Exchange process diffusion of silver adatom on low-index copper surface: case of Cu(110) surface

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The transport properties of the Ag isolated atom (adatom) on the Cu(110) surface have been investigated using molecular dynamics (MD) simulation. A good agreement between our finding for activation energies and those existing in literature is observed. On the other hand, the study of surface atoms vibration via the mean square perpendicular amplitude showed a linear trend ($T \geq 350K$). This investigation has been made between 300K and 500K indicating harmonic behavior of the surface atoms in the temperature interval [350K, 500K]. In addition, the presence of the exchange process is related to the perpendicular amplitude magnitude. The MD simulations (from 375K to 500K) show that the exchange rate has an Arrhenius behavior. Thus, the dynamic activation energy obtained from the Arrhenius plot is in excellent agreement with the static one which is calculated by the drag method at 0K.

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1. Introduction

Knowledge of adatom behavior on metallic surface is of a fundamental interest for understanding epitaxial thin film growth and heterogeneous catalysis. One of the basic elements which can control these processes is the adatome diffusion. The diffusion phenomena have been the subject of many scientific works [1-7]. In this area, adatom self-diffusion on the low index metallic surface has been studied both experimentally [8-9] and theoretically [11-15].

The hetero-diffusion of adatoms on metallic surface is a crucial first step in the study of thin growth morphology. Focusing our attention on systems formed by noble metals, and especially adatom surfaces on copper low-index surface, it was concluded that adatom behavior depends on adatom nature. Examples of such systems are Au/Cu(001) [16], Ag/Cu(001) [17], Au/Cu(110) or Au/Cu(111) [18]. More recently, many works has been made in order to understand the heterogeneous diffusion on the system constituted by silver and copper [19-21].

In the diffusion phenomenon, the adatom starts from a given site, and reaches another one. But, the question is *how*?.

To reach the final position, the adatom could make several diffusion mechanisms such simple jump, long jump or via exchange process. The letter will be the subject of this paper.

Exchange process have been observed in many system such as Cu/Ag(110) [22], Cu/Cu(110) [23], Ag/Ag(110) [24]. This process occurs when the adatom have enough energy to push one adjacent atom of the surface to leave his position. In this case, the adatom becomes atoms of surface, and the apparition of a new adatom is noted. In many systems, the exchange mechanism is found to be predominant than jump process [25,26]. Sometimes, competition between these two mechanism is observed such as during Pb adatom diffusion on Cu(110) at low coverage [27]. From the experiment point of view, the exchange process in homogenous systems in the case of (110) could be observed as across channel jump due to its fastest occurrence.

Using molecular dynamic simulations, the occurrence of exchange has been predicted in many systems such as Cu/Cu(110) [23], Ag/Ag(110) [24] and Au/Au(110) [23].

In this work, molecular dynamics simulation based on embedded atom method (EAM) are carried out, in order to study the Ag adatom on low-index copper surface especially via exchange process. Our attention is focused on Cu(110) surface. The activation energy is calculated for exchange process both in static (0K) and dynamic (T>0K) regime.

The paper is organized as follows: Short potential model description adopted in this work is given in **Sec.2**. All results of this work with discussions are presented in **Sec.3**. The conclusion are summarizes in **Sec.4**.

2. Model

The EAM formalism should not be described in this work and a summary can be found in Ref. 28. The advantage of this energetic model is the time comparing with the calculation using the first principles calculations [29,30] that is still very time-consuming for systems with a large number of atoms per unit cell and for transition metals within the framework of the EAM potential; this has been developed from density functional theory. The total energy of a metallic system is given as a sum of an embedding function $F_i(\rho_i)$ and pair-potential $V_{ij}(R_{ij})$ as:

$$E_{tot} = \frac{1}{2}\sum_{i,j,i\neq j} V_{ij}(R_{ij}) + \sum_{i} F_i(\rho_i).$$

Where the factor ½ is introduced in order not to count the atom couples twice. The quantity ρ_i is the sum of individual electron density characterizing the environment of that atom and R_{ij} is the scalar distance between atom *i* and *j*. In many studies, the semi-empirical many-body potentials lead to reasonable results and their application has helped, at least qualitatively, in understanding diffusion energetics.

The diffusion of Ag adatom on Cu(110) is simulated using a box containing six- layer Cu slab of 120 atoms (20×6). Periodic boundary conditions are applied in the direction parallel to the surface (x and y direction) but not in the perpendicular direction to the surface (z direction). The Ag monomers are placed on Cu (110) on the deep channel on their minimum-energy configuration at zero temperature obtained via the conjugate-gradient algorithm. After relaxation, the system is thermalized during 20 *ps* by keeping constant the number of atoms N, the volume V and the temperature T. Then, the mean program of molecular dynamics simulations is executed at constant temperature.

3. Results and discussion

Before starting our high-temperature molecular dynamic simulations, the activation energy is computed at 0K for the elementary diffusion process using the drag method. As single adatom diffusion via exchange process is the mean subject of this work, data are taken only for this adatom. To our knowledge, no experimental data are available for Ag/Cu(110). For this reason and in the first step, the system Cu/Cu(110) which has been met in many investigations will be considered. The Table 1 reports the computed static energy barrier for diffusion via simple jump E_{simple}, exchange process $E_{exchange}$ and jumping across channel E_{across}. But, the corresponding static energies for Ag/Cu(110) are summarized in Table 2.

Table 1. Static activation energy for diffusion via hopping E_{simple} in the case of Cu/Cu(110), exchange process $E_{exchange}$ and across channel jump E_{across}. All data are in eV.

	E_{simple}	$E_{exchange}$	E_{across}
Our work	0.23	0.29	1.18
Ref.32	0.23	0.29	
Ref.33	0.24	0.30	

For Cu/Cu(110), a good agreement between our findings and those calculated by Mottet *et al.* [31] and Karimi *et al.* [32] is observed as can be seen from the Table 1. In the same context, the reliability of our model is proved in our previous works [22].

Table 2. Static activation energy for diffusion via hopping E_{simple} in the case of Ag/Cu(110), exchange process $E_{exchange}$ and across channel jump E_{across}. All data are in eV.

	E_{simple}	$E_{exchange}$	E_{across}
Our work	0.24	0.32	0.98

From Table 2 and for Ag/Cu(110), the diffusion via simple jump is more favoured than the exchange process. This is due essentially to many factors such as activation energy and the difference of the atomic radius between the Ag adatom and Cu atoms of substrate. On the other hand, the across channel jump is very costly in energy leading to its weak presence (or absence).

In order to simulate the adatom diffusion, many independent microcanonical simulations were run at different temperatures (from 300 to 500K). Since our attention is focused on single adatom diffusion on the perfect surface in the case of heterogeneous system, the simulation is stopped when the exchange process occurs.

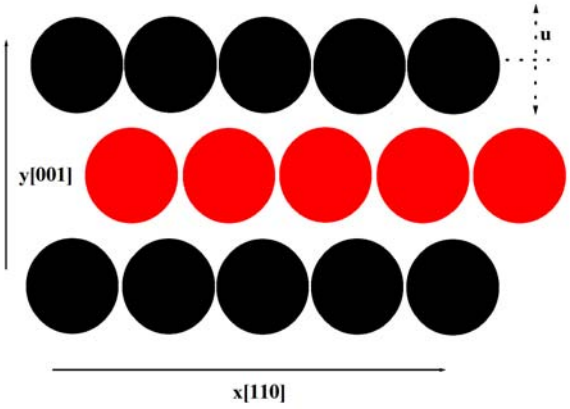

Fig.1. Schematic presentation of the row atom on (110) surface. The black atoms represent the atoms of the substrate which participate in the exchange process with the adatom. The mean square of vibration amplitude (u) is computed for those atoms. The red circles represent the adjacent layer just below the top one.

In the same context, the average square amplitude of the vibration of the top layer atoms of the substrate (Cu atoms) along [001] direction is analysed. The results of this quantity are plotted in Fig. 2.

From Fig.2, one can conclude that the perpendicular vibration of the substrate atoms becomes more important when the temperature exceed 375K. On the other hand, a linear trend of $\langle u^2 \rangle$ is observed showing a harmonic behaviour of this quantity in the range of 350-500K. This increase of the perpendicular vibration amplitude facilitates the perpendicular adatom motion which corresponds to the exchange process. It is worth to mention, that despite this advantage, the exchange process

still presenting a lowest presence than jump process [22] in Ag/Cu(110). The harmonic vibration of the substrate atoms indicates that the correlation between the diffusion processes (such jump-exchange or exchange-exchange) could be neglected. In fact, when the atoms of substrate show anharmonic vibration a correlation between jump process and exchange mechanism is observed such as in Ag/Ag(110) [24]. In conclusion, the presence of exchange process in Ag/Cu(110) is more observed when the temperature exceed 350K . This result leads us to consider only the statistical events accumulated for $T \geq 375K$.

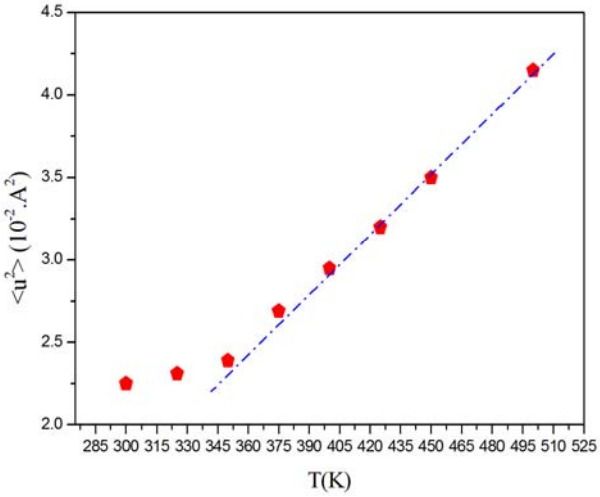

Fig. 2. This graph represents the average square amplitude $<u^2>$ of the vibration of the top layer atoms (atoms in the substrate surface in the [001] surface at different temperatures (from 300 to 500K).

In the same way, this investigation will be more accurate if statistical studies are made in order to compute the dynamic activation energy. This later quantity can be deduced from the Arrhenius plot of the frequency of exchange process (see Fig. 3). Thus, the activation barrier in dynamic regime is found to be $E^{dyn}_{exchange} = (0.31 \pm 0.01)eV$ with a corresponding prefactor of frequency $\sigma_0=2.8ps^{-1}$. It worth to note that the dynamic activation is to lie very close to the corresponding potential energy computed in static regime (0K) indicting that the activation energy for this system can be considered constant even if $T >> 0K$.

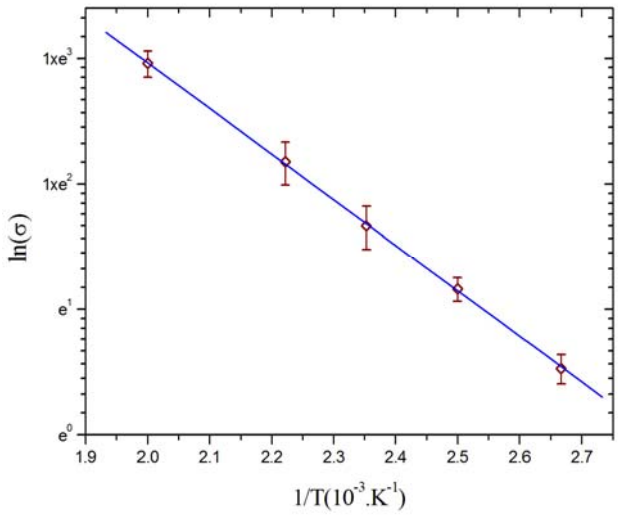

Fig. 3. Arrhenius plot of the exchange rate for Ag adatom on Cu(110) surface. The dashed line represents fit.

4. Conclusion

In this work, a study of Ag adatom diffusion on Cu(110) via exchange is presented. This investigation is started by the determination of the static activation barrier at 0K by the drag method. We find that the EAM offers a good description of adatom diffusion as RGL [25] or EA model [32]. Thus, the values obtained for activation energy are in a good agreement with those available in literature. It has been demonstrated that the occurrence of exchange process in Ag/Cu(110) is related to the perpendicular vibration of the surface atoms of the substrate. On the other hand, a linear trend of the mean square amplitude of those vibrations is shown indicating a harmonic behavior of the atom of the surface.

On the other hand, the MD simulations demonstrate that the exchange rate (or exchange frequency) follows an Arrhenius law. The effective activation energy deduced from this law is found to be $E^{dyn}_{exchange} = (0.31 \pm 0.01)eV$ with $\sigma_0=2.8ps^{-1}$ as a prefactor. The magnitude of the dynamic activation energy is in excellent agreement with the static potential energy computed via the drag method. In addition, the correlated processes such as jump-exchange or exchange-exchange are absent due the harmonic behavior of the atoms row on Cu(110) surface (between 350 and 500K).

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