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A molecular dynamics simulation of TiN film growth on TiN(0 0 1)

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ABSTRACT

The growth of thin TiN films on the TiN(0 0 1) surface during reactive sputtering was simulated by molecular dynamics with the modified embedded-atom method potential. TiN_3 is found to be the smallest epitaxial island and the film grows via the layer mode. Vacancy concentration in the deposited films decreases with increasing the substrate temperature and kinetic energy of incident atoms, resulting from the enhancement of the thermal diffusion and kinetic energy assisted athermal diffusion. To get the stoichiometric TiN film, the N:Ti flux ratio should be larger than unity and be increased with higher incident energy due to the weak adsorption of atomic N on TiN(0 0 1).

1. Introduction

B1 structure TiN exhibits excellent mechanical and distinctive physical properties, such as good resistance to wear and corrosion, golden color, low resistivity and high reflectance in the red and infrared. It has been widely used as hard wear-resistant coatings on cutting tools [1], corrosion-resistant coatings on mechanical parts [2], decorative overlayers on buildings [3], diffusion barriers in microelectronics [4], and antireflective layers on optical components [5]. TiN coatings and films are usually deposited by reactive sputtering (RS), where the effects of various deposition parameters, such as partial pressure of the reactive gas, substrate temperature, ion energy and ion-to-atom ratio, on the growth and properties of TiN coatings and films have been extensively investigated [6–8]. However, the results in literature are sometimes incompatible due to the insufficient knowledge of the growth mechanism of the TiN film and the complexity of RS, e.g., an intended change in one deposition parameter will unintentionally change others [9]. Therefore, increasing reliance is placed upon modeling to explore the growth mechanism of the TiN film and the influence of individual parameter on the growth by fixing the others. Mahieu and Depla [9] reviewed some models explaining the observed TiN film microstructures and crystallographic orientation. Most of them are deduced from experiments without atomic insights, while Gall et al. [10] calculated the binding and diffusion energies of adatoms, molecules, and small clusters on TiN surfaces by *ab initio* method. However, it was restricted in the initial nucleation stage of the film growth due to the large computational cost of the method. Baumann et al. [11] designed a semi-atomic continuum model to simulate the coarsening kinetics of TiN two-dimensional (2D) islands during annealing on the TiN surface, without considering the initial atomic assembly during the film growth. Nevertheless, the detailed understanding of the TiN film growth on the atomic scale is still a challenging topic in research up to date.

Atomic simulations (molecular dynamics (MD) or Monte Carlo) have been confirmed to be able to provide atomic insights into the process of film growth [12–16], but which have not been applied to the TiN film. Therefore, in present work, the TiN film growth on the TiN(0 0 1) surface was simulated by MD with the second nearest-neighbor modified embedded-atom method (2NN MEAM) potential combined with Ziegler–Biersack–Littmark (ZBL) repulsive potential. The adsorption behavior of atomic N and Ti on the TiN(0 0 1) surface was revealed. Furthermore, the effects of the substrate temperature, kinetic energy of incident atoms and N:Ti flux ratio on the film growth were discussed.

2. Simulation methods

2.1. Interatomic potentials

The interatomic potential is a key to MD simulation, which determines the feasibility and reliability of the simulation. For the Ti–N system, several pair potentials have been proposed [17–19], but the potential of pair type is not sufficiently accurate to predict structural properties far from the reference structure to which it is fitted, and induces Cauthy relation in conflict with

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experiments. A potential of many-body type was proposed to analyze the adhesion strength of interfaces between metals and TiN thin films [20], but nothing is known about its universality. Another two many-body potentials based on 2NN MEAM were simultaneously developed by Kim et al. [21] and Yu et al. [22], respectively. Both of them succeed in reproducing some fundamental physical properties of the Ti–N system. However, the former adopts the cohesive energy E_c of TiN deviating from the experimental data [23], while the latter neglects to make the tetragonal rutile structure more stable than the hexagonal ε-Fe_2N structure for Ti_2N. Here, a new set of potential parameters for the Ti–N system combining the advantages of these two potentials was proposed (Table 1) by introducing the experimental E_c of TiN and optimizing the combination of parameters C_{min} and C_{max} in the 2NN MEAM framework. The 2NN MEAM potential parameters for Ti and N were taken from Kim et al. [24] and Lee et al. [25] respectively without any modification. The cutoff distance r_c of all potentials is 4.8 Å, which is between the second and third nearest-neighbor distances of Ti. Some material properties for Ti–N system calculated using the present 2NN MEAM potential are listed in Table 2. It can be noted that the results agree well with the available experimental data and/or first-principles calculations, showing the validity of the potential. To simulate the TiN growth at different temperatures (T = 300–700 K), the corresponding lattice constants a_T were calculated, as listed in Table 3. The thermal linear expansion coefficient is $9.31 \times 10^{-6}\ K^{-1}$ by fitting these data, which is very close to the experimental value of $9.35 \times 10^{-6}\ K^{-1}$.

In MEAM, the energy consists of embedding energy and pair energy. To realistically describe the interatomic collisions at close separation during deposition process, the original pair potential ϕ_{ij} is smoothly joined to the universal ZBL repulsive potential ϕ_{ij}^{ZBL} [30] by introducing a scaled separation a^* [31], resulting in a modified pair interaction term φ_{ij},

$$\varphi_{ij}(R_{ij}) = \begin{cases} \phi_{ij}(R_{ij}), a^* \geqslant -1 \\ f(a^*)\phi_{ij}(R_{ij}) + (1 - f(a^*))\phi_{ij}^{ZBL}(R_{ij}), -3 < a^* < -1 \\ \phi_{ij}^{ZBL}(R_{ij}), a^* \leqslant -3 \end{cases} \quad (1)$$

$$f(a^*) = \{1 - [(a^* + 1)/2]^4\}^2, a^* = (9B\Omega/E_c)^{1/2}(R_{ij}/r_e - 1)$$

where R_{ij} is the distance between atoms i and j, B, r_e and Ω are the bulk modulus, the equilibrium nearest-neighbor distance and atomic volume of the reference structure, respectively. When $a^* < -1$, strong forces act between atoms accounting for collisions.

2.2. MD model of atomic deposition

The TiN film growth during RS is primarily attributed to the fluxes of energetic atomic N and Ti, which react on the surface of substrate [32]. Therefore, RS can be regarded as an atomic deposition process, where the overlay material is deposited atom-by-atom. The schematic of the MD model of atomic deposition is shown in Fig. 1, where the x-, y-, and z-directions are corresponding to [1 0 0], [0 1 0] and [0 0 1] of crystal. The substrate is created from B1 structure with the dimensions of $5a_T \times 5a_T \times 5a_T$. The periodic boundary conditions are applied to the side surfaces, so that the substrate can be regarded as an infinite slab in the x–y plane. The top surface is free to enable deposition on it. The substrate is divided into three regions from bottom to top. The atoms in the fixed region are immovable to prevent the substrate drift due to the incident atom momentum transfer. To simulate the approximately isothermal condition under which growth usually occurs, the isothermal region growing at the same rate as the film growth is set to absorb the kinetic energy of incident atoms and latent heat of condensation, where the velocity of each atom is rescaled at each time step. The atoms in the free region interact freely with incident atoms, through which the energy of incident atoms is transferred to the isothermal region. Before deposition, the substrate was relaxed for 2 ps.

The atomic deposition process was simulated by alternately injecting Ti and N atoms with an incident kinetic energy E_k and normal direction in a time interval of 1 ps from an initial height of 25 Å above the substrate and a random location in the x–y plane. 500 atoms in total, equating to 5 TiN(0 0 1) layers, were deposited on TiN(0 0 1), followed by the whole system relaxation for another 50 ps. During deposition, incident atoms may be reflected by the substrate, meanwhile the atoms in the substrate or deposited film may be sputtered by incident atoms. Sequentially, they may move a far distance from the substrate, and then will not contribute to the film growth any more. To improve the simulation efficiency and get the stoichiometric TiN film, these atoms are reflected and normally deposited onto the substrate with initial E_k when

Table 2
Elastic properties (bulk modulus B and elastic constant C_{ij}, in GPa), unrelaxed surface energy S_{ijk} (in J/m^2), enthalpy of formation ΔH_f, cohesive energy E_c and structural energy difference $\Delta E_{A\to B}$ of B1 structure TiN; lattice constants a and c (in Å), enthalpy of formation ΔH_f and structural energy difference $\Delta E_{A\to B}$ of rutile structure Ti_2N calculated using the present 2 NN MEAM potential, in comparison with experimental data (Exp.) and/or first-principles calculations (Cal.). The unit of energies is eV/atom.

Nitride	Property	MEAM	Exp.	Cal.
TiN (B1)	B	288	288[a]	282[a]
	C_{11}	561	625[a]	598[a]
	C_{12}	152	165[a]	118[a]
	C_{44}	191	163[a]	159[a]
	S_{100}	1.69		1.53[a]
	S_{110}	2.89		2.87[a]
	S_{111}	3.93		5.08[a]
	ΔH_f	−1.82	−1.75[b]	
	E_c	6.69	6.69[c]	7.17[d]
	$\Delta E_{B1\to B2}$	1.25		
	$\Delta E_{B1\to B3}$	0.39		
Ti_2N (rutile)	a	4.777	4.943[e]	
	c	3.048	3.036[e]	
	ΔH_f	−1.63	−1.38[f]	
	$\Delta E_{rutile\to\varepsilon\text{-}Fe_2N}$	0.015		

[a] Ref. [26] and references therein.
[b] Ref. [27].
[c] Ref. [23].
[d] Ref. [10].
[e] Ref. [28].
[f] Ref. [29].

Table 3
Lattice constants a_T of TiN at different temperatures T.

T (K)	300	400	500	600	700
a_T (Å)	4.253	4.256	4.260	4.264	4.269

Table 1
A set of 2 NN MEAM potential parameters for the Ti–N system.

Parameter	E_c (eV)	r_e (Å)	B (GPa)	d	ρ_0^N/ρ_0^{Ti}	Ti–N–Ti		N–Ti–N		Ti–N–N		Ti–Ti–N	
						C_{min}	C_{max}	C_{min}	C_{max}	C_{min}	C_{max}	C_{min}	C_{max}
Value	6.69	2.121	288	0	20	0.16	2.8	0.16	2.8	1.457	2.8	0.81	2.8