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# Theoretical study of the elastic properties of titanium nitride

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The equilibrium lattice parameter, relative volume  $V/V_0$ , elastic constants  $C_{ij}$ , and bulk modulus of titanium nitride are successfully obtained using the *ab initio* planewave pseudopotential (PW-PP) method within the framework of density functional theory. The quasi-harmonic Debye model, using a set of total energy vs molar volume obtained with the PW-PP method, is applied to the study of the elastic properties and vibrational effects. We analyze the relationship between the bulk modulus and temperature up to 2000 K and obtain the relationship between bulk modulus B and pressure at different temperatures. It is found that the bulk modulus B increases monotonously with increasing pressure and decreases with increasing temperature. Moreover, the Debye temperature is determined from the non-equilibrium Gibbs functions.

**KEY WORDS** Elastic constants; Debye temperature; *Ab initio* calculations; Titanium nitride

### 1 Introduction

Like most refractory transition metal nitrides, TiN has a NaCl-type structure (space group FM-3M). The Ti atom occupies the 1a (0, 0, 0) site, and the N atom occupies the 1b (0, 0.5, 0) site. It has been widely used as coating owing to its special properties such as high melting point, high hardness, high corrosion resistance, high specific strength and metallic conductivity<sup>[1-3]</sup>. However, TiN coatings are usually subject to high internal stresses between the coating and the substrate. High internal stress will reduce bonding strength between the substrate and the coating layer. Only when the elastic constants are known, the internal stress can be determined by X-ray diffraction. Sometimes, the same residual stress in the literature may associate with quite different strains. For example, for the well-known thin film TiN, its Young's modulus is widely accepted as 640 GPa<sup>[4]</sup> in Europe, however, in Japan, the value is 250 GPa<sup>[5,6]</sup>.

The single-crystal elastic constants of solids are essential for the interpreting seismic wave velocities and their lateral variations. A study of the elastic properties for materials

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is well motivated by, for example, the understanding that one thereby gains about the chemical bonds and the cohesion of material. Moreover, the elastic constants are also related to the thermal properties according to the Debye theory. Although there exist several research efforts in thin films, the bulk properties of TiN at high temperature are less studied. The aim of this study is to use *ab initio* calculations for getting a new insight on the structural and elastic properties of TiN at high temperatures.

#### 2 Theoretical Method

Firstly, we make a first-principle total energy electronic structure calculation. In our total energy calculation, we use the plane-wave pseudopotential (PW-PP) method<sup>[7]</sup>. The generalized gradient approximation of revised-PBE (RPBE)<sup>[8]</sup> is used for the exchange-correlation energy functional. The initial convergence test guided the choice of 500 eV for the energy cutoff,  $E_{\rm cut}$ . For the cubic Brillouin-zone sampling, we use the  $12 \times 12 \times 12$  mesh<sup>[9]</sup>, which is enough to achieve the self-consistent convergence of the total energy to  $4 \times 10^{-7}$  eV/atom. All total energy calculations are implemented through the CASTEP code<sup>[10]</sup>.

Then, a recent developed Debye-like model (quasi-harmonic Debye model)<sup>[11]</sup> is implemented, and the phononic and the anharmonic effects are also considered. The investigations of elastic properties in this study are done within the quasi-harmonic Debye theory of crystals, without making extensive and complicated lattice dynamics calculations. In this model, the zero pressure bulk modulus  $B_0$  is determined by fitting the calculated energy-volume (*E-V*) data to the Birch–Murnaghan EOS<sup>[12]</sup>

$$\Delta E(V) = E - E_0 = B_0 V_0 \Big[ \frac{V_n}{B'_0} + \frac{1}{1 - B'_0} + \frac{V_n^{1 - B'_0}}{B'_0(B'_0 - 1)} \Big]$$
(1)

where,  $E_0$  is the equilibrium energy. The pressure p vs the relative volume  $V_n$  (= $V/V_0$ , where,  $V_0$  is the equilibrium volume at zero pressure) is obtained by

$$p = -\frac{\mathrm{d}E}{\mathrm{d}V} = \frac{B_0}{B_0'} [V_n^{-B_0'} - 1]$$
(2)

In addition, the bulk modulus B is also investigated under various pressures and temperatures using the quasi-harmonic Debye model. In the quasi-harmonic Debye model, the non-equilibrium Gibbs energy  $G^*(V; p, T)$  of TiN crystal is taken in a form<sup>[13]</sup>

$$G^{*}(V; p, T) = E(V) + pV + A_{vib}(V; T)$$
(3)

where, E(V) is the total energy per unit cell; pV corresponds to the constant hydrostatic pressure condition.  $A_{\rm vib}$  is the vibrational Helmholtz free energy given by the Debye model, which can be written using the Debye model of the phonon density of states as<sup>[14,15]</sup>

$$A_{\rm vib}(\Theta_D;T) = nkT \Big[\frac{9}{8} \frac{\Theta_D}{T} + 3\ln(1 - e^{-\Theta_D/T}) - D(\Theta_D/T)\Big]$$
(4)

where,  $\Theta_D$  is the Debye temperature,  $D(\Theta_D/T)$  represents the Debye integral, and n is the number of atoms per formula unit. The equation of state (EOS) can be obtained by  $\cdot$  148  $\cdot$ 

minimizing the non-equilibrium Gibbs function with respect to volume V as follows

$$\left(\frac{\partial G^*(V; p, T)}{\partial V}\right)_{p,T} = 0 \tag{5}$$

The isothermal bulk modulus is defined as

$$B(p,T) = B(V) = V \left(\frac{\partial^2 G^*(V;p,T)}{\partial V^2}\right)_{p,T}$$
(6)

Instead of solving the Christoffel equations, isotropic approximation is considered to obtain the Debye temperature  $\Theta_D^{[16]}$ 

$$\Theta_D = \frac{h}{2\pi k} [6\pi^2 V^{1/2} n]^{1/3} f(\sigma) \sqrt{\frac{B_{\rm S}}{M}}$$
(7)

where, M is the molecular mass of the crystal, h is the Planck's constant,  $B_S$  is the adiabatic bulk modulus, which is approximately calculated by the static compressibility<sup>[16,17]</sup>

$$B_{\rm S} \approx B(V) = V \Big[ \frac{\mathrm{d}^2 E(V)}{\mathrm{d} V^2} \Big]$$
 (8)

and  $f(\sigma)$  is given in Refs.[18] and [19]. Here, the Poisson's ratio  $\sigma$  is taken as  $0.201^{[20,21]}$ .

It is well known that the elastic constants are calculated by means of Taylor expansion of the total energy,  $E(V, \delta)$ , for the system with respect to a small strain  $\delta$  of the cell volume V. The energy of a strained system is expressed as follows<sup>[22]</sup>:

$$E(V,\delta) = E(V_0,T) + V_0 \left[ \sum \tau_i \xi_i \delta_i + \frac{1}{2} \sum C_{ij} \tau_i \xi_i \delta_i \right]$$
(9)

where,  $E(V_0, T)$  is the energy of the unstrained system with equilibrium volume  $V_0$  at different temperatures,  $\tau_i$  is an element in the stress tensor, and  $\xi_i$  is a factor to consider Voigt index<sup>[22]</sup>. The total energy  $E(V_0, T)$  can be obtained by the quasi-harmonic Debye model. The three independent elastic constants  $C_{11}$ ,  $C_{12}$ , and  $C_{44}$  are resulted from different kinds of strains along certain directions. A detailed description of the calculation method has been reported in Ref.[23].

## 3 Results and Discussion

In Fig.1, we present the relative volumetemperature-pressure diagrams of TiN.

The obtained relative cell volume  $V/V_0$ dependences on temperature T at different pressures p are illustrated in Fig.1. It is noted that as the temperature T increases, the value  $V/V_0$  increases at a given pressure. The effects of the pressure on the relative volume  $V/V_0$  are very small at low temperatures and are increasingly obvious as the temper-



Fig.1 Calculated  $V/V_0$ -p-T relationships of TiN.

ature increases. When the temperature T increases, the curve of  $V/V_0$ -T becomes steeper, indicating that the cell volume of TiN crystal expands considerably easily at high temperatures and low pressures. The higher the temperature, the faster the cell volume increase is.

Now we investigate the dependences of bulk modulus B on temperature T and pressure p. Using the quasi-harmonic Debye model mentioned above, the relationship of the bulk modulus B and the temperature Tis calculated and plotted in Fig.2.



**Fig.2** Bulk modulus B as a function of temperature T at zero pressure.

The calculated bulk modulus  $B_0$  is 280.1 GPa (T=0 K) which is consistent with the experimental data ( $B_0=288$  GPa)<sup>[24]</sup>. From Fig.1, it can be seen that when T<100 K, B remains nearly constant, and the lattice parameter, a, remains nearly constant. When T>100 K, the bulk modulus B decreases dramatically as T increases, which indicates that the cell volume changes rapidly. It is the rapid volume variation that makes the bulk modulus  $B_0$  decrease rapidly. By fitting the B-T data to third-order polynomial, we obtain the following relationship

$$B = 281.82507 - 2.438 \times 10^{-2}T - 1.4517 \times 10^{-5}T^2 + 3.03024 \times 10^{-9}T^3, \text{ for } T < 2000 \text{ K}$$
(10)

From Eq.(9), we obtain the slope of B-T curve

$$K = \left(\frac{\mathrm{d}B}{\mathrm{d}T}\right)_{p=0} = -2.438 \times 10^{-2} - 2.9034 \times 10^{-5}T + 9.09072 \times 10^{-9}T^2 \tag{11}$$

The relationships between bulk modulus B and pressure p at different temperatures (T=0, 500, 1000, and 1500 K) are plotted in Fig.3.

It is noted from Fig.3 that the bulk modulus B increases with pressure p at a given temperature and decreases with temperature T at a given pressure. The dependences of the bulk modulus B on the pressure are nearly linear at various temperatures of T=0, 500, 1000, and 1500 K, respectively. It indicates that the effect of increasing pressure on TiN is the same as the decreasing temperature of the material.



Fig.3 Pressure dependence of the bulk modulus of TiN crystal.

For the cubic structure, there are only three independent elastic constants, namely,  $C_{11}$ ,  $C_{12}$ , and  $C_{44}$ . The zero pressure bulk modulus  $B_0$  of cubic structure is given by the equation

$$B_0 = (C_{11} + 2C_{12})/3 \tag{12}$$

The calculated elastic constants  $C_{ij}$ , bulk modulus  $B_0$ , and lattice parameter *a* are listed in Table 1.

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Table 1 Calculated elastic constants/GPa, bulk modulus/GPa, and lattice parameter for TiN

TiN												
$C_{11}$	$610^{[25]}$	$625 \; (Expt.)^{[26]}$	$497.8 \; (\text{Expt.})^{[20]}$	$600^{[27]a}$	$598^{[27]b}$	589.3 (Calc.)						
$C_{12}$	100	165	128.7	120	118	125.3						
$C_{44}$	168	163	168.1	159	159	160.1						
$B_0$	270	318	236.4	280	278	280.0						
		$B_0 = 288 \text{ GPa}^{[24]} \text{Expt.}$	$a{=}0.425$ nm	$a{=}0.422 \text{ nm}^{[28]}$		$a{=}0.423~\mathrm{nm}$						

Note: a. Obtained by CASTEP code with the Perdew-Wang 1991 GGA functional;

b. Obtained by CASTEP code with the Perdew-Burke-Ernzerhof 1996 GGA functional.

From Table 1, it is known that agreements between experimental data and our calculated results for lattice parameter a, elastic constants  $C_{11}$ ,  $C_{12}$ ,  $C_{44}$ , and  $B_0$  are excellent. The calculated  $B_0$  consists of the value obtained by the quasi-harmonic Debye model  $(B_0=280.1 \text{ GPa})$ . Another elastic property of TiN is the elastic anisotropy A, which is defined by the following relation for a cubic crystal<sup>[29]</sup>

$$A = 2C_{44}/(C_{11} - C_{12}) \tag{13}$$

In Table 2, we present the temperature dependences of elastic constants  $C_{ij}$ , bulk modulus B, and elastic anisotropy A at the temperature interval of 300–1800 K.

From Table 2, it can be found that all elastic constants  $C_{ij}$  and bulk moduli decrease monotonously when the temperature is enhanced. The effect of temperature on the elastic constants of TiN crystal is large. The elastic constant  $C_{11}$ , which corresponds to the longitudinal wave  $v_{p1}$  propagated along [001], decreases dramatically with the increasing temperature.  $C_{44}$  decreases very slowly with the elevated temperature, which indicates that the velocity of shear wave  $v_{s1}$  propagated along [110] or [001] will be slower as the temperature increases. We can find that the elastic anisotropy factor A for the TiN crystal increases with the increasing temperature, which indicates that the elastic anisotropy for TiN crystal will gradually be strengthen with the increasing temperature. The bulk moduli obtained from the quasi-harmonic Debye model are in agreement with the values obtained from the elastic constants. Unfortunately, no experimental or theoretical data of elastic constants are available for our comparison.

**Table 2** Elastic constants  $C_{ij}$ /GPa, bulk modulus/GPa, and Debye temperature at high temperatures for TiN at zero pressure

T/K	$B^{\mathbf{a}}$	$B^{\mathrm{b}}$	$C_{11}$	$C_{12}$	$C_{44}$	A	$\Theta_D/\mathrm{K}$
300	268.3	261.5	559.4	112.5	157.2	0.7035	579.2
450	263.0	257.5	550.6	111.0	156.7	0.7129	574.5
600	257.1	252.4	539.6	108.9	156.2	0.7253	569.3
750	251.6	247.9	529.0	107.4	155.5	0.7376	563.9
900	245.8	242.1	516.5	104.8	154.6	0.7510	558.3
1050	239.7	238.9	506.2	105.3	153.9	0.7678	552.7
1200	233.1	231.8	491.8	101.8	153.2	0.7856	546.8
1350	227.1	227.2	479.7	101.0	152.4	0.8048	540.7
1500	220.7	222.2	467.5	99.6	151.7	0.8246	534.6
1650	214.0	213.8	451.1	95.2	150.9	0.8480	528.2
1800	208.1	209.8	439.4	95.0	149.9	0.8705	521.6

**Note**: a. Obtained from the quasi-harmonic Debye model;

b. Obtained from the elastic constants.

Another fundamental parameter of solids is the Debye temperature  $\Theta_D$ , which is closely related to specific heat, elastic constants, thermal coefficients, and rigidity. At 300 K, we obtain the Debye temperature  $\Theta_D$ =579.2 K, which is in excellent agreement with the experimental data ((580±20) K<sup>[30]</sup>). From Table 2, it can be seen that the Debye temperature  $\Theta_D$  decreases with temperature T. As the temperature increases, the Debye temperature  $\Theta_D$  decreases more quickly when T>600 K than at low temperature region.

## 4 Conclusion

In summary, the temperature dependence of bulk modulus, relative volume  $V/V_0$ , elastic constants  $C_{ij}$ , and Debye temperature of TiN are obtained using the *ab initio* planewave pseudopotential (PW-PP) method. The temperature effects have been defined using the quasi-harmonic Debye model exploiting the total energy calculations. It is found that the bulk modulus *B* is nearly a constant when T < 100 K, whereas it decreases dramatically with the increment of temperature *T* when T > 100 K. The bulk modulus *B* increases monotonously as the pressure increases. Moreover, the temperature dependence of Debye temperature is also successfully obtained. The Debye temperature decreases with *T* at low temperatures and gradually approaches a linear increase at high temperatures, and then the increasing trend becomes steeper. Our study on the properties of TiN will be helpful for further understanding of TiN crystal.

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