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Formation processes of ultrafine metal particles on MgO(100) as investigated by molecular dynamics and computer graphics

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Abstract

A new molecular dynamics (MD) code was developed to simulate the formation processes of ultrafine metal particles on substrate surfaces. In this methodology, the number of metal atoms deposited over substrate surfaces is increased one by one. The metal atoms are shot to the surface after regular time intervals with definite velocity. We applied this new MD code and computer graphics (CG) technique to the investigation of the formation processes of ultrafine Au particles on a MgO(100) plane at 300 K. The dynamic behavior of the Au atoms and the atomistic mechanism of the formation processes were revealed. The effect of deposition rates of Au atoms on the formation processes was also investigated. Decreasing the deposition rates of Au atoms was found to increase the number of fixed Au atoms on a MgO(100) plane. The effect of a groove in the MgO(100) plane was also investigated. It was revealed that surface defects greatly affect the configuration and location of Au clusters on the MgO(100) plane, in agreement with the experimental results.

1. Introduction

Much attention has been given to the behaviors of ultrafine metal particles on metal oxide surfaces, in relation to heterogeneous catalysis and metal–ceramic heterojunctions in advanced materials (e.g., Refs. [1–3]). Although great advances in the preparation and characterization of ultrafine metal particles on metal oxide substrates have been made experimentally, theoretical approaches (e.g., Ref. [4]), such as molecular dynamics (MD), quantum chemistry (QC), Monte Carlo simulation (MC) and computer graphics (CG) would be also desirable for the atomistic understanding of the structure and dynamics of ultrafine metal particles on metal oxides (e.g., Ref. [5]).

By using MD and CG, we have investigated structures and dynamics of various materials, including zeolites, clays, bioceramics, metal oxides, oxide superconductor films, magnetic materials, carbon nanotubes and supported metal catalysts (e.g., Refs. [6,7]). Furthermore, the methods have been applied to the investigation of the structure and dynamics of MgO crystal, MgO(100) plane, Au crystal, and Au_{32} cluster, as well as the deposition processes of Au_{32} cluster on a MgO(100) plane [8] and the sintering processes of two Au_{32} clusters on a MgO(100) plane [9]. These results suggest that MD and CG are effective for investigating various topics relating to ultrafine metal particles deposited on metal oxide substrates.

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A number of interesting experimental works have been done for the structure of Au clusters on MgO surfaces by using various techniques, such as MBE, SEM, HRTEM, RHEED, LEED etc. (e.g., Refs. [10–14]), because of its importance as a catalyst and as an electronic device material. In our previous study [8], the formation process of ultrafine Au particles was not clarified, because only one Au_{32} cluster was deposited on the MgO(100) plane to understand the structure and dynamics of ultrafine Au particles on the surface. In the present study, we developed a new MD code to simulate the formation processes of ultrafine metal particles on substrate surfaces when atomic metal is continuously deposited one by one on the surface. The objectives of the present study are to investigate: (i) the migration process of one Au atom on the MgO(100) plane, (ii) the formation processes of the ultrafine Au clusters on the MgO(100) plane, (iii) the effect of the deposition rates of the Au atoms on the structure of deposited Au clusters on the MgO(100) plane, and (iv) the effect of a groove in the MgO(100) plane on the structure of deposited Au clusters.

2. Methods

For the present MD calculations, we developed a new MD code, on the basis of the MXDORTO code developed by Kawamura [15]. The MXDORTO code is very useful and effective for calculating the bulk properties of inorganic materials, such as metal oxides, metals, glasses, and zeolites, however it is not available for calculating the surface properties of inorganic materials, such as the formation processes of ultrafine metal particles on substrate surfaces. Fig. 1 shows the model system of these MD simulations which consists of two parts, namely a substrate and a source of deposited atoms. The deposition rates of metal atoms can be varied, and the wide variation, namely 180, 540, 720, and 1080 m/s, which correspond to the kinetic energies of Au atoms at 300, 2713, 4822, and 10850 K respectively, was used in this study. Here, the deposition rates are defined as the initial velocities of metal atoms at the source of metals whose direction is [100]. The number of metal atoms deposited over the substrate surface is increased one by one. The metal atoms are shot to the surface after regular time intervals with definite velocity. The distance between MgO(100) plane and source of deposited Au atoms, the time interval between the deposition of Au atoms, and the temperature of the MgO(100) plane are variable parameters. In the present calculations these values are 10 Å, 2000 steps, and 300 K, respectively. The horizontal positions of the emerged Au atoms over MgO(100) plane were randomly selected.

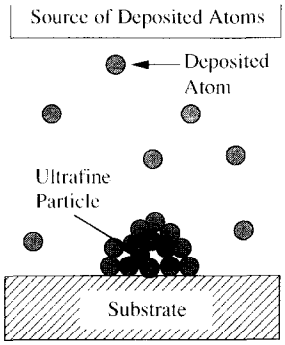

Fig. 1. The model system for simulating the formation processes of ultrafine metal particles on substrate surfaces.

The Verlet algorithm was used for the calculation of the atomic motions, while the Ewald method was applied for the calculations of the electrostatic interactions. Temperature were controlled by means of scaling the atom velocities. The calculations were performed for 30 000–70 000 steps with a time step of 2.0×10^{-15} s. The two-body, central force interatomic potential,

$$u(r_{ij}) = Z_i Z_j e^2 / r_{ij} + f_0(b_i + b_j) \times \exp\left[(a_i + a_j - r_{ij})/(b_i + b_j)\right] + D_{ij}\left\{\exp\left[-2\beta_{ij}(r_{ij} - r_{ij}^*)\right] - 2\exp\left[-\beta_{ij}(r_{ij} - r_{ij}^*)\right]\right\}, \quad (1)$$

was used for all calculations. In Eq. (1), the first, second, and third terms refer to Coulomb, exchange repulsion, and Morse interactions, respectively. Z_i is the atomic charge, e the elementary electric charge, r_{ij} the interatomic distance, and f_0 a constant. The parameters a and b in Eq. (1) represent the size and stiffness, respectively, in the exchange repulsion interaction, while D_{ij}, r_{ij}^*, and b_{ij} represent bond energy, equilibrium bond distance, and stiffness, re-

spectively, in the Morse function. The parameters of Eq. (1) were determined to reproduce the structures of various metal oxides and metal crystals.

Calculations were performed with Hewlett-Packard HP9000 Model-710 and Model-715 workstations, while the visualization was made with a Silicon Graphics IRIS-4D/25TG workstation and BIOSYM Insight II software. Dynamic features in the formation processes of ultrafine metal particles were also investigated by using the real-time solid modeling visualization with the MOMOVIE code developed in our laboratory on the OMRON LUNA-88K workstation.

3. Results and discussion

3.1. Migration process of one Au atom on the MgO(100) plane

On the basis of previous investigations of the metal–metal oxide interactions (e.g., Refs. [3,8]), both Au–Mg and Au–O interactions were taken into consideration in the calculation. Because of the lack of detailed potential parameters for Au–Mg and Au–O interactions, the effect of D_{ij} values for Au–Mg and Au–O on the structure of the Au cluster was clarified in the previous study by depositing one Au_{32} cluster on the MgO(100) plane [8]. When D_{ij} for Au–Mg and Au–O was taken to be 2.24 kcal/mol, namely 20% of D_{ij} for the Au–Au bond, the shape of the Au_{32} cluster on the MgO(100) plane was very similar to that reported by the experimental results [13]. Hence, in the present study those values were used for MD simulation.

Detailed understanding of the migration process of one Au atom on the MgO(100) plane has an important role to clarify the formation processes of ultrafine Au particles on the surface. Fig. 2 shows the positions of a single Au atom after every 1000 steps of MD simulation at 300 K, after it was deposited on the MgO(100) plane. The configuration of the atoms of the MgO surface are fixed in Fig. 2, since the geometry of the MgO(100) plane did not change markedly during the deposition. The Au atom possessed high mobility on the MgO(100) plane, even when the deposition rate was very slow, namely 180 m/s. This behavior is in marked contrast to that in the deposition of a metal oxide cluster such as TiO_2 on the $SrTiO_3(100)$ plane during the simulation of the layer-by-layer homoepitaxial growth of the $SrTiO_3(100)$ plane [16]. In the latter case, after the metal oxide cluster is deposited on the $SrTiO_3(100)$ plane, it does not migrate with high mobility on the surface, even for the high deposition rate of the metal oxide cluster as fast as 5×10^4 m/s. The different behavior can be interpreted in terms of the weaker bond between the Au atom and the MgO(100) plane than that between the metal oxide cluster and the $SrTiO_3(100)$ plane, in terms of Coulomb interaction. Furthermore, it was observed that the migration direction of the Au atom is fixed to be [011], [01$\bar{1}$], [0$\bar{1}$1], or [0$\bar{1}\bar{1}$], in other words the Au atom is in contact with the Mg^{2+} ions during the migration. In the previous study [8], the importance of the crystallographic fit between the metal and the metal oxide for the fixation of ultrafine metal particles on a metal oxide surface was discussed. In addition, the present results suggest that the crystal morphology has a significant role on the migration processes of metal atoms over metal oxide surfaces.

3.2. Formation processes of ultrafine Au particles on the MgO(100) plane

The dynamic process of the Au atoms in the formation of Au clusters on the MgO(100) plane was simulated by MD and CG. Fig. 3 shows the formation process of an Au cluster on a MgO(100) plane

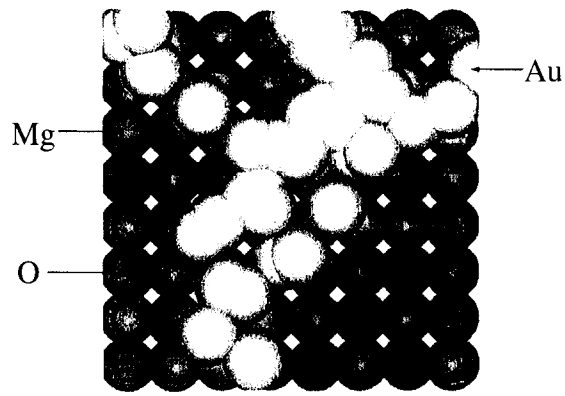

Fig. 2. The positions of a single Au atom after every 1000 steps of MD simulation at 300 K, after it was deposited on a MgO(100) plane. Deposition rate of the Au atom is 180 m/s.

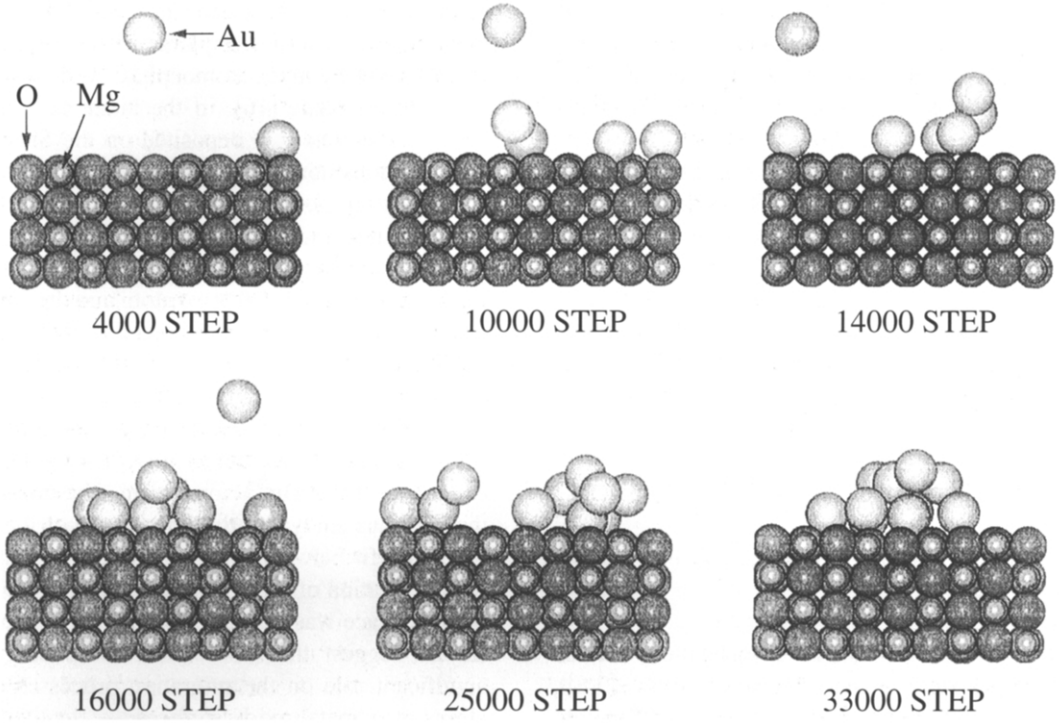

Fig. 3. The formation process of an Au cluster on a MgO(100) plane at 300 K. Deposition rates of Au atoms are 180 m/s.

at 300 K, when 10 Au atoms with the deposition rate of 180 m/s were deposited one by one after every 2000 steps. When any Au atom approached the MgO(100) plane, initially it migrated on the surface with high mobility, similar to the behavior shown in Fig. 2. After the Au atoms aggregated gradually, finally a hemispherical Au_{10} cluster was formed on the MgO(100) plane. The shape of the Au cluster was quite similar to that obtained by the simulation of Au_{32} cluster deposition on a MgO(100) plane [8]. Thus, the dynamic behavior of the Au atoms leads to the formation of an Au cluster and the interaction between Au atoms and the MgO surface is the cause of the final shape of the Au cluster. These results

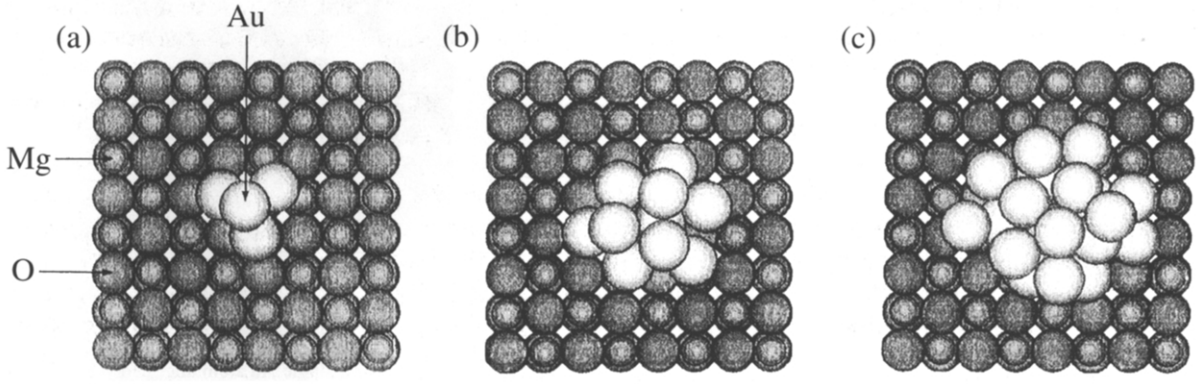

Fig. 4. The final shapes of the Au clusters formed on the MgO(100) plane at 300 K. Deposition rates of Au atoms are (a) 720 m/s, (b) 540 m/s, and (c) 180 m/s.

validate the applicability of the new MD code for the atomistic understanding of the formation processes of ultrafine metal particles on substrate surfaces which cannot be derived from experimental studies.

3.3. Effect of the deposition rates of Au atoms on the formation processes of ultrafine Au particles on a MgO(100) plane

In relation to the metal deposition by evaporation, sputtering, or molecular beam epitaxy, the effect of the deposition rates of metal atoms on the ultrafine metal particle formation over substrate surfaces is an interesting phenomena. MD simulations with various deposition velocities of Au atoms were performed at 300 K. Since the deposition rates of Au atoms in the above simulation studies were very slow, namely 180 m/s, the deposition process of 20 Au atoms with a deposition rate of 1080 m/s on the MgO(100) plane was simulated. All of the Au atoms were repelled by the MgO(100) plane and no Au atoms were fixed on the surface. Figs. 4a, 4b and 4c represent the final shapes of the Au clusters on MgO(100) plane, when 20 Au atoms were deposited with deposition rates of 720, 540, and 180 m/s, respectively. When the deposition rate was 720 m/s (Fig. 4a), 4 Au atoms were fixed on MgO(100) plane and other Au atoms were repelled from the surface. When the deposition rates of Au atoms were 540 m/s (Fig. 4b) and 180 m/s (Fig. 4c), 10 and 19 atoms were fixed on the surface, respectively. It was found that the slower deposition rates of Au atoms lead to a larger number of fixed Au atoms on the MgO(100) plane. Although the number of fixed Au atoms on the MgO(100) plane cannot be quantitatively discussed from these results, decreasing the deposition rates of Au atoms is effective to fix Au atoms efficiently on MgO(100) plane.

3.4. Effect of a groove in the MgO(100) plane on the formation processes of ultrafine Au particles

It has been experimentally shown that surface defects, such as grooves, steps, kinks, and vacancies greatly affect the structure of metal clusters on substrate surfaces [10–12,17,18]. The effect of a groove in the MgO(100) plane on the formation processes of ultrafine Au particles was also investigated by MD and CG. Fig. 5 shows the formation process of an Au cluster at 300 K, when 10 Au atoms were

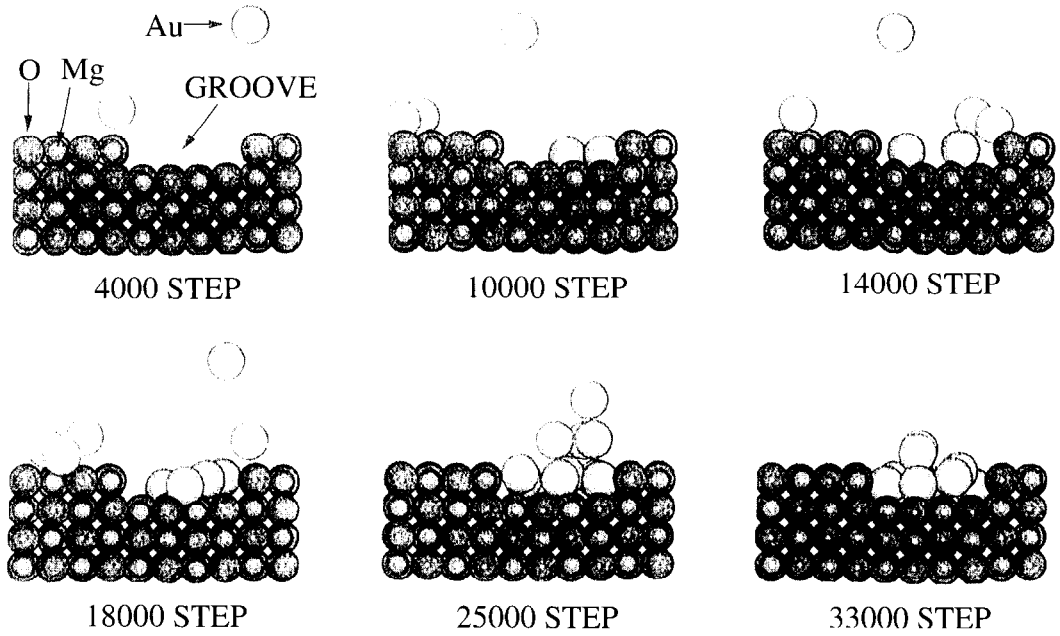

Fig. 5. The formation process of an Au cluster on a MgO(100) plane with a groove at 300 K. Deposition rates of Au atoms are 180 m/s.

deposited on a MgO(100) plane with a groove, which is approximately 8 Å wide and 2 Å deep. Initially Au atoms migrated on the MgO(100) plane with high mobility, and finally a hemispherical Au_{10} cluster was formed only in the groove on the MgO(100) plane. It was found that the surface defects greatly affect the configuration and location of Au clusters on the MgO(100) plane, in agreement with the experimental results [10–12]. The specific interaction of the Au atoms and groove in the MgO surface is due to the configuration and location of the Au cluster. Furthermore, the dynamics of the Au cluster in the groove on the MgO(100) plane was less than that on the flat MgO(100) plane. This result suggested that modification of the MgO(100) plane is effective to reduce the mobility of the Au cluster, and hence stabilize the ultrafine Au particles on the MgO(100) plane.

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