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Computer simulation of the interface in Cu/Ni multilayer films

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X-ray diffraction of Cu/Ni (1 0 0) bicrystalline multilayer thin films was studied by atomistic simulation. Atomic position equilibrium was reached by using a molecular dynamics method to simulate interface structure with Morse potentials to model interatomic interactions. It was found that X-ray profiles were sensitive to the interface structure and some "extra" peaks appeared other than the regular peaks of copper or nickel crystals. The number of "extra" peaks increased with increasing modulation length of the multilayer. The "extra" peaks result from the diffraction between interfaces and also from the diffraction of the modulated structure. The variation of spacing normal to the interface could be described as a near-square wave. The interface region approximately includes five atomic layers for Cu/Ni (1 0 0) multilayer thin film when its modulation length is not too small. When the modulation length is small enough, the interface regions overlap, and the average atom potential energy is high.

1. Introduction

Interfaces have attracted considerable attention in recent years. Because it is widely recognized that interfaces govern many of the mechanical, chemical and electric properties of important materials [1], much work has been done on the interface structure and bonding. With the advantage of high-speed computers, computer simulation has been developed as a helpful theoretical method and has been used in many research fields. Here we use a molecular dynamics method to study interface structure. The challenge to computer simulation is now to devise a simple potential capable of describing correctly the interatomic interaction with a reasonable accuracy. The *ab initio* [2] calculation is precise, but the computational effort is enormous. At present it is restricted to the system with a small number of atoms. There are also semiempirical [3, 4] and empirical classical potential methods applied. These two kinds of methods require less computational work but are not as rigorous as the *ab initio* one. Considering that pair potential is often chosen to study the mechanical properties of materials, and the result is generally good for metals whose structure is f c c, we have used empirical pair potential to describe interatomic interaction. Here we chose Morse potential, which had been used in many studies [5] and the results were very good for copper and nickel.

X-ray diffraction is a good method to study structure and composition of materials. It can also be used to study interfaces [6]. If the X-ray diffraction of interfaces is studied experimentally as well as theoretically using computer simulation, we can test and adjust the model by comparing the two results instead of simply fitting to the physical properties, as is usually done. This paper presents some preliminary work on this idea. The calculated interface structures and X-ray profiles of Cu/Ni (1 0 0) bicrystal multilayer thin film are reported. The modulation length of the thin film is changed to ascertain its effects on interface structure and X-ray profile. We intend to determine what the X-ray profile is like when the interfaces play a major role, and how the profile changes when the interface structure changes. Because the number of atoms in the interfaces is much smaller than that in the bulk, the effects of interfaces are covered by those of the bulk, and a multilayer thin film is used to enhance the effects of the interfaces.

2. Computation approach

We simulated the interface structure by molecular dynamics [5] using the Morse potentials to model the interatomic interactions in order to save computational work. The most popular form of the Morse potential is

$$U(r_{ij}) = D\{\exp[-2\alpha(r_{ij}-r_0)] - 2\exp[-\alpha(r_{ij}-r_0)]\} \quad (1)$$

where r_{ij} is the distance between atom i and atom j. D, α, r_0 are parameters. r_0 is defined as the nearest distance between atoms at 0 K. The values of D, α, r_0 are determined by fitting to the experimental lattice constant and elastic constants. The values for copper and nickel shown in Table I are taken from Milstein's paper [7]. Those values for Cu–Ni interactions are calculated under the geometric hypothesis or

TABLE I Morse potential parameters

	D (10^{-12} erg)	α (nm)	r_0 (nm)
Cu	0.56774	0.13393	0.28850
Ni	0.35059	0.24877	0.25275
Cu–Ni	0.45920	0.18253	0.27063

TABLE II Atom configuration of the computational cell

Cell	Z direction	X–Y plane
1	BAbabABAbabAB	Cu 4×4 Ni 4×4
2	ababABABABABababa	Cu 4×4 Ni 4×4
3	bababababABABABABABABABABababababab	Cu 4×4 Ni 4×4

[a] A, B, Ni atoms; a, b, Cu atoms.

arithmetic hypothesis as

$$D_{\text{Cu-Ni}} = (D_{\text{Cu}} + D_{\text{Ni}})/2 \quad (2)$$

$$\alpha_{\text{Cu-Ni}} = (\alpha_{\text{Cu}} + \alpha_{\text{Ni}})^{1/2} \quad (3)$$

$$r_0^{\text{Cu-Ni}} = (r_0^{\text{Cu}} + r_0^{\text{Ni}})/2 \quad (4)$$

By solving the differential equations numerically, using the Verlet algorithm [8] we calculate the forces acting on atoms in the computational cell. When the energy of the system becomes minimum, the atomic equilibrium positions are gained. Then the reflected wave amplitude and intensity can be calculated. From X-ray diffraction theory [9], we have

$$A(S) = \sum_n f_n \exp[-4\pi i(\sin\theta/\lambda)l_n]e^{-M} \quad (5)$$

$$I(S) = A(S) \times A(S)$$

where l_n is the projection in the z-axis of the position vector of the nth atom, f_n is the atomic scattering factor, M is the Debye–Waller temperature factor. Here the absorption of X-rays by materials was not taken into account because our films were not very thick.

In this study we calculated Cu/Ni (1 0 0) interface structures and their X-ray profiles. We constructed three computational cells with different modulation lengths. As we know, the atoms stack is ABABAB ... along the [1 0 0] direction in f c c structure. So in each copper or nickel layer, we arrange atoms according to this rule. Because the lattice parameters of copper and nickel are only slightly different, $a_{\text{Cu}} = 0.36153$ nm (20 °C), $a_{\text{Ni}} = 0.35238$ nm (20 °C), we chose the average of the two as a common lattice parameter to construct the initial interface regions, the value is $a = (a_{\text{Cu}} + a_{\text{Ni}})/2 = 0.35696$ nm. We also supposed that the computational cells were perfect without any kinds of defects. The three cells contain 12, 14 and 30 atom planes, respectively. Each atom plane has 32 atoms, so the whole atom number of each cell is 384, 448 and 960, respectively. The details of the cells are listed in Tables II and III, and the shape of computational cell is drawn in Fig. 1.

We simulated the X-ray diffraction of Cu/Ni (1 0 0) thin film when the atoms in these cells were relaxed to reach the equilibrium positions. The wavelength of the applied X-ray radiation, Cr$K_{\alpha 1}$ is 0.22897 nm. The irradiated volumes of the three thin films are $11 \times 11 \times 11$, $11 \times 11 \times 11$, $11 \times 11 \times 5$, respectively, where $11 \times 11 \times 11$ means that the length of the three sides in the x, y, z direction of the irradiated body is $11L_x$, $11L_y$, $11L_z$, respectively. In order to enhance the interface effects, multilayer thin films are modelled by applying periodic conditions in three directions. In this study we kept the atom number, temperature and computational cell volume unchanged. Temperature was fixed at 300 K by periodically scaling the kinetic energy to the fixed temperature according to the formula

$$E_{\text{K}} = 3NKT/2 \quad (6)$$

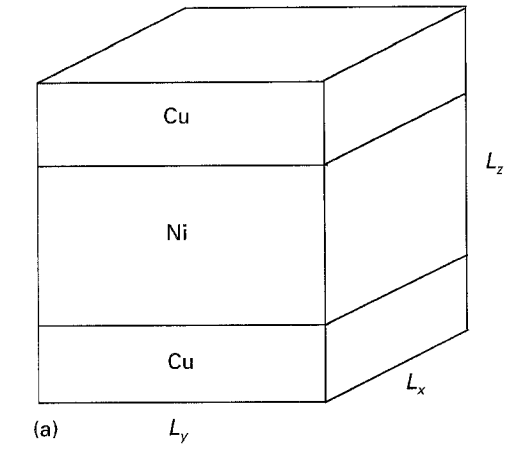
where E_{K} is the kinetic energy of all N atoms in the cell, T the temperature, and K Boltzmann's constant.

3. Results and discussion

We calculated the distances in the z-axis direction between two adjacent atom planes of the three computational cells after relaxation. The results are shown in Figs 2–4. A common character of the three curves is that the variation of spacing can be described as a near-square wave, even when the number of copper (or nickel) atom planes is reduced to three. The period of the square wave is determined by the modulation of thin film. There are atom drifts near the copper/nickel phase boundary. This area is termed the interface region. For a system with $N = 960$, the drifts in the copper region extend to 3 atomic planes, while in the nickel region they extend to 2 atomic planes; we can then define the interface region as including approximately five atomic planes. If we increase the modulation length of the thin film the drift area will not increase. However, for systems with $N = 384$ and 448, the drift area shrinks. We consider this phenomenon to result from the interface interaction and overlap. From the spacing variation curve, it is clear that copper and nickel atoms do not interdiffuse and that the composition changes abruptly. This is in agreement with experiment. It can also be seen that there

TABLE III Number of atoms in cells

Cell	Number of atoms, N	L_z (nm)	Irradiated volume $lx \times ly \times lz$ (nm^3)	L_x (nm)
1	384	2.3480	11 × 11 × 11	0.44491
2	448	2.6017	11 × 11 × 11	0.44491
3	960	5.4574	11 × 11 × 5 11 × 11 × 11	0.44491



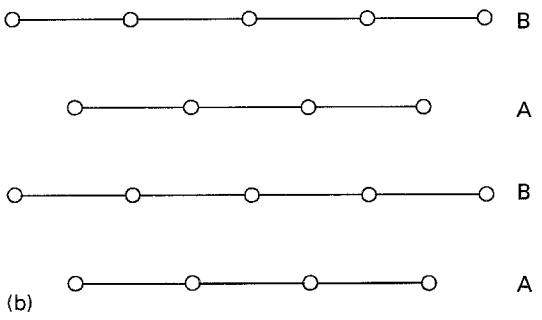


Figure 1 (a) The shape of the computational cell. L_x, L_y, L_z are the lengths of the three sides along the X, Y, Z directions, respectively. (b) Atom stacking pattern for copper or nickel along the [1 0 0] direction. A(B) represents the atomic plane which is the projection in the Z–Y($Z-X$) plane.

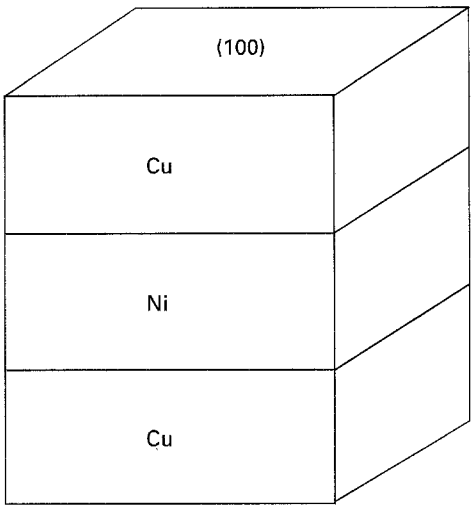


Figure 2 Variation of the interplanar spacing along the Z direction for cell 1: $N = 384$, $lz = 2.3480$ nm. "depth" represents the sequence number of the atomic plane normal to the z-axis.

is an expansion of copper and a shrinkage of nickel regions. The percentage expansion of copper is much larger than that of shrinkage of the nickel region. This is probably because the bulk modulus of nickel is much larger than that of copper. The ratios for copper and nickel are listed in Table IV.

It was found that the atom arrangement retains the fcc structure in the x–y plane, but that the average distance between atoms along the x-axis (or y-axis) changes. The curves for the three cells are shown in

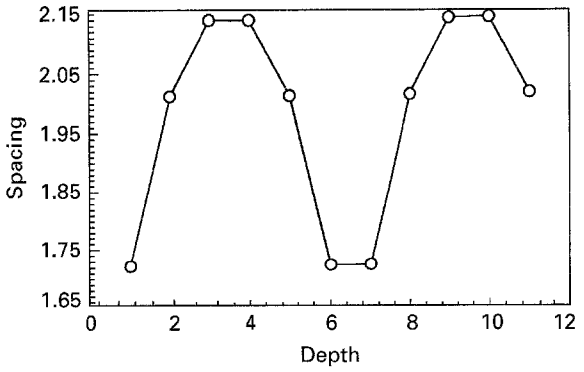


Figure 3 Variation in interplanar spacing along the Z direction for cell 2: $N = 448$, $Lz = 2.6017$ nm.

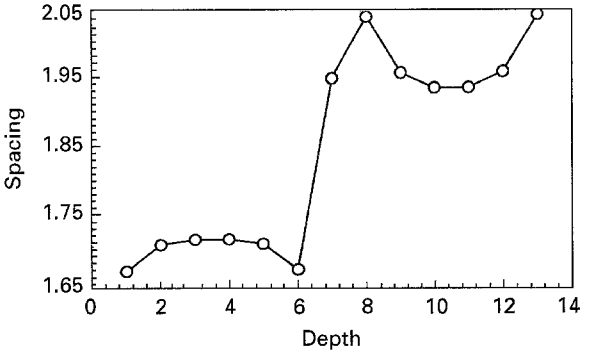


Figure 4 Variation in interplanar spacing along the Z direction for cell 3: $N = 960$, $Lz = 5.4574$ nm.

TABLE IV The variation of ratios of the average lattice parameters of cells in the z-axis direction. (−) shrinkage, (+) expansion. $\bar{d}$ is the average distance between [1 0 0] atomic planes in cells, $\bar{\theta}$, corresponding to the second diffraction angle. $\theta°$ is the position of the zero-peak of the calculated X-ray profile

	Cell		
	1	2	3
Ni	− 2.4%	− 2.4%	− 3.5%
Cu	18.4%	7.3%	5.1%
$\bar{d}$ (nm)	0.396 48	0.375 86	0.370 36
$\bar{\theta}$ (deg)	35.3	37.5	38.2
$\theta°$ (deg)	36.0	38.0	37.5

Figs 5–7. It was found that there is an expansion of nickel and a shrinkage of the copper region in the x–y plane. This coincides with the expansion of copper and shrinkage of the nickel region along the z-axis for a fixed volume. The average atom potential energy in the interface region is high when the modulation length is small. This is because the interface regions overlap each other. When the repeat period increases, the interface regions move apart. The average atom energy drops and the interface becomes more steady.

We calculated the X-ray profile of a single computational cell. It shows a small peak whose intensity is very low. However when we simulated the diffraction of multilayer thin films described as before, we found some "extra" peaks, which were not "pure" peaks of copper or nickel. They are shown in Figs 8–10. The

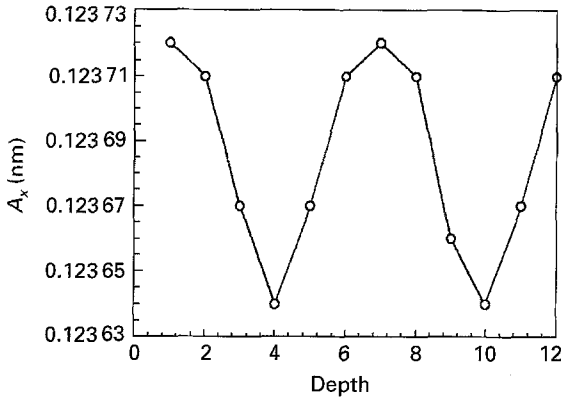


Figure 5 Variation of average distance between atoms along the X direction for cell 1.

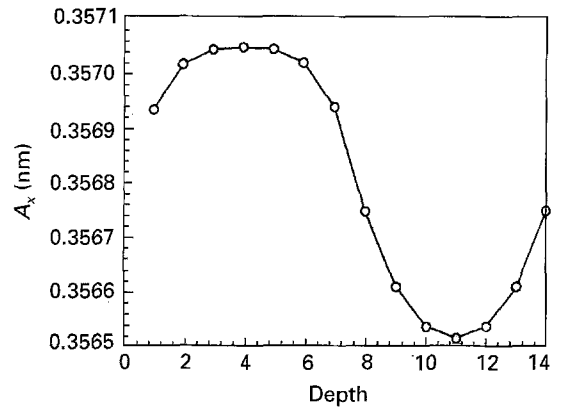


Figure 6 Variation of average distance between atoms along the X direction for cell 2.

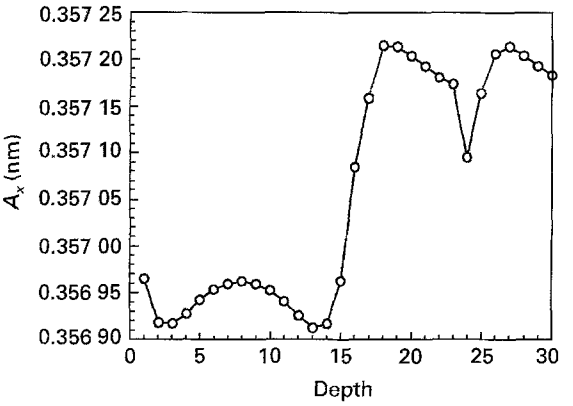


Figure 7 Variation of average distance between atoms along the X direction for cell 3.

smaller the modulation length, the fewer were the peaks. When the modulation length was large enough, peaks of pure copper or nickel appeared. For example, the profile of a system with $N = 960$ contains a (2 0 0) peak of copper at 39.3° and a (2 0 0) peak of nickel at 40.5°. These indicate that the "extra" peaks are due to the diffraction between interfaces, and they contain the interaction of interfaces. When the repeat period increases, the effects of the bulk increase, and then the peaks of pure copper or nickel appear. These phenomena were also seen by Chaudihuri and Alyan's [6] experimental results for Au/Ni multilayer thin films.

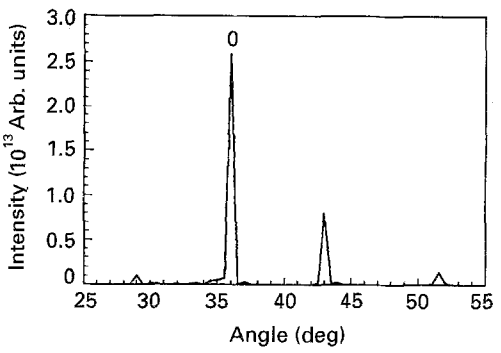


Figure 8 X-ray diffraction profile for cell 1. The irradiated volume is $11 \times 11 \times 11$. 0, zero-peak.

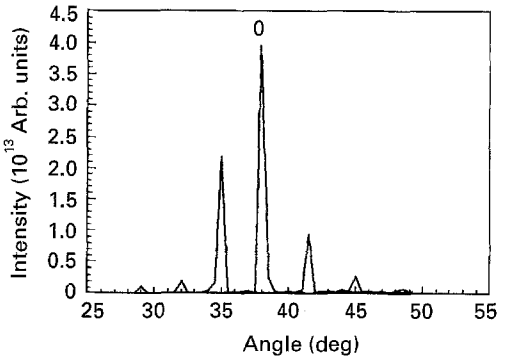


Figure 9 X-ray diffraction profile for cell 2. The irradiated volume is $11 \times 11 \times 11$. 0, zero-peak.

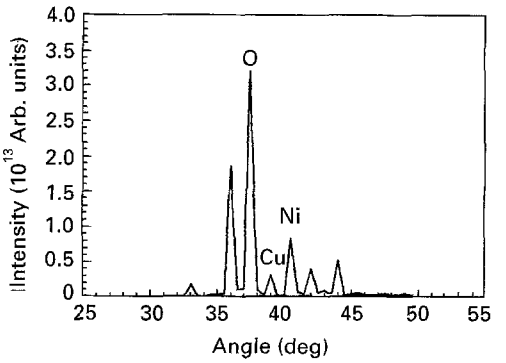


Figure 10 X-ray diffraction profile for cell 3. The irradiated volume is $11 \times 11 \times 5$. 0, zero-peak.

The zero-peak is the average result of the bulk and the interface diffraction and its position is seriously affected by the structure of the interface region. To see that, we calculated the average distance, $\bar{d}$, between the (1 0 0) atomic planes of the three cells, together with the corresponding second diffraction angles, $\bar{\theta}$, calculated from

$$2\bar{d}\sin\bar{\theta} = 2\lambda \quad (7)$$

All the results are listed in Table IV. By comparing $\bar{\theta}$ with the zero-peak position, $\theta°$, of the X-ray profile, the two are seen to coincide on the whole. The position of the zero-peak is seen to be different for different interfaces, appearing to exhibit a trend to move to the high-angle direction, $\bar{\theta}_1 < \bar{\theta}_2 < \bar{\theta}_3$. However, we note that $\theta_2° > \theta_3°$, this may be caused by the different atom

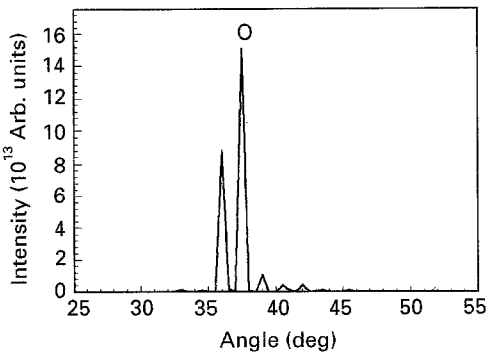


Figure 11 X-ray diffraction profile for cell 3. The irradiated volume is $11 \times 11 \times 11$. 0, zero-peak.

arrangements in the x–y plane shown in Figs 6 and 7. Some satellite peaks also exist around the zero-peak in the X-ray profile; these peaks are produced by the diffraction of the modulation structure. The numbers and positions of these peaks for different interfaces are very different. Thus, the X-ray profile is sensitive to interface structure. This character was used by us to adjust the interatomic interaction model by comparing the theoretical calculation with experimental results.

We also calculated another X-ray profile for the system with $N = 960$ by increasing the irradiated volume to $11 \times 11 \times 11$. This is shown in Fig. 11. It was found that the positions of low-order peaks were unchanged and those of high-order peaks exhibited small changes. The intensity of the low-order peaks increased much more rapidly than that of high-order peaks. Thus, it seems that the theoretical analysis can be performed more correctly and simply by increasing the number of layers in the multilayer thin film.

Jones and Slotwinski [4] also obtained the near-square character of the Cu/Ni (1 0 0) interface using embedded atom method (EAM). In the present work, similar results were obtained using the much simpler Morse potential. Therefore, this is a good method to obtain simple and nearly correct models by modifying the Morse potential. Because the X-ray profile is sensitive to the interface structure, it can be expected that the interface model could be improved by comparing theoretical X-ray profile calculations with experimental results.

4. Conclusion

X-ray diffraction profiles of Cu/Ni (1 0 0) multilayer thin films were calculated. Atomic position equilibrium was reached by using a molecular dynamics method to simulate interface structure with Morse potentials to model interatomic interactions. We found that X-ray profiles are sensitive to the interface structure and some "extra" peaks appeared. The number of "extra" peaks increases with increasing modulation length of the thin film. The "extra" peaks result from the diffraction between interfaces and also from the diffraction of the modulated structure. The variation of spacing normal to the interface can be described as a near-square wave. The interface region approximately includes five atom layers for the Cu/Ni (1 0 0) multilayer thin film when its modulation length is not too small. When the modulation length is small enough, the interface regions overlap, and the average atom potential energy is high.

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References

1. R. W. BALLUFFI, M. RÜHLE and A. P. SUTTON, *Mater. Sci. Eng.* **89** (1987) 1.
2. R. CAR and M. PARRINELLO, *Phys. Rev. Lett.* **55** (1985) 2471.
3. S. MURRAY and M. I. BAKE, *Phys. Rev. B* **29** (1984) 6443.
4. R. S. JONES and J. A. SLOTWINSKI, *ibid.* **45** (1992) 13624.
5. HANS C. ANDERSON, *J. Chem. Phys.* **72** (1980) 2384.
6. J. CHAUDIHARI and S. M. ALYAN, *Thin Solid Films* **219** (1992) 63.
7. F. MILSTEIN, *J. Appl. Phys.* **44** (1973) 3825.
8. D. W. HERMANN, "Computer Simulation in Theoretical Physics" (Springer, Berlin, 1986).
9. Y. M. WANG, "X-ray Diffraction of Amorphous Solid and Crystal Defects" (Science Publishing House, China, 1988) (in Chinese).

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