded in a temperature range from 4 to 300 K.

III. Results and Discussion

Figure 1 shows an electron micrograph and the diffraction pattern of a palladium(Pd)-(011)MgO composite film prepared at 350°C. The diffraction pattern shows that palladium grows with an epitaxial orientation parallel to a MgO single crystal. Multiply twinned particles are not observed as in the vacuum-deposited films on MgO. In the micrograph, palladium crystallites are identified with a size of 1 to 2 nm with dark contrast. The 111 and 200 lattice fringes appearing in the crystallite regions are identified as those of palladium or MgO, depending on the defocus condition of microscope. The phenomenon is a kind of selective imaging in high-resolution electron microscopy⁽³⁾, when two crystals with different lattice spacings are overlapped. The feature is similar to that of gold(Au)-MgO composite films⁽⁵⁾. The lattice misfit of (200) planes between palladium and MgO is 7.6%, which is larger than that of Au-MgO composite films. Discontinuity of the 111 lattice fringes at the boundaries is sometimes observed as indicated by arrows, which may be due to existence of dislocations. The growth features in respect of the density and size-distribution of the palladium crystallites are similar to those of previous Au-MgO composite films⁽⁴⁾⁽⁵⁾⁽⁷⁾.

Figure 2 shows electron micrographs of Au-MgO composite films with different deposition rates of gold and

with constant deposition of MgO. The films were prepared at a time using a specially designed deposition apparatus, which can control the deposition rate on each of the films⁽⁷⁾. We have noticed from the electron micrographs that the density of the crystallites reduces by one-half from $3.2 \times 10^{12}/\text{cm}^2$ (a) to $1.4 \times 10^{12}/\text{cm}^2$ (c), but the average lateral size of the crystallites is relatively unchanged as indicated by arrows. The decrease of the density with the similar average size increases the separation distance between the crystallites, which affects the electron transport property as shown in Fig. 3.

From the results of the present and previous studies of vacuum-deposited films, it is inferred that the surface migration of metal atoms on the growing MgO surface is depressed by MgO vapor in the simultaneous deposition and the coalescence process between metal crystallites is also suppressed. The phenomena make the size of the crystallites relatively small and similar.

Figure 3 shows data on the specific resistivity (ρ) of Au-MgO and Pd-MgO composite films against volume fraction of the metals as evaporated. With increasing the volume fraction, the resistivity drops drastically. The tendency is similar to those of other cermet films below the percolation threshold⁽²⁾. Low resistivity of Pd-MgO films is due to more connection of palladium crystallites than gold ones even in the similar deposition condition. Specimen 'Au-2' is prepared by an inclined deposition.

Figure 4 shows data on the temperature dependence of the resistivity (ρ) of Au-MgO composite films prepared on a substrate at 350°C and annealed after the first measurement. The resistivity changes apparently linearly

Fig. 1 High-resolution electron micrograph and the diffraction pattern of a Pd-(011)MgO composite film. The Pd crystallites are identified with dark contrast. Arrows indicate misfits of 111 lattice fringes at the boundaries between Pd and MgO.

Fig. 2 Electron micrographs of Au-MgO composite films prepared with changing the deposition rate of gold and with constant rate of MgO. With decreasing the gold deposite ((a)→(c)), the density of the Au crystallites decreases, although the size is relatively unchanged. Arrows indicate typical Au crystallites.

Fig. 3 Specific resistivity(ρ) of Au-MgO and Pd-MgO composite films against volume fraction of the metals. The specimen, 'Au-2' is prepared by an inclined deposition.

Fig. 4 Temperature dependence of specific resistivity(ρ) of an as-grown Au-MgO composite film and annealed ones. The temperature coefficient is negative from 20 to 100°C, and the resistivity increases from 100 to 220°C for the as-grown film.

with a negative temperature coefficient from 20 to 100°C and increases gradually from 100 to 220°C for the as-grown film. When the as-grown specimen is annealed at 220°C for 2 h, the resistivity rises up from a point (a) to a point (b). When the annealed specimen is heated from room temperature, the resistivity passes through again the point (b) and begins to increase as shown in the second curve. The increase is thus due to an irreversible process occurring inside the films.

The data in the apparently linear regions are plotted in scales with $\log(1/\rho)$ versus $1/T^{(8)}$, $\log(1/\rho)$ versus $1/\sqrt{T}^{(9)}$ and $\log(T/\rho)$ versus $1/T$ (hopping model). Since the difference for the fitness between the $1/T$ and $1/\sqrt{T}$ plots is not appreciable in the temperature range measured here, we try to interpret the data through the $1/T$ plot based on a model by Neugebauer⁽⁸⁾: Electrons are transported by tunneling between charged metal crystallites separated by insulators, where the charging is caused by the thermal activation from the neutral state. Based on the model, the activation energies are determined to be 0.026, 0.022 and 0.013 eV for composite films of volume fraction of gold, 12, 18 and 36%, respectively. It is also found that the activation energies are scarcely changed by annealing up to 300°C, where the resistivity increases as shown in Fig. 4.

We have successfully observed what kind of change occurs inside the composite films before and after the annealing. Figure 5 shows a pair of 'off-Bragg' high-resolution images of a Au-(011)MgO film as-grown and annealed at 200°C for 0.5 h. The off-Bragg microscopy was developed by the present authors in order to identify atom clusters without disturbance of lattice fringes of MgO⁽¹⁰⁾. Some atom clusters become smaller and some

disappear after the annealing as indicated by the arrows. On the other hand, larger crystallites of a few nm in size do not apparently change their separation distances and positions, although their sizes are changed a little. According to the previous study⁽⁴⁾, a shape of gold crystallites was changed by annealing at 400°C due to surface diffusion of gold atoms. We may conclude that constituent atoms of the gold clusters diffuse into the larger crystallites (absorption) and then the small clusters disappear. The disappearance of the atom clusters may change the tunneling property between the gold crystallites through the MgO matrix. The overall resistivity thus changes. Existence of the atom clusters has been inferred also by a combination of the atomic absorption spectroscopy of metal content in the composite films and the measurement of volume of the crystallites from the electron micrographs.

This result suggests that the electric resistivity of these composite films including single atoms and atom clusters has a term connected with an irreversible process caused by heating, as well as another term due to a reversible one. Initial annealing for an appropriate time exhausts the former term. After that, the latter term with a negative temperature coefficient remains, which is determined mainly by the separation distance and size of the crystallites. The present specimens are easier to obtain information on them by using electron microscopy, than those of previous cermet films with amorphous matrices and randomly oriented metal crystallites.

Figure 6 shows an electron micrograph and the diffraction pattern of an iron(Fe)-(001)MgO composite film including nm-sized iron crystallites and atom clusters⁽⁶⁾. The diffraction pattern shows that the iron crystallites have a b.c.c. structure (α -Fe) and two kinds of epitaxial orientations as (1) $(01\bar{1})[100]_{\text{Fe}} // (001)[100]_{\text{MgO}}$ and (2) $(001)[110]_{\text{Fe}} // (001)[100]_{\text{MgO}}$. Iron oxides have not been apparently detected in the diffraction pattern. From the micrograph, the lateral size of the iron crystallites is estimated to be 1.0 to 2.0 nm. A vertical length of the crystallites along the z -direction ($[001]$ direction) has been estimated from another micrograph taken at a tilted incidence by 20° from the $[001]$ axis. The vertical length depends on the deposition time for a deposition ratio of iron and MgO. For the composite films of 20 nm in thickness, the length of the iron crystallites is 3 to 5 nm.

When the as-grown films are annealed at 450°C for 1 h, the size and separation distance does not seem to change. However, migration and diffusion of iron atoms in MgO crystals may be expected on the analogy of Au-MgO films. When the as-grown films are annealed above 550°C, most of the α -iron crystallites embedded in MgO transform into γ -iron ones⁽⁶⁾. Some of the α -iron crystallites remain with the same structure. After the transformation, the neighboring crystallites make a coalescence. A strain is generated at the periphery of the γ -iron crystallites, which is for accommodation of lattice misfit between γ -iron ($a=0.36$ nm) and MgO ($a=0.41$ nm). The coalescence process continues up to 800°C. After annealing over 900°C, nucleation of spinel,

Fig. 5 Pair of off-Bragg high-resolution electron micrographs of Au-MgO composite films at the same region: as-grown (a) and annealed one at 200°C for 0.5 h (b). Arrows indicate atom clusters less than 1 nm in size.

Fig. 6 High-resolution electron micrograph and the diffraction pattern of a Fe-(001)MgO composite film. The α -iron crystallites of b.c.c. structure are embedded with two kinds of epitaxial orientations (A, B).

Fe_2MgO_4 was observed⁽⁶⁾⁽¹¹⁾.

Recently we have found a growth of γ -iron crystallites in as-grown composite films prepared at 350°C. Figure 7 shows electron micrographs of Fe-(001)MgO composite films with a change of the thickness of composite films (deposition time). For the film with a thickness of 1.8 nm (a), the diffraction pattern shows a growth of γ -iron crystallites. The existence is confirmed also by moiré fringes with spacing of 1.36 nm in the image⁽⁶⁾. For the

Fig. 7 Electron micrographs and the diffraction patterns of Fe-MgO composite films with changing the total thickness: $t=1.8$ nm (a) and $t=7.2$ nm (b).

film with a thickness of 7.2 nm (b), the diffraction pattern and moiré fringes of 0.45 nm in the image indicate an existence of α -iron in MgO. The lower temperature of the formation of the γ -iron crystallites is interesting because the transformation temperature from α - to γ -iron is 906°C for bulky iron.

The above transformation with increasing the thickness may be interpreted in terms of the size effect in the growth process: The vertical length along z -direction becomes longer with deposition time as described before. The lateral sizes of the crystallites are not so much changed with deposition time. It is thus inferred that the transformation is caused by the increase of the size along the z -direction.

Figure 8 shows a high-resolution electron micrograph of the as-grown Fe-(001)MgO composite film including the γ -iron crystallites. The 200 lattice fringes of the γ -iron bend at the periphery as indicated by the arrows. The bending was observed also in γ -iron crystallites prepared by annealing at 550 to 800°C⁽⁶⁾. The bending is due to strain of γ -iron lattices to accommodate the lattice misfit between γ -iron and MgO⁽⁶⁾.

Figure 9 shows thermo-magnetic curves of the γ -iron-MgO composite film shown in Fig. 8 as well as those of the α -Fe-MgO composite film shown in Fig. 6. The curves change in two ways with temperature depending on zero field cooling (ZFC) and field cooling (FC). The ZFC curves have a maximum whose temperature (T_g) is ranging from 30 to 100 K depending on the volume fraction of iron in MgO. With increasing external magnetic field (H), the temperature (T_g) shifts to lower values and ultimately approaches 4 K, where the maximum does not seem to be observed and only a Curie-Weiss type curve (FC curves) remains. Most of studies about magnetic

Fig. 8 High-resolution electron micrograph of γ -Fe crystallites in MgO. The 200 lattice fringes bend at the periphery due to accommodation of lattice misfit between γ -Fe and MgO.

Fig. 9 Thermo-magnetic curves of a γ -Fe-(001)MgO composite film as shown in Fig. 8 as well as α -Fe-(001)MgO one in Fig. 6. The notation, FC means the field cooling curves and ZFC, zero-field cooling ones.

properties of aggregates of fine iron crystallites were concerning with the FC curves due to high external field⁽¹²⁾. Initial magnetization curves as the ZFC curves which can be measured at lower external field such as 3.97 kA/m (50 Oe), were discussed only in some papers^{(13)–(15)}. In the present experiment, use of a SQUID magnetometer enables us to focus on the ZFC curves. Although measurements of both ZFC and FC curves are common in studies of spin glass state in diluted magnetic alloys.

With increasing volume fraction of iron, the characteristic temperature (T_g) shifts to higher values up to R.T. The values of magnetization and the characteristic temperature were scarcely changed before and after the an-

nealing at 450°C for 1 h. During the annealing, iron atoms and clusters may diffuse in MgO films as discussed before. This result suggests that nm-sized iron crystallites observable in electron microscope images such as those shown in Fig. 6 may be responsible for the magnetization curves.

Figure 10 shows an electron micrograph (a) and the thermo-magnetic curve (b) of an α -Fe-MgO composite film similar to that shown in Fig. 6, prepared at R. T. In the micrograph, the size of iron crystallites becomes less than 1 nm, which is about by half smaller than that in Fig. 6. The separation distance between the crystallites is 1 to 2 nm, which is not so much different from that in Fig. 6. In the thermo-magnetic curves, the characteristic temperature (T_g) is 28 K, which is the lowest value in the course of the study. Magnetic property of an iron-doped MgO single crystal where iron atoms are randomly distributed, is also measured with the same external field. The thermo-magnetic curves are similar to the Curie-Weiss type ones without the characteristic maximum. Therefore, the curves in Figs. 9 and 10 can be continuously related to those of the iron-doped MgO crystals. Incidentally, the magnetic properties of Co-MgO and Ni-MgO composite films prepared by the same method showed a similar nature, although the magnetization decreases in this order.

The behaviors of the curves with changing the volume fraction (concentration of iron) and external magnetic field are similar to those of spin glass state observed in diluted magnetic alloys such as Au-Fe⁽¹⁶⁾. The composite films may be categorized as 'insulating spin glass'⁽¹⁴⁾ in place of 'metal spin glass'. In the metal spin glass, spins located on atoms correlate with each other by the RKKY interaction. The present result could be interpreted in models with (1) anti-ferromagnetic coupling of nm-sized iron crystallites (superparamagnetic for themselves in R.T.) with tunneling electrons between thermally charged crystallites⁽⁸⁾ or with electro-magnetic forces, (2) crystalline anisotropy of individual iron crystallites or (3) correlation between iron atom and atom clusters such as dimer⁽¹⁷⁾. Based on the second model, Chien *et al.*⁽¹⁵⁾ discussed the effect of the anisotropy in the case of Fe-SiO₂ cermet films, and concluded that the estimated anisotropic energy of their iron crystallites observed by electron microscopy is much larger than that of bulky iron. In the present specimen, however, the effect of iron atom clusters and single atoms on the magnetic property may not be so much, because (1) annealing at 450°C for 1 h does not change the characteristic temperature (T_g), and (2) decrease of the size of the iron crystallites changes the characteristic temperature from 100 K to less than 30 K as shown in Fig. 10. We have to thus search for the origin of the magnetic property in the first and second models based on nm-sized crystallites.

In previous studies of aggregates of iron crystallites prepared by the gas evaporation technique⁽¹²⁾, the origin of the magnetic properties was sought in the crystallites with magnetic moment caused by ferromagnetic coupling of spins. On the other hand, the magnetic properties of

Fig. 10 Electron micrograph and the thermo-magnetic curve of an Fe-MgO composite film prepared at R.T.; α -iron is embedded in MgO as smaller crystallites than those prepared at 350°C in Fig. 6.

diluted iron alloys such as Au-Fe⁽¹⁶⁾ have been interpreted in terms of randomly distributed spins with interaction by conduction electrons. Recent studies of spin glass in Au-Fe and Cu-Fe alloys, however, suggested the existence of iron clusters of a few atoms in noble metal matrices as the origin of the magnetic properties⁽¹⁸⁾. As shown in Fig. 10, in the ultimate case of our composite films, the size of iron crystallites is about 0.6 nm, which are composed of tens of iron atoms. The state is not so much different from the spin glass state in the diluted iron alloys, although the matrix is insulator. We thus believe that the present study of the magnetic property of Fe-MgO composite films may be useful for interconnecting the studies of magnetic properties of the aggregates of crystallites and the diluted alloys.

In conclusion, the present composite films prepared by the simultaneous vacuum-deposition are composed of nm-sized crystallites and atom clusters embedded in MgO crystals. Existence of the clusters may be reasonably accepted in viewpoints of the crystal growth. The atom clusters play an important role for the electric resistivity in the Au-MgO films and not so much for the magnetic property in the Fe-MgO films. The analyses of the crystallites and clusters as well as interfaces between the crystallites and matrices are essentially important for understanding physical properties of these kinds of composite films.

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