Physica B 407 (2012) 3617–3621

Contents lists available at SciVerse ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Structural and elastic properties of TiN under high pressure

Ke Liu [a,b], Xiao-Lin Zhou [a,*], Hai-Hua Chen [b], Lai-Yu Lu [a]

[a] Department of Physics, Sichuan Normal University, Chengdu 610066, PR China
[b] Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, PR China

ARTICLE INFO

Article history:
Received 7 November 2011
Received in revised form
4 February 2012
Accepted 12 May 2012
Available online 19 May 2012

Keywords:
Equation of state
Elastic constants
High pressure
Debye temperature
TiN

ABSTRACT

We have investigated the structural and elastic properties of TiN at high pressures by the first-principles plane wave pseudopotential density functional theory method at applied pressures up to 45.4 GPa. The obtained normalized volume dependence of the resulting pressure is in excellent agreement with the experimental data investigated using synchrotron radial x-ray diffraction (RXRD) under nonhydrostatic compression up to 45.4 GPa in a diamond-anvil cell. Three independent elastic constants at zero pressure and high pressure are calculated. From the obtained elastic constants, the bulk modulus, Young's modulus, shear modulus, acoustic velocity and Debye temperature as a function of the applied pressure are also successfully obtained.

1. Introduction

Face-centered cubic titanium carbide and nitride belong to the group of so-called hard refractory metals. Their high melting point, hardness, brittleness, and metallic conductivity are common to all carbides and nitrides of the Group IV and V transition metals [1]. TiN is presently one of the most important materials for hardness and corrosion resistant coating. Presently interest is also developing within the microelectronic industry for the use of TiN as an electrically conducting barrier [2].

There are large number of experiments devoted to various aspects of TiN film growth [3–5] and many theoretical calculations about elastic modulus for TiN [2,6,7]. Zhao et al. [8] investigated the behavior of TiN using axial x-ray diffraction under high pressure to 30.1 GPa. Their experimental results suggested an isostructural phase transition at about 7 GPa as shown by the discontinuity of V/V_0 data with pressure.

The knowledge of elastic constants is essential for many practical applications related to the mechanical properties of a solid: load deflection, thermoelastic stress, internalstrain, sound velocities, and fracture toughness [9]. Moreover, the elastic constants are also related to the thermal properties according to the Debye theory. At present, the investigations of the elastic constants of TiN at zero pressure have been experimentally [2] and theoretically [2,10] investigated successfully. Chen et al. have reported the elastic constants of TiN at high temperature [11]. However, to the best of our knowledge, there are lack of theoretical investigations on the high-pressure elastic constants of TiN. Therefore, we here make first-principles calculations on the structural and elastic properties of TiN under high pressure.

2. Theoretical method

2.1. Total energy electronic structure calculations

In this work, all first-principles calculations were performed with the CASTEP code [12]. The ultrasoft pseudopotential [13] was employed to describe the interaction between ions and electrons. Both the local-density approximation (LDA) [14] and the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) [15] were used to describe the exchange and correlation potentials. Wave functions of valence electronics expand in the form of plane wave basis sets. Pseudo atomic calculations are performed for N 2s2 2p3 and Ti 3s2 3p6 3d2 4s2. A kinetic cut-off of plane wave 350 eV and a $10\times10\times10$ Monkhorst–Pack [16] grid for Brillouin-zone sampling are used throughout. The threshold of 10^{-7} eV/atom is used to determine whether the self-consistent progress has been converged.

2.2. Elastic constants

The elastic constants are calculated as the second derivatives of the internal energy with respect to the strain tensor. The elastic constants of MgB_2 [17–19], AlB_2 [20] and c-BN [21] using the theoretical method proposed by Sin'ko and Smirnov [22] are

* Corresponding author.
E-mail addresses: Zhouxl_wuli@163.com, lkworld@126.com (X.-L. Zhou).

0921-4526/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.physb.2012.05.038

successfully obtained. Only a brief description of this method is made as follows.

For TiN with lattice constant a, the Bravais lattice vectors are normally written in the form of

$$\mathbf{R} = \frac{1}{2}\begin{pmatrix} 0 & a & a \\ a & 0 & a \\ a & a & 0 \end{pmatrix} \quad (1)$$

Consider a crystal isotropic compressed to the density $\rho_1 = 1/V_1$, where V_1 is the distorted volume due to the strain tensor $\varepsilon=[\varepsilon_{ij}]$ with small lattice distortion $\varepsilon_{ij}(i,j=1,2,3)$, which takes every Bravais lattice point $\mathbf{R}$ of the undistorted lattice to a new position $\mathbf{R}'$ in the strained lattice, $\mathbf{R}_i' = \sum(\delta_{ij}+\varepsilon_{ij})\mathbf{R}_j$. For a homogeneous strain the parameters ε_{ij} are simply constants with $\varepsilon_{ij}=\varepsilon_{ji}$, where the subscripts i, j indicate Cartesian components and each ranges over three values, δ_{ij} is the Kronecher delta.

Since a cubic crystal structure possesses three independent elastic constants, we thus use the three independent strains listed in Table 1. All these stains are not volume-conserving. The atomic positions are optimized at all strains. For each strain, a number of small values of γ are taken to calculate the total energies E for the strained crystal structure. The calculated E–γ points are then fitted to a second-order polynomial $E(\rho_1,\gamma)$, and the third-order derivatives of $E(\rho_1,\gamma)$ with respect to γ are easily obtained.

3. Experimental method

We investigated the compression behavior of TiN using synchrotron radial x-ray diffraction (RXRD) technique under nonhydrostatic compression up to 45.4 GPa in a diamond-anvil cell. We obtained the hydrostatic compression equation of state of TiN. Fitting to the third-order Birch–Murnaghan equation of state, the bulk modulus derived from nonhydrostatic compression data varies from 232 to 353 GPa, depending on angle Ψ, the orientation of the diffraction planes with respect to the loading axis. The RXRD data obtained at $\Psi=54.7^\circ$ yield a bulk modulus $B_0=282\pm9$ GPa with pressure derivative B_0' fixed at four, which reported by us earlier [23].

Table 1
Strains used to calculate the elastic constants of TiN. In the second column, all unlisted elements of strain tensors are set to zero.

Strains	Distortion	$\rho_1 \frac{\partial^2 E(\rho_1,\gamma)}{\partial\gamma^2}\Big\vert_{\gamma=0}$
1	$\varepsilon_{11}=\varepsilon_{22}=\gamma$	$2(C_{11}+C_{12})$
2	$\varepsilon_{13}=\varepsilon_{31}=\gamma$	Θ_D
3	Θ_D	Θ_D

4. Results and discussion

It is well known that GGA usually overestimates the lattice constants and underestimates the elastic constants, while LDA underestimates the lattice constants and overestimates the elastic constants [24,25]. For this reason, both the GGA and LDA methods were used to obtain the lattice parameters, bulk modulus and elastic constants of TiN.

We, using both the GGA and the LDA, take a series of lattice constants a to obtain the total energy E of TiN and the corresponding primitive cell volume V, then an energy–volume (E–V) curve can be obtained by fitting the calculated energy–volume (E–V) data to the Birch–Murnaghan equation of state (EOS) [26]. The obtained lattice constant, bulk modulus and its pressure derivative are listed in Table 2, together with our experimental data and other experimental and theoretical results. The agreement among them is good.

In Fig. 1, we illustrate the GGA- and LDA-calculated normalized primitive cell volume V/V_0 (V_0 is the zero-pressure equilibrium primitive cell volume) as a function of pressure P. For comparison, our experimental data observed by RXRD method at $\Psi=54.7^\circ$ up to 45.4 GPa are also presented. It is shown that the calculated results, especially the LDA-calculated EOS, agree well with the experimental data. The correspondence of the calculated EOS in this work with the experimental data gives us confidence to investigate the elastic behavior of TiN at high pressure. By fitting LDA-calculated data to second-order polynomials of the applied pressure, we obtained the following relationship at $T=0$ K:

$$V/V_0 = 0.99896 - 0.00302P + 10^{-5}P^2 \quad (2)$$

In Table 3, we present the calculated three independent elastic constants both in the GGA and LDA at zero pressure. Previous experimental data and the other theoretical results at zero pressure are listed in Table 3. On the whole, our results are in agreement with the experimental data and those from other theoretical calculations. On the other hand, it is found that the LDA results are larger than the GGA ones, which are consistent with the law of LDA underestimates the lattice constants and overestimates the elastic constants [24,25].

Table 2
Our GGA- and LDA-calculated lattice constants (Å), bulk moduli (in GPa), pressure derivative of bulk modulus B_0' of TiN at zero pressure, compared with experimental and other calculated results.

Present calculation			Other calculation	Experiment
a/Å	4.246(GGA)	4.175(LDA)	4.26[a], 4.18[b],4.175/4.236/4.237/4.260[e], 4.24[g],4.32[h],4.253[k]	4.240[i],4.235[j]
B_0/GPa	277.99	320. 60	286[a], 322[b] 270[c], 310[d], 319/282/282/266[e],305[g],389[h],280[k]	282 ± 9(present) 320[c],282[f],288[h]
B'_0	4.30	4.25	4.3/4.2/4.2/4.2[e]	4(present)

[a] From the FLAPW-GGA method [25].
[b] From the FLAPW method [25].
[c] From the GGA method [2].
[d] From the LDA method [2].
[e] From the LDA/ PW91/ PBE/ RPBE method [6].
[f] Ref. [27].
[g] From the LAPW method [28].
[h] From the LMTO-ASA method [29].
[i] Ref. [30].
[j] Ref. [31].
[k] Ref. [7]