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Mechanical deformation modes and anisotropy of IVB transition metal nitrides



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1. Introduction

The IVB transition metal nitrides, namely, TiN, ZrN, and HfN, are a group of ceramic materials with special properties. These compounds not only possess excellent electric and thermal conductivity but also share the properties of covalent compounds, such as high melting point, high hardness, and high corrosion resistance. These compounds have long attracted considerable attention among researchers [1–8]. In the field of industrial application, IVB transition metal nitrides mostly serve as cutting materials, ultra-wear-resistant materials, and thermal barrier coating. Thus, these compounds have a significant function in basic research and technical research. The mechanical properties [1–5] and thermal properties [6–8] of these compounds have been extensively studied.

Elastic modulus has always been the focus of mechanical research. The nitrides of IVB transition metals have large Young's modulus and relatively high hardness. TiN, ZrN, and HfN are mainly prepared through hot pressing and thin film deposition. However both preparation methods can facilitate the production of internal stress in materials, thereby affecting lattice structure and configuration. These changes result in the anisotropic distortion of the crystal lattice and significant differences in the measured data for the physical properties of the material. Furthermore, thermal properties are jointly affected by electron and phonon. Therefore, the influence of the thin film and substrate on electron property and lattice vibration should be considered when studying thin films. The anisotropy of mechanical elasticity and

ABSTRACT

This paper studies the deformation modes and anisotropy of the IVB transition metal nitrides TiN, ZrN, and HfN using the plane-wave density functional theory. The values of elastic modulus and hardness of the TiN, ZrN, and HfN are calculated and analyzed in detail. This result suggests typical elastic anisotropy, which increases in the order of TiN \rightarrow ZrN \rightarrow HfN. This phenomenon results in inevitable lattice distortion and microcracks. The minimum value of thermal conductivity of the polycrystalline system decreases in the order of TiN \rightarrow ZrN \rightarrow HfN. The thermal conductivity of single crystals in each crystal orientation presents a nearly anisotropic thermodynamic property.

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thermal properties of IVB transition metal nitrides are still not completely clear. Therefore, calculating the structural parameters and elastic constants of the single crystal structures of TiN, ZrN, and HfN is very important for revealing the mechanical and thermal properties of IVB transition metal nitrides.

Using the first-principles method, this research studies the deformation modes and elastic constants of TiN, ZrN, and HfN. A detailed investigation on the mechanical and thermal properties of these materials as well as anisotropic conditions is also performed.

2. Computational methods and theory

2.1. Calculation parameter

This research is conducted using the CASTEP [9] program and first-principles density functional theory [10]. We use the periodic boundary condition and Ceper-ley–Alder–Perdew–Zunger method under local density approximation (LDA) [11] and Perdew–Burke–Ernzerhof method under generalized gradient approximation (GGA) for electronic exchange–correlation energy [12]. Crystal wave function is expanded by the plane wave basis set, and the interaction potential for ion core and valence electron is determined based on the ultrasoft pseudopotential [13]. In wave vector K space, plane wave cut-off energy is 450 eV. Then, we perform the Brillouin-Zone integration using $10 \times 10 \times 10$ special Monkors–Park K point. Using the experimental value as the lattice constant for structural optimization calculation, we use the Broyden–Fletcher–Goldfarb–Shanno algorithm [14–18] to optimize the crystal model structure and position of the atom in the lattice to determine the structure with the lowest energy. Based on this method, the elastic properties and thermal conductivity are calculated.

2.2. Structural properties

After the geometry optimization for each degree of freedom of the crystal structure, we determine the lattice parameters that match the experimental value. Next, we calculate the elastic constants and elastic modulus for each ground-state crystal





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through linear fitting of stress-strain curves. To calculate the bulk modulus and shear modulus, we refer to the model of Voigt [19] and Reuss and Angew [20], respectively.

$$B_V = B_R = (C_{11} + 2C_{12})/3 \tag{1}$$

$$G_V = (C_{11} - C_{12} + 3C_{44})/5 \tag{2}$$

$$G_R = 5(C_{11} - C_{12})C_{44} / [4C_{44} + 3(C_{11} - C_{12})]$$
(3)

Based on extreme value principle, Hill [21] has proved that Voigt's and Reuss's models are the upper and lower limits of the elastic constant, respectively. The arithmetic mean Voigt-Reuss-Hill (VRH) value is closer to the experimental result.

$$B = (B_V + B_R)/2 \tag{4}$$

$$G = (G_V + G_R)/2 \tag{5}$$

Using Hill's value of bulk modulus and shear modulus, we obtain the Young's modulus and Poisson Ratio for each material under polycrystalline system.

$$E = (9BG)/(3B+G)$$
(6)

 $v = (3B - 2G)/[2(3B + G)] \tag{7}$

3. Calculation results and discussion

TiN, ZrN, and HfN have the face-centered cubic lattice like NaCl. Table 1 lists the lattice constant, elastic constants, and elastic modulus of TiN, ZrN, and HfN obtained using the LDA and GGA methods. The LDA calculation has underestimated the lattice constants but overestimated the elastic constants. The GGA calculation has overestimated the lattice constants but underestimated the elastic constants. A cubic system has three independent elastic constants, namely, C_{11} , C_{12} , and C_{44} . The basis for determining the mechanical stability is as follows [22]:

$$C_{11} > 0, C_{44} > 0, C_{11} > |C_{12}|, C_{11} + 2C_{12} > 0$$
 (8)

The elastic constants listed in Table 1 meet this criterion, indicating that the structure of the three nitrides is mechanically stable. Bulk modulus *B* and shear modulus *G* are calculated using the VRH method. Young's modulus *E* and Poisson ratio *v* are calculated using Formulas (6) and (7), respectively. Poisson ratio *v* of TiN, ZrN, and HfN shows an increasing trend, indicating material incompressibility. According to the Pugh criterion [23], materials with G/B > 0.5 generally shows brittleness, and materials with G/B < 0.5 are generally tough. All of the three nitrides belong to brittle materials. The compressibility and brittleness decreases with the change in Poisson ratio *v* and *G/B* value. Hardness represents the ability of a material to resist elastic deformation, plastic deformation, or failure. We calculate bond population based on the first-principle and analyze the intensity of the internal bond per unit volume. The hardness of the material is easily predicted based on the following formula [30]:

$$H_{\rm V} = A P \, v_{\rm h}^{-\frac{2}{3}} \tag{9}$$

where *A* is the proportionality factor relative to diamond hardness, *P* is the bond population, and v_b is bond volume. The relevant data for determining hardness are listed in Table 2. The data show no significant difference in the bond populations of Ti–N, Zr–N, and Hf–N. However, the high hardness of TiN suggests higher bonding strength per unit volume.

3.1. Electron structure

The energy band structure and the density of states for TiN, ZrN and HfN are shown in Fig. 1, in which the red dashed line represents Fermi level. The properties of the material are determined by the properties of the electrons at the Fermi surface. It can be seen from Fig. 1 that all the three nitrides have energy band, in which valence band passes through Fermi level to enter conduction band, suggesting the existence of free electrons near the Fermi level. Considering the analysis results for density of states, we know that this is the contribution of Ti, 3d, Zr, 4d, Hf and 5d state electrons, respectively. Thus the electron transmission property and charge carrier type of TiN, ZrN and HfN could be settled, and the three compounds have metallic conductivity.

The total density of states (TDOSs) of TiN, ZrN and HfN and partial density of states (PDOSs) reflect the specific composition of the electronic state in the energy band structure, and the peak with the minimum amount of energy at the valence band appears near -15.44, -15.23 and -16.12 eV, respectively. They are mainly made up of 2s orbital electron of N atom, with very small contribution of d orbital electron of metal atom. Within the energy range of from -9 eV to -3 eV, there is orbital hybridization between d orbital of metal atom and 2p orbital of N atom. The contribution to density of state from d orbital of metal atom is significantly lower than that of 2p orbital of N atom. The narrow widening of orbital hybridization peaks and state density distribution indicate that the bond is ionic and the pseudogap in state density occurs near -2.47 eV (TiN), -2.83 eV (ZrN) and -3.10 eV (HfN). There is significant difference in the structural properties of electrons near the Fermi level on the left and right of the pseudogap. The density of states mainly

Table 1

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Lattice constants of TiN, ZrN, and HfN (Å);density (g cm⁻³); elastic constant C_{ij} (GPa); bulk modulus *B* (GPa); shear modulus *G* (GPa); *G*/*B*; Young's modulus *E* (GPa); and Poisson ratio v.

Species	TiN			ZrN			HfN		
Method	LDA	GGA	Expt.	LDA	GGA	Expt.	LDA	GGA	Expt.
a, b, c ρ	4.175 5.65	4.249 5.36	4.238 ^a	4.522 7.56	4.591 7.22	4.585 ^d	4.574 13.36	4.645 12.75	4.682 ^g
C ₁₁	670.58	559.83	625 ^b	633.37	542.42	611 ^e	709.54	602.93	694 ^e
C_{12} C_{44}	145.55	167.19	163 ^b	129.56	120.80	129 ^e	103.86	92.26	134 ^e
B	319.22	274.01	325 ^b 102 ^b	282.81	249.08	215 ^b 157 ^e	314.25	273.82	306 ^e 202 ^e
G/B	0.657	0.674	132	0.611	0.618	157	0.511	0.506	202
E v	516.23 0.230	452.43 0.225	509 ^c	430.52 0.246	382.91 0.244	380 ^t	411.69 0.282	355.75 0.283	387 ^r

^a [24],

^b [25],

^c [26],

^d [27],

° [28],

^f [5], ^g [29].

Table 2
Bond lengths of TiN, ZrN, and HfN (Å); population; bond volume; (Å ³); and hardness (GPa).

	Bond	Method	Length	Population	V_b	H_V	H_V^{exp}
TiN	Ti–N	LDA GGA	2.08740 2.12446	0.69 0.70	6.06333 6.39250	25.33 23.53	24.5 ^a
ZrN	Zr-N	LDA GGA	2.26080 2.29534	0.60 0.62	7.70333 8.06250	14.78 14.15	13.4 ^b
HfN	Hf–N	LDA GGA	2.28698 2.32260	0.71 0.71	7.97417 8.35250	16.51 15.28	16.0 ^c

[31].

^a ^b [3∠ ^c [2]. [32].



Fig. 1. The graphs for the energy hand structure and density of states for TiN, ZrN and HfN, respectively, in which the red dashed line represents Fermi level and the blue one the location of pseudogap. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

comes from the contribution of d orbital electrons of metal atom, showing the metallicity of the material. The pseudogap is red shifted in sequence, which indicates that the electronic state near the Fermi level is predominantly under the control of d orbital electrons of metal atom. The metallicity increases in the sequence $TiN \rightarrow ZrN \rightarrow HfN.$

3.2. Mechanical deformation modes

To study the deformation mechanism of TiN, ZrN, and HfN, we calculate the tensile (shear) stress-strain curve in the crystal orientation [001], [110], and [111], respectively (Fig. 2). In other words,

we obtain the pattern of variation in stress from the elastic region to the unstable region and ultimate breakdown under the strain. Within the initial strain range, each curve shows linear variation. The slope is consistent with the data for Young's modulus in Table 1. When the elastic deformation reaches its limit, a turning point appears in the tensile (shear) curve, which means that the atom breaks away from the control of adjacent atoms and spontaneously slides from the original lattice position to a new one to attain the minimum total energy of the system [33]. Fig. 2a shows the comparison of the stress-strain status of different materials in the stretching along the same crystal orientation. TiN presents the maximal tensile strength along [100] and [110]. The tensile



Fig. 2. Stress-strain curves for the stretching of TiN, ZrN, and HfN along the [001], [110], and [111] crystal orientations.

strength of ZrN along [111] is higher. Fig. 2b shows the significant anisotropy of the stress–strain variation of the lattice for different crystal orientations. The [110] and [111] present the most obvious difference in the shape of the curve. The curve in [110] has undergone longer plastic deformation with less obvious variation in stress, indicating high toughness. In [111], no significant yielding stage is observed between the elastic deformation stage and fracture stage, indicating material brittleness. Furthermore, the ideal tensile strength τ in the three crystal orientations is shown in the following variation pattern:

 $\tau[001] < \tau[110] < \tau[111]$

The tensile (shear) stress-strain curve shows obvious anisotropy because marked changes have appeared in the stress of the crystal cell when the stretching occurs along different crystal orientations. The details are presented as follows:

- (1) In the stretching along [001], the bond involved in tensile deformation is the X–N bond (X = Ti, Zr, Hf) in [100]. The tensile stress s in the same direction as the bonding.
- (2) During the stretching along [110], the X–N bond in [010] and [100] are involved. The inclusion angle between the tensile stress and initial orientation of the bonding is 45°, which decreases as the stretching progresses.
- (3) During the stretching along [111], the bond involved in tensile deformation is the X–N bond along [100], [010], and [001]. The inclusion angle between the tensile stress and initial orientation of the bonding is approximately 35.3°, which decreases with stretching.

During the stretching along [001], the bond length rapidly changes and the stage of elastic deformation shortens. The stress reaches the ideal strength when the bonding reaches its elasticity limit, followed by yielding and fracture. The processes confirm the brittleness of these materials corresponding to Push criterion exactly. The stretching process along [110] and [111] results in

changes in bond length and bond angle (Fig. 3). The elastic deformation stage of the tensile curve along the two crystal orientations becomes significantly longer because bond length and bond angle also contribute to the stretching of materials. The change in bond angle weakens the effect of tensile stress on bond length. The tensile stress along the [110] has the maximum inclusion angle with the initial direction of bonding. However, the deformation rate of the bond angle is faster than that in the [111] and reaches the elasticity limit more quickly. Thus, the elastic deformation stage along the [110] is shorter than that in the [111]. Considering that the stretching process only causes changes in the bond length and angle on the (100) plane, a high degree of freedom for deformation is observed. Therefore, the plastic deformation stage along [110] is the longest of the three orientations. On the contrary, the stretching in the [111] has the longest elastic deformation stage, which indicates the maximum ideal strength during stretching. However, the stretching process is directly related to the change in the bond length and angle in the crystal cell. The deformation of [111] has the lowest degree of freedom among the three orientations. Once the stretching curve reaches the ideal strength, it instantly transits to the fracture stage without passing through any obvious yielding stage.

Electron density difference further explains the modes behind the tensile deformation of the materials (Fig. 4). The stretching in [001] strengthens the effect of the electron transfer of the X–N bond in the transverse direction and weakens the effect of the electron transfer of the X–N bond of each crystal cell on the (100) plane along the stretching direction. The relaxation process enables the crystal cell to reach a new equilibrium state under the influence of tensile stress with minimal total energy of the system. The strengthening of the effect of some of the electron transfers along [110] and [111] is also influenced by the relaxation process. Given the inclusion angle between the direction of the tensile stress and bond, the direction for the strengthened electron transfer is slightly different from that for the strengthened elog [001]. The difference is mainly observed in the direction of unpaired



Fig. 3. Changes in the bond length (a) and bond angle (b) of TiN, ZrN, and HfN during stretching along the [110] and [111] crystal orientations, respectively.



Fig. 4. Electron density difference for the stretching of TiN (a), ZrN (b), and HfN (c) along the (100) [001], (001) [110], and (11 $\overline{2}$) [111] with a strain of 0%, 10%, and 25%, respectively. The blue ball is Nitrogen atom, and the light color ball is Ti, Zr, and Hf atom in (a), (b), and (c), respectively. The value order from low to high is black (zero) \rightarrow blue \rightarrow green \rightarrow yellow \rightarrow red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

electrons. Under the same condition of tensile deformation, the effect of the electron transfer of the X-N bond in the longitudinal direction weakens at a slower rate, corresponding to the stable tensile property in this crystal orientation. Furthermore, when the TiN crystal cell stretches by 25% along [111], the atom location significantly changes, and the electron transfer between the Ti and N atoms disappear. This finding is in agreement with the stress-strain results in Fig. 3.

3.3. Anisotropy

The influence of microcracks and lattice distortion are generally considered when studying the mechanical properties of a material. The anisotropy of elastic property is often the essential condition for the emergence of microcracks and lattice distortion. Therefore, research on elastic anisotropy is beneficial for improving the mechanical durability of materials. The bond has high directionality in NaCl-like configurations. Therefore elastic properties along the face diagonal and body diagonal may significantly differ. To conduct quantitative research on the anisotropy of a single crystal, we calculate the universal anisotropic index A^U [34] and the Zener factor A^Z [35], which describes the anisotropy of single crystal elasticity for cubic crystals.

$$A^U = 5G_V/G_R + B_V/B_R - 6 \ge 0 \tag{10}$$

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

Since $G_{100} = C_{44}$ and $G_{110} = (C_{11} - C_{12})/2$, $A^Z = G_{100}/G_{110}$ refers to the shear anisotropic factor. Similarly, we define the Young's anisotropic factor $A^E = E_{100}/E_{110}$ for cubic crystals as follow:

$$A^{E} = (C_{11}^{2} + C_{11}C_{12} - 2C_{12}^{2} + 2C_{11}C_{44})/[4(C_{11}C_{44} + C_{12}C_{44})]$$
(12)

In formula (9), $A^U = 0$ refers to a locally isotropic single crystal; as for A^Z and A^E , the large deviation from 1 indicates the elastic anisotropy of a single crystal. However, the bulk anisotropic factor $A^B = B_{100}/B_{110}$ is always equal to 1 for cubic crystals, indicating the isotropic bulk modulus. All of the anisotropic values of TiN, ZrN, and HfN are listed in Table 3. The calculation results show that the Young's modulus and shear modulus of TiN, ZrN, and HfN for single crystals are anisotropic. And the degree of anisotropy increases in the order of TiN \rightarrow ZrN \rightarrow HfN.

To observe clearly how the elastic modulus of a single crystal changes in all directions, we construct a three-dimensional diagram (Fig. 5a) for the Young's modulus. The calculation formula is as follows [36]:

$$E^{-1} = s_{11} - 2(s_{11} - s_{12} - s_{44}/2)(l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2)$$
(13)

Here s_{ij} is the elastic compliance coefficient, and l_1 , l_2 , and l_3 are the direction cosines. However a shear modulus is decided by two factors. One is the force-exerting plane, and the other is the force-exerting direction. The later has infinite possibility on the plane. Therefore a shear modulus cannot be plotted in 3D space. But the torsion modulus can be plotted, which is the average shear modulus over all possible directions. Fig. 5b and c show that the torsion (shear) modulus [37] and bulk modulus [38] are calculated according to the following formulas:

$$T^{-1} = s_{44} + 4[(s_{11} - s_{12}) - s_{44}/2)](l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2)$$
(14)

$$B^{-1} = (s_{11} + 2s_{12})(l_1^2 + l_2^2) + (2s_{13} + s_{33})l_3^2$$
(15)

Many physical properties of a crystal are determined by lattice vibration. Lattice vibration in turn can be reflected by the phonon system. Acoustic wave, as a key physical quantity, has a significant function in studying the thermal conductivity of a material. This paper calculates the wave speed of the transverse and longitudinal acoustic waves for TiN, ZrN, and HfN in the [100], [110], and [111] crystal orientations, respectively. Table 3 shows the results, and the calculation formula is as follows [39]:

$$v_l[100] = \sqrt{C_{11}/\rho}, v_{t1}[010] = v_{t2}[001] = \sqrt{C_{44}/\rho}$$
(16)

$$v_{l}[110] = \sqrt{(C_{11} + C_{12} + 2C_{44})/2\rho}, v_{t1}[110]$$

= $\sqrt{(C_{11} - C_{12})/2\rho}, v_{t2}[001] = \sqrt{C_{44}/\rho}$ (17)

$$v_{l}[111] = \sqrt{(C_{11} + 2C_{12} + 4C_{44})/3\rho}, v_{t1}[112] = v_{t2}$$
$$= \sqrt{(C_{11} - C_{12} + C_{44})/3\rho}$$
(18)

where C_{ij} is the elastic constant, and ρ is the density. For facecentered cubic crystals, the phonon spectrum shows two dispersion curves between Γ [000] and X[100], which correspond to the longitudinal acoustic wave and degenerate transverse acoustic wave, respectively [40]. Therefore, the two transverse acoustic waves along [100] have the same wave speed. The acoustic wave in [111] is similar to that in [100]. In [110], all of the phonon dispersion curves are in a non-degenerate state, so the two transverse acoustic waves propagate at different wave speeds. The distributions of the two transverse acoustic waves on the phonon spectrum significantly differ. Table 4 shows the comparison of the calculation results and experimental values of the CaO acoustic wave speed for face-centered structure. The results are in good agreement, indicating that this calculation method is reliable.

Acoustic wave speed is closely related to the thermal conductivity of a material. At high temperatures, thermal conductivity decreases with increasing temperature [42]. Thus, determining the minimum value at high temperature is important for exploring the application of materials under extreme conditions. In this paper, the calculation for the thermal conductivity of polycrystalline TiN, ZrN, and HfN is based on the Clark Model [42] and Cahill Model [43].

(1) Clark Model:
$$\kappa_{\min} = 0.87 k_B M_a^{-2/3} E^{1/2} \rho^{1/6}$$
 (19)

(2)Cahill Model :
$$\kappa_{\min} = k_B p^{2/3} (v_l + 2v_t)/2.48$$
 (20)

In the Formula, *E* is the Young's modulus, ρ is the density, k_B is the Boltzman constant, $M_a = [M/(n \cdot N_A)]$ is the average mass for the atom in the lattice, *M* is the molar mass for molecules, n is the number of the atoms, N_A is the Avogadro's constant, *p* is the number of atoms per unit volume, and v_l and v_t are the average wave speed for transverse acoustic wave and longitudinal acoustic wave, respectively. Based on the two models, we can calculate the lower limit for lattice thermal conductivity. The calculation results are shown in Table 5. We also calculate the thermal conductivity for cubic ZrO₂ and compare the value with the experimental value to verify the accuracy of the calculation method. The results show that the Cahill value for high-temperature thermal conductivity is slightly higher than the Clark value. the Cahill value is also closer to the experimental value. The high-temperature thermal conductivity ity for TiN, ZrN, and HfN sequentially decreases.

Compared with the Clark model, the calculation of the thermal conductivity using the Cahill model is based on the wave speed of lattice vibration. In the formula, v_t and v_t correspond to the acoustic wave in the crystal orientation. Thus, we can calculate the thermal conductivity for the lattice in different lattice orientations. The formula is then changed into [43]

$$\kappa_{\min} = k_B p^{2/3} (\nu_l + \nu_{t1} + \nu_{t2}) / 2.48 \tag{21}$$

This paper calculates the minimum thermal conductivity of the three structures in [100], [110] and [111]. The detailed results are presented in Table 5. The difference in the wave speed for the acoustic wave in different crystal orientations results in the

Table 3

The calculated A^U, A^E, A^G, E_[100], E_[110], E_[111], T_[100], T_[110], and T_[111] of TiN, ZrN, and HfN.

Species	A ^U	A^E	A ^Z	E[100]	E[110]	E[111]	T _[100]	T[110]	T[111]
TiN	0.176	1.273	0.683	619.96	487.05	462.27	180.00	187.43	189.38
ZrN	0.627	1.589	0.493	602.16	378.86	346.72	129.56	138.33	140.71
HfN	1.446	2.058	0.350	676.64	328.76	291.31	103.86	113.04	115.59



(c) Bulk modulus of TiN, ZrN, and HfN

Fig. 5. Three-dimensional diagrams for the elastic moduli of TiN, ZrN, and HfN. (a) the Young's moduli, (b) the torsion moduli, and (c) the bulk moduli.

anisotropy in the thermal conductivity. For the lattice with isotropy in thermal conductivity, $\kappa_{\min}[100] = \kappa_{\min}[110] = \kappa_{\min}[111] = \kappa_{\min}$. Thus, we can determine the degree of anisotropy for lattice thermal conductivity by comparing $\kappa_{\min}(avg) = (\kappa_{\min}[100] + \kappa_{\min}[110] + \kappa_{\min}[111])/3$ and κ_{\min} [hkl]. As listed in Table 6, the values of $\kappa_{\min}[100]$, $\kappa_{\min}[110]$, and $\kappa_{\min}[111]$ are quite different. Therefore IVB transition metal nitrides are the thermal conducting anisotropy. The difference between $\kappa_{\min}[100]$ and

 $\kappa_{\min}[110]$, $\kappa_{\min}[110]$ and $\kappa_{\min}[111]$, $\kappa_{\min}[111]$ and $\kappa_{\min}[100]$ are 2.1%, 0.8%, and 3.1% for TiN respectively; those for ZrN are 4.1%, 1.9%, and 6.2% respectively; and those for HfN are 6.2%, 3.3%, and 10.1%, respectively. Thus the degree of anisotropy shows a trend of slight increase in the sequence of TiN \rightarrow ZrN \rightarrow HfN. From [45], the thermal conductivity for ZrN is 6.27(Wm⁻¹ K⁻¹) at 1100 °C, larger than 1.964(Wm⁻¹ K⁻¹), the lowest limit at high temperature. The result is reasonable.

Table 4

Anistropic acoustic wave speeds of TiN, ZrN, and HfN (km s⁻¹).

Direction	[100]		[110]			[111]	
	$v_{t1,2}$ [100]	<i>v</i> _l [100]	$v_{t1} [1 \bar{1} 0]$	v_{t2} [001]	v _i [110]	$v_{t1,2} [11\bar{2}]$	v _i [111]
TiN	5.639	10.884	6.823	5.639	10.184	6.453	9.9395
ZrN	4.139	9.151	5.896	4.139	8.131	5.375	7.761
HfN	2.788	7.287	4.710	2.788	6.220	4.169	5.821
CaO _{cal}	4.704	8.101	7.030	4.703	7.944	4.879	7.887
CaO _{exp} ^a	4.936	8.208	7.023	4.936	8.189	4.956	8.183

^a [41].

Table 5

Average mass (g) of atoms, transverse acoustic wave and longitudinal wave speed (km s⁻¹), atomic number per unit volume, and minimum high-temperature thermal conductivity (W m⁻¹ K⁻¹) for polycrystalline TiN, ZrN, and HfN.

	Clark		Cahill	Cahill				
	$M_a 10^{-23}$	κ_{\min}	v_t	v_l	$p\times 10^{28}$	κ_{\min}		
TiN	5.142	2.635	6.088	10.286	11.009	2.872		
ZrN	8.740	1.773	4.779	8.237	8.653	1.938		
HfN	15.988	1.274	3.467	6.289	8.357	1.407		
ZrO_2	6.827	1.735	4.306	8.143	9.452	1.936	2.2 ^a	

^a [44].

Table 6

Minimum thermal conductivity (W m⁻¹ K⁻¹) at high temperatures and $\Delta \kappa_{min}$ = - $\kappa_{min}(avg) - \kappa_{min}$ for TiN, ZrN, and HfN.

	κ _{min} [100]	κ _{min} [110]	κ _{min} [111]	κ_{\min} (avg)
TiN	2.834	2.896	2.921	2.884
ZrN	1.898	1.979	2.016	1.964
HfN	1.369	1.459	1.507	1.445

4. Conclusion

Using the pseudopotential plane-wave method of first-principle density function theory, this paper analyzes mechanical deformation modes, and the anisotropy of elasticity and the minimum thermal conductivity at high temperature for the IVB transition metal nitrides. All elastic modulus, except for the bulk modulus, show anisotropy, and the thermal conductivity displays a slight anisotropy. The degree of anisotropy increases in the following order: $TiN \rightarrow ZrN \rightarrow HfN$. Among the IVB transition metal nitrides, TiN has the highest hardness and the lowest anisotropy. Hence it is usually used as cutting materials and ultra-abrasion-resistant materials. On the other hand, HfN, occupying the minimum thermal conductivity at high temperature, is the best candidate for a thermal barrier coating.

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References

- [1] M. Zhang, J. He, Surf. Coat. Technol. 142 (2001) 125.
- [2] S.H. Jhi, J. Ihm, S.G. Louie, M.L. Cohen, Nature 399 (1999) 132-134.
- [3] T. Liao, J.Y. Wang, Y.C. Zhou, Phys. Rev. B 73 (2006) 214109.

- [4] Q. Yang, W. Lengauer, T. Koch, M. Scheerer, I. Smid, J Alloys Comp. 309 (2000) 5-9.
- [5] X.J. Chen, V.V. Struzhkin, Z. Wu, M. Somayazulu, J. Qian, S. Kung, A.N. Christensen, Y. Zhao, R.E. Cohen, H. Mao, R.J. Hemley, Proc. Nat. Acad. Sci. U.S.A. 103 (2005) 3198.
- [6] W. Grzesik, Int. J. Mach. Tools Manuf 39 (1999) 355.
- [7] S.W. Wendell, J. Am. Ceram. Soc. 49 (1965) 156.
- [8] M.O. Mark, G.T. Inna, J.W. Eric, A.Z. James, J.C. Samuel, J. Eur. Ceram. Soc. 19 (1999) 2405.
- [9] M.D. Segall, P.L.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, M.C. Payne, J. Phys.: Condens. Matter 14 (2002) 2717.
- [10] P. Hohenberg, W. Kohn, Phys. Rev. 136 (1964) 864.
- [11] D.M. Ceperley, B.J.J. Alder, Phys. Rev. Lett. 45 (1980) 566.
- [12] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
- [13] D. Vanderbilt, Phys. Rev. B 41 (1990) 7892.
- [14] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188.
- [15] C.G. Broyden, J. Inst. Math. Appl. 6 (1970) 222.
- [16] R. Fletcher, Comput. J. 13 (1970) 317.
- [17] D. Goldfarb, Math. Comput. 24 (1970) 23.
- [18] D.F. Shanno, Math. Comput. 24 (1970) 647.
- [19] W. Voigt, Lehrbuch der Kristallphysik, B.G. Teubner, Leipzigz, 1928.
- [20] A. Reuss, Z. Angew, Math Mech 9 (1929) 49.
- [21] R. Hill, Proc Phys Soc A (London) 65 (1952) 349.
- [22] Z.J. Wu, E.J. Zhao, H.P. Xiang, X.F. Hao, X.J. Liu, J. Meng, Phys. Rev. B 76 (2007) 054115.
- [23] S.F. Pugh, Philos. Mag. 45 (1954) 823.
- [24] M. Hasegawa, T. Yagi, J Alloys Comp. 403 (2005) 131.
- [25] J.O. Kim, J.D. Achenbach, P.B. Mirkarimi, M. Shinn, S.A. Barnett, J. Appl. Phys. 72 (1992) 1805.
- [26] H. Yao, L. Ouyang, W.Y. Ching, J. Am. Ceram. Soc. 90 (2007) 3194.
- [27] A.N. Christensen, Acta Chem. Scand. A 29 (1975) 563.
- [28] C. Sarioglu, Surf. Coat. Technol. 201 (2006) 707.
- [29] Y.G. Zainulin, S.I. Alyamovskii, G.P. Shveikin, P.V. Gel'd, Teplofiz. Vys. Temp. 9 (1971) 496.
- [30] F.M. Gao, Phys. Rev. B 73 (2006) 132104.
- [31] W.J. Chou, G.P. Yu, J.H. Huang, Surf. Coat. Technol. 149 (2002) 7.
- [32] C.S. Chen, C.P. Liu, C.Y.A. Tsao, H.G. Yang, Script. Mater. 51 (2004) 715.
- [33] D.M. Teter, R.J. Hemley, Science 271 (5245) (1996) 53.
- [34] S.I. Ranganathan, M. Ostoja-Starzewski, Phys. Rev. Lett. 101 (2008) 055504.
 [35] C. Zener, Elasticity and Anelasticity of Metals, University of Chicago Press, Chicago, 1948.
- [36] J.F. Nye, Physical Properties of Crystals, Clarendon Press, Oxford, 1964.
- [37] R.F.S. Hearman, An Introduction to Applied Anisotropic Elasticity, Oxford University Press, 1961.
- [38] K. Brugger, J. Appl. Phys. 36 (1965) 768.
- [39] C. Kittel, Introduction to Solid State Physics, John Wiley & Sons, New York, 1997.
- [40] J. Wong, M. Krisch, D.L. Farber, R. Xu, T.C. Chiang, A.J. Schwartz, Phys. Rev. B 72 (2005) 064115.
- [41] G. Crimvall, Thermo Physical Properties of Materials, North Holland, Amsterdam, 1999.
- [42] D.R. Clarke, Surf. Coat. Technol. 163 (2003) 67.
- [43] D.G. Cahill, S.K. Watson, R.O. Pohl, Phys. Rev. B 46 (1992) 6131.
- [44] R. Vassen, X. Cao, F. Tietz, D. Basu, D. Stöver, J. Am. Ceram. Soc. 83 (2000) 2023.
- [45] J.F. Shackelford, W. Alexander, Materials Science and Engineering Handbook, CRC Press, 2001.