Study of the surface relaxation and single vacancy formation in very thin Cu (001) film by using MAEAM

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Abstract: The surface relaxation and the formation of a single vacancy in very thin Cu (001) film formed by 2 ~ 14 atomic layers have been studied by using MAEAM and MD simulation. For the surface relaxation, the highest surface energy is in the \( l = 2 \) atomic layers. The multilayer relaxation mainly occurs between the first two atomic layers, and the maximum contractive displacement is obtained in the very thin Cu (001) film formed by \( l = 3 \) atomic layers. For the vacancy formed in \( l' = 1 \) of the very thin Cu (001) film formed by \( l = 2 \sim 14 \) layers, the most difficult site in the film formed by \( l = 3 \) atomic layers.

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Keywords: surface relaxation • vacancy • MAEAM • thin film

1. Introduction

It has been known that the mechanical properties of metallic thin films are quite different from those of bulk materials [1]. However, for nanostructured metallic thin films, the atomic process in nanostructured metal may not be an extension of that in its bulk [2–5]. It has been reported that capping of Cu films brings about suppression of diffusional creep [6] and internal stress relaxation [7, 8] for atomic transport in the surface of nm-scale Cu films, which results in mechanically weak Cu/low-dielectric-constant-material interconnects for semiconductor devices [9, 10]. Understanding of the surface relaxation and single vacancy formation in nm-scale Cu film is important.

In this paper, the surface relaxation and the formation of a single vacancy in very thin Cu (001) film formed by 2 ~ 14 atomic layers have been studied by using modified analytic embedded atom method (MAEAM) and molecular dynamic (MD) simulation. The MAEAM [11–14] is obtained by modifying the analytic embedded-atom method (AEAM) of Johnson [15–17] that is originated in embedded-atom method (EAM) of Daw and Baskes [18, 19], which is a reasonable potential models in constructing the inter-atomic potentials. By using the MAEAM, the self-diffusion dynamics behaviors of Pd small clusters respectively on Pd (111) and (001) surfaces and Zr small cluster on Zr (0001) surface have been studied successfully [20–22].
2. MAEAM method

In the MAEAM, the total energy of a system $E_i$ is written as [23]:

$$E_i = \Sigma F(p_i) + \frac{1}{2} \Sigma \phi(r_{ij}) + \Sigma M(p_i),$$

(1)

where $F(p_i)$ is the energy to embed an atom in site $i$, $p_i$ is the electron density that is induced at site $a$ by all other atoms in the system and is taken in the original form [15]:

$$p_i = \Sigma f(r_{ij})$$

(2)

where $r_{ij}$ is the separation distance of atoms $i$ and $j$. $M(p_i)$ is the energy modification term and is written as [23]:

$$M(p_i) = a \left\{ \frac{1}{1 - \exp \left[ - \left( \frac{P_i}{P_e} \right)^2 \right]} \right\},$$

(3)

where $P_i$ is taken as [24]:

$$P_i = \sum f^2(r_{ij}).$$

(4)

The embedding function $F(p_i)$ and atomic density $f(r_{ij})$ are taken as the forms used by Johnson [16]:

$$F(p_i) = -F_0 \left[ 1 - n \ln \left( \frac{P_i}{P_e} \right) \right] \left( \frac{P_i}{P_e} \right) \alpha,$$

(5)

$$f(r_{ij}) = f_e \left( \frac{r_{ij}}{r_e} \right) 6,$$

(6)

where subscript $e$ indicates the equilibrium state, $F_0 = E_e - E_{1f}$, $E_e$ and $E_{1f}$ are the cohesion energy and mono-vacancy formation. $f_e$ is taken as [12]

$$f_e = \frac{\sqrt{E_e}}{\Omega},$$

(7)

where $\Omega = \frac{a^3}{2}$ is the atomic volume in face-centered cubic (FCC) metals and $a$ is the lattice constant. The cut-off distance for FCC metal’s potential lies between fifth and sixth neighbor distance, i.e. $r_{1e} = r_5 + k_{ee}(r_6 - r_5)$, $k_{ee}$ is a model parameter that needs to be fitted. If the distance $r_{ij}$ is smaller, or equal to this distance, the potential function is taken as the following [25]:

$$\phi(r_{ij}) = k_0 + k_1 \left( \frac{r_{ij}}{r_{1e}} \right)^6 + k_2 \left( \frac{r_{ij}}{r_{1e}} \right) + k_3 \left( \frac{r_{ij}}{r_{1e}} \right)^6 + k_4 \left( \frac{r_{ij}}{r_{1e}} \right)^{12} + k_5 \left( \frac{r_{ij}}{r_{1e}} \right)^{10},$$

(8)

otherwise $\phi(r_{ij})$ goes to zero.

The model parameters (such as $a$, $n$, $k_{ee}$, $k$ and those values in the potential function) are determined by fitting the potentials to available physical parameters such as lattice constant $a$, cohesive energy $E_e$, mono-vacancy formation energy $E_{1f}$, and elastic constants $C_{11}$, $C_{12}$, $C_{44}$. The input physical parameters and the calculated model parameters for FCC metal Cu are listed in Table 1 and 2, respectively.

| Table 1. | The input physical data for FCC metal Cu [26]. |
| :-----: | :-----: | :-----: | :-----: | :-----: | :-----: |
| $\sigma$(nm) | $E_e$(eV) | $E_{1f}$(eV) | $C_{11}$(GPa) | $C_{12}$(GPa) | $C_{44}$(GPa) |
| 0.36147 | 3.49 | 1.17 | 169 | 122 | 75.3 |

The lattice relaxation resulting from the existence of the surface or the vacancy is simulated with the molecular dynamic (MD) method [27]. The forces applied to the $i$-th atom from the other atoms are calculated by

$$f_i^\alpha = -\frac{\partial E_i}{\partial r_{ij}} = - \left[ F'(p_i) \sum_{j \neq i} f'(r_{ij}) \frac{r_{ij}^\alpha}{r_{ij}} + \frac{1}{2} \sum_{j \neq i} \phi'(r_{ij}) \frac{r_{ij}^\alpha}{r_{ij}} + 2M'(p_i) \sum_{j \neq i} f'(r_{ij}) \frac{r_{ij}^\alpha}{r_{ij}} \right].$$

(9)

Where the superscript $\alpha (= x, y$ and $z$ ) in $f_i^\alpha$ and $r_{ij}^\alpha$ represents the $\alpha$ th component of the force $f_i$ and the separation distance $r_{ij}$ of the atom $j$ from atom $i$. $E_i = F(p_i) + \frac{1}{2} \sum_{j \neq i} \phi(r_{ij}) + M(p_i)$ is the energy contribution from atom $i$. The position vector of the $i$ th atom, $\vec{r}_i$, is a function of time. When the increment of time $\Delta t$ is one minute, $\vec{r}_i$ can be approximated by a Taylor series. So the coordinate $\vec{r}_i(t + \Delta t)$ of atom $i$ at time $t + \Delta t$ can be obtained from the coordinate $\vec{r}_i(t)$ of the atom at time $t$ by the predictor-corrector method [28],

$$\vec{r}_i^p(t + \Delta t) = \vec{r}_i(t) + \vec{r}_i(\Delta t) + \frac{1}{2} \frac{\vec{v}_i(\vec{r}_i)}{m}(\Delta t)^2.$$

(10)

Where $\vec{v}_i(\vec{r}_i)$ is the coordinate predicted at time $t + \Delta t$, $i(\Delta t) = \frac{\vec{v}_i(t)}{m}$ is the velocity of atom $i$ at time $t$ and $\vec{v}_i(\vec{r}_i) = \frac{\partial \vec{r}_i}{\partial t}$ is the resultant force applied to atom.

3. Calculation process and results

The very thin Cu (001) film is a double-sided slab that formed by $2 \sim 14$ atomic layers. A computational cell $5a \times 5a \times \frac{5(1-1)l_{\text{atom}}}{2}$ is selected in the calculation, $l_{\text{atom}}$ is the film
The schematic diagrams of the relaxed Cu(001) film structure formed by $l = 2(a), 3(b), 4(c)$ and $5(d)$ layers viewed from the [100] direction.

### Table 2. The model parameters for FCC metal Cu.

| $\alpha$ | $n$ | $k_0$ (eV) | $k_1$ (eV) | $k_2$ (eV) | $k_3$ (eV) | $k_4$ (eV) | $k_5$ (eV) |
|-----------|-----|------------|------------|------------|------------|------------|------------|
| 0.003297  | 0.6 | 0.3        | 1.499487   | -0.650171  | 0.097645   | -0.000056  | 0.098837   | -1.178326  |

3.1. **Surface relaxation**

Surface relaxations were studied by optimizing the atomic positions in the slab. However, only the displacements of the atoms along the surface normal direction are needed to be considered. From the total energy of the computational cell minimization, the schematic diagrams of the relaxed Cu (001) film structure formed by $l = 2, 3, 4$ and 5 layers can be obtained as shown in Fig. 1. The surface energy can be expressed as

$$E_s = \frac{NE_{coh} - E_{slab}}{2A}, \quad (11)$$

where $E_{slab}$ is the total energy of the slab, $N$ is the number of atoms in the slab, and $A$ is the surface area. $E_{coh}$ is the bulk cohesive energy.

The results of the surface energies are given in Table 3 with the other calculated data and experimental value [29–33]. We can see that the highest value is for the $l = 2$ atomic layers. With the increase in the layer number, the surface energy decreases gradually. From $l = 9$, the surface energy is no longer affected by the atomic layer and the value is very close to the other calculated and experimental values.

The multilayer relaxations for the clean surfaces are calculated (Table 4) as the percentage difference in the surface interlayer spacing, $d_{ij}$, from the layer spacing of the same orientation in the geometry optimized bulk structure, $d_{bulk}$.

$$\Delta d_{ij} = \frac{d_{ij}}{d_{bulk}} \times 100. \quad (12)$$

From Table 4, we can see that the atom displacement mainly occurs between the first two surface atomic layers and the contraction of the first interlayer spacing and expansion of the second are in excellent agreement with the other calculation and experiment. However, the contractive degree of the $\Delta d_{12}$ is $-1.7540$ in Cu film formed by $l = 3$ is the biggest. When the thin film thickness is greater than or equal to $2a$, i.e., $l \geq 5$, the atom multilayer relaxations for the clean surfaces are equal to the bulk. In our simulation model, the smaller the distance between atomic layers, the higher the atom density in the surface. So the maximum atom density is obtained in the very thin Cu (001) film that formed by $l = 3$ atomic layers. This result will affect the formation of a single vacancy in the surface as we can see in the following study.

3.2. **The formation of a single vacancy in the different (001) atomic layers**

A single vacancy is created by removing an atom from the center of atomic layers $l'$ in the computational cell, $l' = 1 \sim \frac{1}{2}$ when $l$ is even or $l' = 1 \sim \frac{14}{7}$ when $l$ is odd. The formation energies $E_{f}^{l'}$ for the Cu vacancies are obtained by the following formula:

$$E_{f}^{l'} = E_{rel}(m - 1) - E_{rel}(m) + E_{s}, \quad (13)$$

where $E_{rel}(m-1)$ and $E_{rel}(m)$ are the total energies of the relaxed system with and without a single vacancy, respectively. For the very thin Cu film formed by $l = 2 \sim 9$ atomic layers, the calculated formation energies for a single vacancy in the different (001) atomic layers along the surface normal direction are listed in Table 5. In order to make these more intuitive, the formation energies of a single vacancy in the layers ($l' = 1 \sim 7$) in the very thin Cu film formed by $l = 2$, 3 and 4 atomic layers, $l = 5$ and 6 layers, and $l = 9$ and 10 layers, respectively, are
Table 3. Relaxed surface energies $E_s (\text{meV} \cdot \text{Å}^{-2})$ for the very thin Cu film formed by $l = 2 \sim 9$ atomic layers.

| Layer number($l$) | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|-------------------|---|---|---|---|---|---|---|---|
| This paper        | 80.8395 | 79.4100 | 79.2141 | 79.2062 | 79.2058 | 79.2054 | 79.2053 | 79.2056 |
| SC [29]           | 76.15 |
| EAM [30]          | 78.71 |
| DFT [31]          | 91.13 |
| MM [32]           | 118.02 |
| Experiment [33]   | 110.48 |

Table 4. Multilayer Relaxation of the Cu (001) surface in very thin Cu film formed by $l = 2 \sim 9$ atomic layers, $\Delta d_{ij}$ represents the difference from the bulk spacing for the distance between the $i - j$ layer spacing, where 1 denotes the top layer. The positive value denotes expansion, while the negative value signifies contraction.

| Layer number($l$) | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|-------------------|---|---|---|---|---|---|---|---|
| $\Delta d_{12}$ (%) | -1.3991 , -1.7540 , -1.2328 , -1.1996 , -1.1996 , -1.1996 , -1.1996 , -1.1996 |
| DFT [31]          | -1.62 |
| Experiment [33]   | -1.1 |
| $\Delta d_{23}$ (%) | +0.1222 , +0.1111 , +0.1111 , +0.1111 , +0.1111 , +0.1111 |
| DFT [31]          | +2.57 |
| Experiment [33]   | +1.7 |

Table 5. The formation energies of a single vacancy in the layers ($l' = 1 \sim 7$) in the very thin Cu (001) film formed by $l = 2 \sim 14$ layers.

| $l' = 1$ | $l' = 2$ | $l' = 3$ | $l' = 4$ | $l' = 5$ | $l' = 6$ | $l' = 7$ |
|----------|----------|----------|----------|----------|----------|----------|
| $l = 2$  | 0.5050   |
| $l = 3$  | 0.5054   | 1.2082   |
| $l = 4$  | 0.4916   | 1.2212   |
| $l = 5$  | 0.4897   | 1.2059   | 1.2292   |
| $l = 6$  | 0.4896   | 1.2039   | 1.2138   |
| $l = 7$  | 0.4896   | 1.2038   | 1.2117   | 1.1983   |
| $l = 8$  | 0.4896   | 1.2038   | 1.2117   | 1.1964   |
| $l = 9$  | 0.4896   | 1.2038   | 1.2117   | 1.1963   | 1.1944   |
| $l = 10$ | 0.4896   | 1.2038   | 1.2117   | 1.1963   | 1.1943   |
| $l = 11$ | 0.4896   | 1.2038   | 1.2117   | 1.1963   | 1.1943   | 1.1942   |
| $l = 12$ | 0.4896   | 1.2038   | 1.2117   | 1.1963   | 1.1943   | 1.1942   | 1.1942   |
| $l = 13$ | 0.4896   | 1.2038   | 1.2117   | 1.1963   | 1.1943   | 1.1942   | 1.1942   | 1.1942   |
| $l = 14$ | 0.4896   | 1.2038   | 1.2117   | 1.1963   | 1.1943   | 1.1942   | 1.1942   | 1.1942   | 1.1942   |

Table 5. The formation energies of a single vacancy in the layers ($l' = 1 \sim 7$) in the very thin Cu (001) film formed by $l = 2 \sim 14$ layers.

4. Conclusions

The surface relaxation and the formation of a single vacancy in very thin Cu (001) film that formed by $2 \sim 14$ atomic layers have been studied by using MAEAM and MD simulation. The following conclusions can be drawn.

a) For the surface relaxation, the highest surface energy is in the $l = 2$ atomic layers. From the beginning of the $l = 9$, the surface energy is no longer affected by atomic layer. The multilayer relaxations mainly occur between the first two surface atomic layers, and the maxium atom displacement that is contractive is obtained in the very thin Cu (001) film formed by $l = 3$ atomic layers.

b) For the vacancy formed in $l' = 1$ of the very thin Cu (001) film formed by $l = 2 \sim 14$ layers, the vacancy formation is the most difficult in the very thin film formed by $l = 3$ atomic layers.

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Figure 2. The formation energies of a single vacancy in the layers \( l = 1 \sim 7 \) for the (001) surface of Cu thin film in \( l = 2 \), 3 and 4 layers, \( l = 5 \) and 6 layers and \( l = 9 \) and 10 layers respectively.

Figure 3. The formation energies of a single vacancy in the layers \( l = 1 \) and \( l' = 2, 3, 4, 5 \) and 6 layers respectively for the (001) surface of Cu thin film in \( l = 2 \sim 14 \) layers.

References

[1] R.W. Hoffman, In: H.G.F. Wilsdorf (Ed), Thin films (Metal Park, OH, American Society for Metals, 1964)
[2] H. Mizubayashi et al., J. Metastab. Nanocryst. 24-25, 61 (2005)
[3] N. Yagi et al., J. Metastab. Nanocryst. 24-25, 503 (2005)
[4] B.S. Berry, A.C. Pritchet, J. Phys. 42, C5-1111 (1981)
[5] S. Sakai et al., Scripta Mater. 45, 1313 (2001)
[6] M.J. Kobrinsky, C.V. Thompson, J. Appl. Phys. 89, 91 (2001)
[7] D. Gan et al., J. Appl. Phys. 97, 103531 (2005)
[8] J. Peng et al., Mater. Sci. Forum. 524-525, 595 (2006)
[9] K.N. Tu, J. Appl. Phys. 94, 5451 (2003)
[10] C.S. Hau-Riege, Microelectron. Reliab. 44, 195 (2004)
[11] W.Y. Hum, M. Fukumoto, Modelling Simu. Mater. Sci. Eng. 10, 707 (2002)
[12] W.Y. Hu et al., J. Phys.: Cond. Matt. 13, 1193 (2001)
[13] W.Y. Hu et al., J. Mater. Sci. Tech. 15, 336 (1999)
[14] H.Q. Deng et al., Appl. Surf. Sci. 221, 408 (2004)
[15] R.A. Johnson, Phys. Rev. B 39, 3924 (1988)
[16] R.A. Johnson, Phys. Rev. B 39, 12554 (1989)
[17] R.A. Johnson, Phys. Rev. B 41, 9717 (1990)
[18] S.M. Foiles et al., Phys. Rev. B 33, 7983 (1986)
[19] S.M. Foiles, M.S. Daw, Phys. Rev. B 38, 12643 (1988)
[20] F.S. Liu et al., Modelling Simul. Mater. Sci. Eng. 18, 045010 (2010)
[21] F.S. Liu et al., Comp. Mater. Sci. 47, 505 (2009)
[22] F.S. Liu et al., Nucl. Instrum. Meth. B 267, 3267 (2009)
[23] B.W. Zhang et al., Phys. Rev. B 48, 3022 (1993)
[24] B.W. Zhang et al., Phys. B 262, 218 (1999)
[25] X.L. Shu, In: Ph.D. Dissertation (Ed), Study on the physical properties, point defects and atomic diffusion in intermetallics by a modified analytic EAM model (P. R. China, Hunan University, Changsha, 2001)
[26] C.J. Smithells, In: E. A. Brandes (Ed), Smithshells Metals Reference Book (Butterworths, London, 1983)
[27] R.W. Smith, D.J. Srolovitz, Phys. Rev. B 79, 1448 (1996)
[28] J.R. Beeler Jr, Radiation Effects Computer Experiments (North Holland, New York, 1983)
[29] T.D. Daff et al., Surf. Sci. 603, 445 (2009)
[30] J. Cai, Y.Y. Ye, Phys. Rev. B 54, 8398 (1996)
[31] T.D. Daff et al., J. Phys. Chem. C 113, 15714 (2009)
[32] H. Cox et al., Mol. Phys. 96, 921 (1998)
[33] H.L. Davis, Surf. Sci. 126, 245 (1983)