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Hetero-diffusion of small clusters on Ag(111) surface

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Abstract. The investigation reported in this paper is an attempt to analyze and understand the hetero-diffusion of small clusters on the (111) surface of Ag. This work has been realized using molecular statics simulations based on semi-empirical many body potentials described by the embedded atom method. For this study, we have considered three heterogeneous systems $\mathrm{Cu}_n/\mathrm{Ag}(111)$, $\mathrm{Ag}_n/\mathrm{Ag}(111)$ and $\mathrm{Au}_n/\mathrm{Ag}(111)$, where n is the number of cluster atoms ($n = 1$, 2, 3, 4 or 5). Our findings show that the clusters diffuse on the (111) surface via two different diffusion processes, namely the zigzag motion and the concerted jump. Moreover, the activation energy increases from adatom, dimer, to trimer, and goes down at tetramer, and then rises again for pentamer. This behavior is similar for the three systems under study and also to the one obtained by the density-functional theory for the homogenous systems.

1 Introduction

Understanding phenomena on surfaces at the atomic scale has been one of the long term goals of material science because of their technological applications that have direct influence in improving human life [1–3]. This effort has been intensified with the introduction of powerful experimental tools such as the scanning tunneling microscopy (STM) [4–6] and the field ion microscope (FIM) [7,8] that are used to see surfaces and to manipulate atoms, clusters, and molecules so as to control diffusion, other reactions and microscopic events [9,10]. In fact, these experimental measurements are unable to detect the atomistic processes which proceed in the time scale of nanoseconds. For this reason, a number of theoretical efforts were also performed to provide support and rationale for experimental findings, such as molecular dynamics (MD) simulations based on realistic interatomic potentials as effective medium potentials [11], embedded-atom potentials [12], glue potential [13] and second-moment tight-binding potentials [14].

For a long time, the scientific research has been focused on the study of the clusters diffusion on crystal terraces, which play a fundamental role in numerous applications (epitaxial thin film growth, catalysis, etc. . . .). On the atomic scale, understanding how small clusters move across the surface is therefore essential for developing an atomic model for crystal growth of thin films. As compared to the diffusion of single atoms, cluster diffusion involves additional information emerging from interactions of atoms within the cluster. Because the energetics and the mechanisms can be affected by these interactions, they are important for better understanding growth kinetics [15]. Moreover, the diffusion of a multi-atom system is an important step of the early stages of nucleation. Since it involves the diffusion of more than a single-atom, cluster diffusion brings a bit more challenge originating from the competition between the interactions within the cluster atoms and that of the cluster-substrate. These interactions may affect diffusion energetics and diffusivity that ultimately control nucleation. Furthermore, the number of possible diffusion processes for a cluster is far more complex to be determined as compared to that for a single-atom. In this context, several works have been devoted to study the self-diffusion of small clusters on metal surfaces [16–22], but little is known about the cluster hetero-diffusion [23–25].

A prior molecular dynamics study for the homogeneous systems using the semi-empirical methods reported that the diffusion energy increases strongly from adatom, dimer, to trimer, but decreases at tetramer, and then rises again for pentamer [26–29]. To our knowledge, for the heterogeneous systems there are no theoretical and experimental results

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concerning the activation energy of the clusters diffusion in the literature. This will allow us to ask the following question: *Can the same behavior be observed for heterogeneous systems?* In this regard, we have addressed this paper to tackle this issue. Towards this end, we are interested by the hetero-epitaxial growth of Cu, Ag and Au clusters on the close-packed (111) surface of Ag. These metals constitute a particularly simple prototype system for the various growth modes. In fact, they are chemically very similar and crystallize both in the face centered-cubic (*fcc*) lattice structure. These properties should minimize the interfacial and the strain energies of the film. An intermixing at the interface seems unlikely for close packed *fcc* (111) surfaces. This study has been realized using molecular dynamics (MD) computer simulations combined with embedded atom method potentials (EAM), with parameterization by Foiles *et al.* [30]. These potentials have had important success in revealing the characteristics of transition metals (the subject of the research presented here) and their alloys [28–34]. In addition, the EAM potentials have been widely tested and shown to reliably produce the properties of several transition metallic systems (pure and alloys). The ultimate goal of the study undertaken in this paper is to gather knowledge that will help build materials with the desired physical and chemical properties.

The rest of this paper is organized as follows. In sect. 2 we give a detailed description of our model together with the method of calculation. In sect. 3 our numerical calculations about static activation energy E_a are presented and discussed for heteroepitaxial systems of interest here. Finally, our conclusions are drawn in sect. 4.

2 Model and computational details

As emphasized above, in order to study the systems considered in this work, we have performed the embedded atom method (EAM) potentials proposed by Foiles *et al.* [30]. The key advantage of these interaction potentials is that they are much faster compared to the first-principle calculations. Therefore, an accurate potential of this kind is a quite valuable tool to study systems with large time and length scale. The EAM atomistic approach has been fully described in refs. [12,30] and also in our previous work [35], therefore only a brief summary will be presented here. Thus, the total potential energy of an assembly of atoms is written as the sum of two terms

$$E_{\mathrm{tot}} = \frac{1}{2}\sum_{i,j}\phi_{ij}\left(r_{ij}\right) + \sum_{i}F_i(\rho_i), \tag{1}$$

where

$$\rho_i = \sum_{i(i\neq j)}\rho_j^{\alpha}(r_{ij}), \tag{2}$$

ρ_i is the sum of individual electron density provided by the other atoms of the system, $F_i(\rho_i)$ is the energy required to embed the atom i into the local electronic charge density ρ_i, $\phi_{ij}(r_{ij})$ is a pairwise electrostatic interaction between atom i and atom j separated by the distance r_{ij} and ρ_j^{α} is the electron density contributed by atom j.

Here, we have paid our attention to the diffusion of Ag, Cu and Au clusters (from one to five atoms) on Ag(111) surface. The motivation behind this study is to reveal the atomistic processes responsible for the diffusion of metallic clusters. This study is performed using LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) code [36]. The Verlet algorithm [37] is used to solve the Newton's equations of motion for atoms with a time step of 10^{-15} s. The simulations have been carried out for a substrate with free surface on two sides, containing 14 (111) atomic layers having (10×10) atoms in one layer. Here x- and y-axes lie in the surface plane, while z-axis is perpendicular to the surface. 2D clusters are formed by placing several atoms close to each other on the free surface. In the surface plane the periodic boundary conditions were performed but not in the z-direction. The geometry optimization is performed at 0 K by minimizing their energy with a conjugate-gradient method [38] during 3 *ps*. In these static investigations, the activation energy is calculated using the drag method [39], which is the simplest and the most commonly used method to find the transition state. In this method, the adatom is dragged from its departure site to the nearest neighboring one along the reaction path in small increments. At each step on the diffusion path, the total energy of the system is minimized.

3 Results and discussion

In this section, we will present and discuss the results of embedded atom method based calculations for the activation energies for the diffusion of clusters (Cu, Ag or Au) on Ag(111). The systems in which we have carried out are Cu_n/Ag(111), Ag_n/Ag(111) and Au_n/Ag(111). We mention that, all the calculations are realized using static molecular simulation at 0 K combined with EAM potential. We recall that the reliability of this potential has been discussed earlier by our researches group in their previous work [40]. In fact, the obtained results have shown a very good agreement with DFT calculations, supporting the validity of the EAM. These allow us to approach the rest of our investigations in confidence.

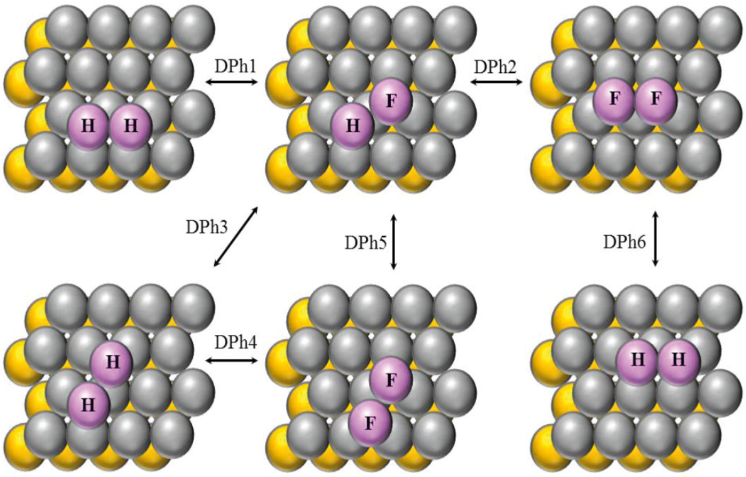

Fig. 1. Diffusion paths of dimers on Ag(111) surface. H and F labels on the adatoms define the adatom location at the hcp and fcc sites, respectively. Arrows are used to show the direction along which the dimer performs the diffusion process with the corresponding label.

Table 1. Diffusion energy of Cu_2/Ag(111), Ag_2/Ag(111) and Au_2/Ag(111) systems.

System	E_a (eV)					
	DPh1	DPh2	DPh3	DPh4	DPh5	DPh6
Cu_2/Ag(111)	0.07	0.07	0.07	0.21	0.07	0.11
Ag_2/Ag(111)	0.03	0.03	0.02	0.09	0.03	0.05
Au_2/Ag(111)	0.05	0.03	0.05	0.09	0.03	0.06

3.1 Monomer diffusion on Ag(111)

In reality, the adatoms may diffuse on metallic substrate by either simple or long jump, or through an exchange process. In fact, several previous works have shown that the adatoms diffuse on the fcc (111) surfaces only through a jump mechanism [41,42]. This is due to its densely packed structure. In our previous work [35], we have calculated the activation energy corresponding to this specific mechanism from fcc site to *hcp* one and vice versa for three systems under study such as Ag/Ag(111), Au/Ag(111) and Cu/Ag(111) and others. However, for the Ag/Ag(111) system, we found that the adatom needs a value of 0.06 eV to move from the fcc to the *hcp* sites and vice versa, while for Au/Ag(111) it required just 0.047 eV. Since the values of the activation energy for these systems are extremely similar for both paths (fcc to *hcp* and *hcp* to fcc), we can conclude with confidence that the silver and gold adatoms have a very small preference for sitting in any adsorption site at the diffusion temperature. On the other hand, for the Cu/Ag(111) system the adatom must have a value of 0.079 eV to displace from the fcc to *hcp* site and 0.067 eV from the *hcp* to fcc site.

3.2 Dimer diffusion on Ag(111)

This subsection shed light on the diffusion properties of Cu_2, Ag_2 and Au_2 *dimers* on Ag(111) surface. For this purpose, we have illustrated in fig. 1 the possible diffusion paths of our dimers on Ag(111) surface. As can be seen from this figure, the dimers can diffuse through six possible paths. However, the barriers corresponding to these paths are calculated and presented in table 1. In this effort, we have found that there are two types of motions in the dimer diffusion: zigzag and concerted jump. Note that in the zigzag motion, only one atom moves at a time, while in the concerted jump process the dimer atoms move together. In fig. 1, a migration path combining a zigzag motion [DPh1 ↔ DPh2, DPh1 ↔ DPh3 and DPh1 ↔ DPh5] with a concerted jump motion [DPh4 and DPh6] is shown. The obtained results of table 1 show that the path with the lowest activation energy is generally corresponding to the zigzag motion for the three considered systems. Thus, in this zigzag motion the energy barrier in the three different diffusion paths (see DPh1 ↔ DPh2, DPh1 ↔ DPh3 and DPh1 ↔ DPh5 in fig. 1) is 0.14 eV, 0.06 eV and 0.08 eV for Cu_2/Ag(111), Ag_2/Ag(111) and Au_2/Ag(111) respectively. Moreover, if the dimer atoms are forced to diffuse together through the DPh4 path, then the energy barrier is 0.09 eV for Au_2/Ag(111) and Ag_2/Ag(111) and 0.21 eV for Cu_2/Ag(111). In the same context, Morgenstern *et al.* [43] have studied experimentally the diffusion of Cu dimer on Ag(111) surface by using low-temperature scanning tunneling microscopy between 6 and 25 K. In this range of temperature, the authors found that the most favorable diffusional motion of the Cu dimer is identified as a zigzag motion with an energy barrier of 73 meV [43,44]. On the theoretical side, to our knowledge, the results for diffusion on Ag(111) surface are available

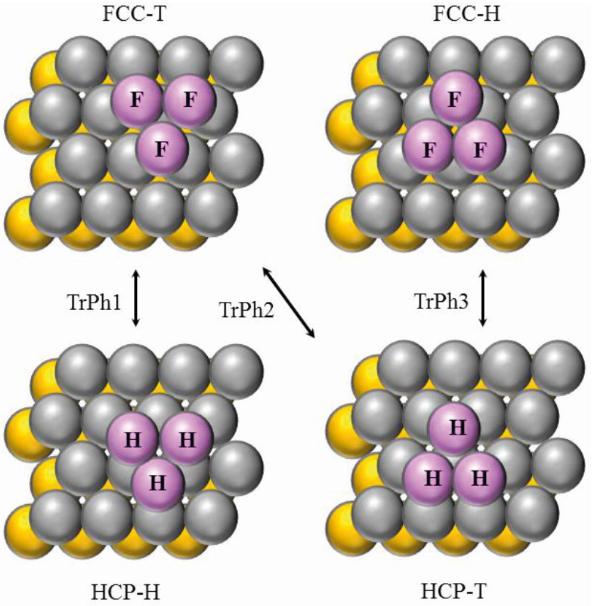

Fig. 2. Structures and diffusion paths for trimer on Ag(111) surface. FCC-H and FCC-T mean that the trimer atoms sitting at *fcc* sites and the center of their mass are on the hollow site and on the top site, respectively. HCP-H and HCP-T show that the trimer atoms sitting at *hcp* sites and the center of their mass are on the hollow site and on the top site, respectively.

Table 2. Diffusion energy of Cu_3/Ag(111), Ag_3/Ag(111) and Au_3/Ag(111) systems.

System	E_a (eV)		
	TPh1	TPh2	TPh3
Cu_3/Ag(111)	0.39	0.46	0.25
Ag_3/Ag(111)	0.18	0.59	0.16
Au_3/Ag(111)	0.16	0.66	0.15

in the literature only for Cu and Ag dimers. Concerning the Cu dimer on Ag(111), Hayat *et al.* [45] have successfully used MD simulations and DFT calculations to confirm the experimental observation. Their DFT calculations showed that the diffusion barrier for zigzag motion amounts to 72 meV, which is in excellent agreement with the experimental value [43]. The slightly lower barrier for the zigzag motion made it the chief diffusion mechanism. On the other hand, Kinetic Monte Carlo calculations [46] found that the effective diffusion barrier for Ag dimer on Ag(111) is about 121 meV. Recent MD simulations [47] of up to 10 ns have obtained a diffusion barrier for the Ag dimer on Ag(111) of 94 meV, thus confirming the effective diffusion barriers reported by Shah *et al.* [48] and Chang *et al.* [19]. Overall, all the above results indicate that the role of zigzag motion is major in the diffusion of the Cu and Ag dimers on Ag(111).

3.3 Trimer diffusion on Ag(111)

The trimer is the smallest cluster that can have a one-dimensional (linear form) or a two-dimensional (compact triangular form and non-compact triangular form) structure. On the fcc of (111) surface, the only detailed experimental study of which we are mindful for the diffusion behavior of clusters larger than dimers was carried out using the field ion microscope (FIM) [49] for Ir_n/Ir(111) [50,51]. For a theoretical study of the trimer diffusion on *fcc* (111) surface, there exist a large number of calculations for homogenous system such as Ir_n/Ir(111) [52], Ni_n/Ni(111) [53], Al_n/Al(111) [19, 54] and Ag_n/Ag(111) [48,55]. However, all these calculations show that the compact triangular form is more stable than the two other forms. For this reason, we are interested only in the compact triangular form of our trimers. For this form, the trimers can have four configurations identified as FCC-H, FCC-T, HCP-H, and HCP-T (see fig. 2). In fig. 2, we have illustrated three kinds of diffusion mechanisms such as translation between FCC-T and HCP-H (TrPh1), translation between FCC-H and HCP-T (TrPh3) and rotation process between FCC-T and HCP-T (TrPh2) configurations. The FCC and HCP nomenclatures are used to show the trimer atoms sitting at fcc sites or hcp sites, respectively. However, the “T” or “H” means that the mass center of the trimer is on the top site (T) or hollow site (H). Similarly to the dimers study, the same calculations of the activation energy have been performed for Cu, Ag and Au trimers on the Ag(111) surface (see table 2). Our results show that the translation between FCC-H and HCP-T (TrPh3) is the most stable configuration for all trimers with an energy barrier of 0.25 eV for Cu_3, 0.16 eV for Ag_3 and 0.15 eV for Au_3. Our results for the activation energies of various concerted processes for the Ag trimer on Ag(111) is in good agreement with those obtained from effective medium theory (EMT) potential as reported in [48].

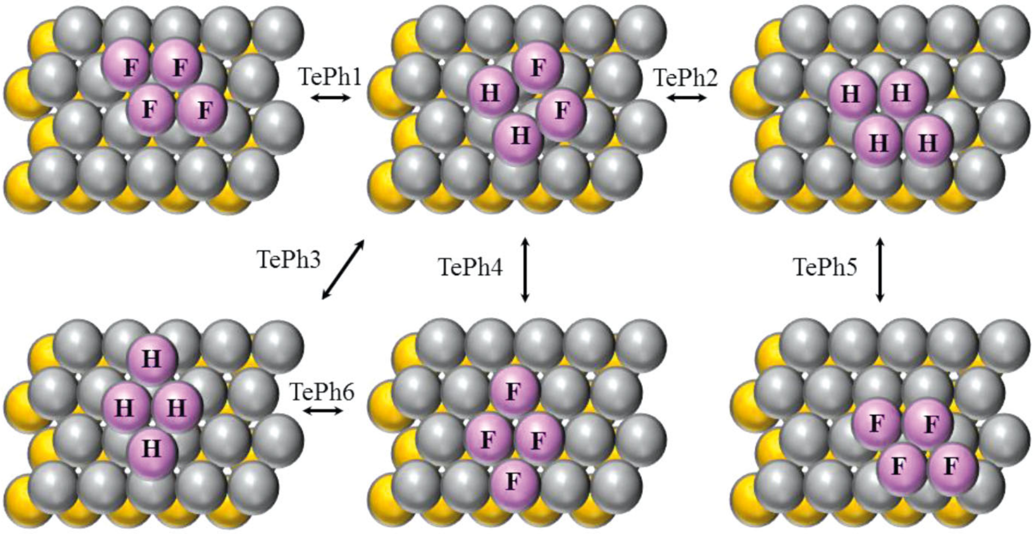

Fig. 3. Structures and diffusion paths for tetramer atoms on Ag(111) surface.

Table 3. Diffusion energy of the three systems under study on the (111) surface.

System	E_a (eV)					
	TePh1	TePh2	TePh3	TePh4	TePh5	TePh6
Cu_4/Ag(111)	0.50	0.31	0.31	0.50	0.45	0.45
Ag_4/Ag(111)	0.56	0.36	0.36	0.53	0.23	0.23
Au_4/Ag(111)	0.29	0.14	0.11	0.12	0.28	0.28

3.4 Tetramer diffusion on Ag(111)

We will report, in this part, the molecular static calculations for Cu, Ag and Au *tetramers* diffusion on Ag(111) substrate. Before presenting the results concerning the activation energy, we will first present in fig. 3 how tetramers diffuse on Ag(111) surface. This figure shows that the tetramer can diffuse through four kinds of motion such as translation (TePh1 ↔ TePh2), rotation by zigzag motion (TePh1 ↔ TePh3 or TePh1 ↔ TePh4), concerted intracell (TePh5) and concerted intercell (TePh6) diffusion. Arrows are used to show the direction along which the tetramer performs the diffusion process with the corresponding label. Table 3 contains the values of the E_a for the three systems under study. From this results we note that the barrier for zigzag motion is 0.31 eV for Cu_4/Ag(111), 0.36 eV for Ag_4/Ag(111) and 0.14 eV for Au_4/Ag(111). Moreover, for the concerted intracell and intercell diffusion, the activation energy takes the value of 0.45 eV for Cu_4/Ag(111), 0.23 eV for Ag_4/Ag(111) and 0.28 eV for Au_4/Ag(111). Besides, the tetramer diffusion lowest energy barrier is not related to the same diffusion path but it is depending on the nature of the diffusing adatoms (*e.g.*, TePh2 is the favorable mechanism for Cu, TePh5 for Ag and TePh3 for Au). This point is not observed for dimer and trimer configurations. To our knowledge, the results for tetramers diffusion on Ag(111) surface are existing only for Ag and Cu clusters. Indeed, in ref. [47] Rehman and Hayat have been investigated the thermal diffusion behavior of small two-dimensional Ag-islands on Ag(111) using molecular dynamics simulations in the frame of semi-empirical potentials. The authors showed that the tetramer prefers to diffuse through concerted motion for the low temperatures with an effective energy barrier about 205 meV. On the other hand, for Cu tetramer on Ag(111), Hayat *et al.* [56] determined that the smaller islands (2 to 4 atoms) diffusion occurs mostly via concerted motion with an effective barrier about (200 ± 5) meV. In fact, our results for TePh5 and TePh6 paths seem to be in good agreement with these findings.

3.5 Pentamer diffusion on Ag(111)

In this subsection, we will concentrate on the diffusion properties of pentamers on Ag(111) surface. In fact, the energetically more favorable compact pentamer configuration is obtained by adding an adatom to a rhombus-shaped tetramer. Further, pentamers having all adatoms on fcc sites are found to be energetically most stable than their hcp analogues or those occupying both kinds of occupancy sites. The various paths of pentamers are shown in fig. 4. The values of the static barrier are presented in table 4. From this table, we note that, for the three systems studied, the static activation energy takes low values in the PaPh2 diffusion path. We found 0.27 eV, 0.44 eV and 0.62 eV for Cu_5/Ag(111), Ag_5/Ag(111) and Au_5/Ag(111) respectively. But, when diffusion is carried out in the PaPh3 path, the

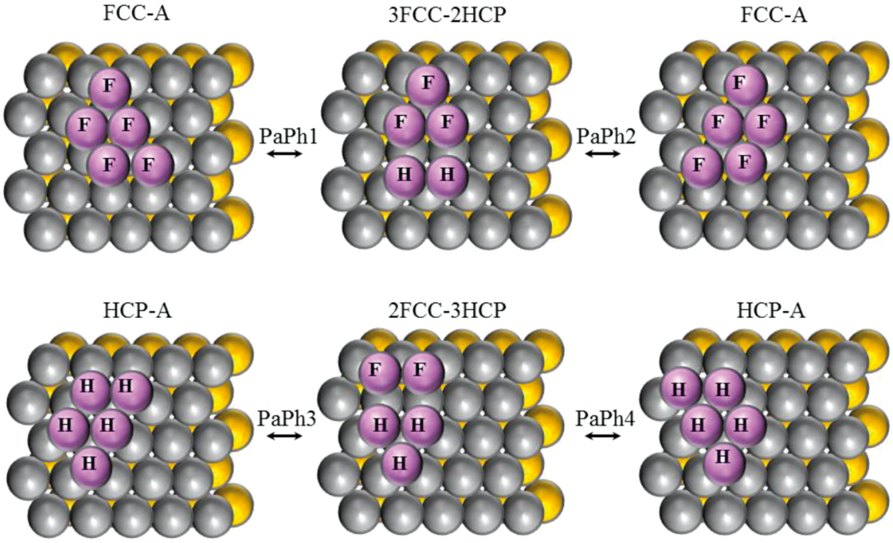

Fig. 4. Atomistic process for pentamer cluster on Ag(111) surface.

Table 4. Activation energy of Cu, Ag and Au pentamers on Ag(111) substrate.

System	E_a (eV)			
	PaPh1	PaPh2	PaPh3	PaPh4
Cu_5/Ag(111)	0.67	0.27	0.81	0.32
Ag_5/Ag(111)	0.47	0.44	0.46	0.46
Au_5/Ag(111)	0.62	0.62	0.63	0.63

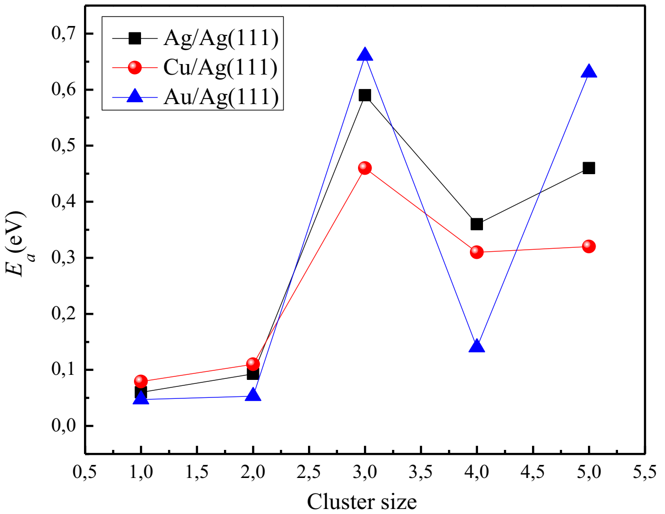

Fig. 5. Static barrier as a function of cluster size for self- and hetero-diffusion on Ag(111) surface.

atoms will need to have an important value of the activation energy: 0.81 eV for Cu_5/Ag(111), 0.46 eV for Ag_5/Ag(111) and 0.63 eV for Au_5/Ag(111). From these results, we conclude that the most favorable diffusion process for the pentamer is the rotational mechanism, in which only two atoms need to move. This diffusion kinetics trend of the pentamer islands on the (111) surface was found earlier by Chang *et al.* [19].

The behavior of the static barrier as a function of the cluster size for three systems Cu_n/Ag(111), Ag_n/Ag(111) and Au_n/Ag(111) is reported in fig. 5. As can be seen from this figure, the E_a has qualitatively the same behavior for all the systems, where the value of the static barrier increases from adatom, dimer to trimer, but decreases at tetramer, and rises again for pentamer. This behavior is quite similar to that found in previous studies of Al_n/Al(111) system [19] and Ir_n/Ir(111) system [14]. The explanation of this phenomenon back to that in the tetramer diffusion is that only two atoms are needed to move at each step by zigzag motion, while for the trimer diffusion all adatoms move together by concerted motion.

4 Conclusion

In this work, we have investigated the diffusion properties of Cu_n, Ag_n and Au_n small clusters on Ag(111) surface by calculating their activation barriers using molecular statics simulations combined with a semi-empirical metal potential which includes a many-body term. Our results have shown that the dimer diffuses on Ag(111) via concerted motion accomplished by zigzag motion. For trimer, the three atoms are preferred to diffuse by concerted motion. Tetramer diffusion is similar to that for the dimer, in which the diffusion is accomplished by zigzag motion where only two of the tetramer atoms move at a time, whereas the pentamer prefers the rotational process. Concerning the behavior of the activation energy as a function of the cluster size, we have found a general trend of diffusion barriers on (111) surfaces of fcc metals. That is, the activation energy increases sharply from adatom, dimer, to trimer, drops (or stays constant) at tetramer, and then rises again for pentamer. A comparison of our results with those existing in the literature show generally minor quantitative differences and overall qualitative agreement.

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