Solid State Communications 150 (2010) 1818–1821

Contents lists available at ScienceDirect

Solid State Communications

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

Revisiting the Phillips ionicity of conductors and the quantitative determination of the hardness of carbides and nitrides of transition metals using the LDA + *U* technique

C. Li, J.C. Li *, Q. Jiang *

Key Laboratory of Automobile Materials, Ministry of Education, and School of Materials Science and Engineering, Jilin University, Changchun 130022, China

ARTICLE INFO

Article history:
Received 7 April 2010
Received in revised form
4 June 2010
Accepted 4 July 2010
by Y.E. Lozovik
Available online 14 July 2010

Keywords:
A. Metallic bonding
D. Ionicity
D. Hardness

ABSTRACT

The Phillips ionicity is modified, simulated and calculated for conductors. The results show that the percentage of metallic bonding in multiplex chemical bonds of transition metal (TM) carbides and nitrides is large; this affects the Phillips ionicity. The redefinition of Phillips ionicity has been applied to estimate the hardness of TM carbides and nitrides; the values obtained are in agreement with experimental and theoretical evidence. In addition, materials with the zinc blende structure are harder than those with rock salt structure.

1. Introduction

Transition metal (TM) carbides and nitrides, which show high melting point, hardness, strength and diffusion activation energy, have been used widely as tools, coatings [1], and diffusion barriers for Cu interconnects [2]. The chemical bonds, which consist of ionic, covalent, and metallic components, determine the material properties, such as mechanical, structural, optical and magnetic properties [3–5]; the separation of the chemical bonds into these components is meaningful for understanding the physical background of these properties.

The chemical bond in insulators and semiconductors has been divided into a covalent part E_h and an ionic part C by Phillips; the Phillips ionicity is defined as $f_i = C^2/(C^2 + E_h^2)$ [6]. Recently, He et al. rewrote this as $f_i = [1 - \exp(-|P_c - P|/P)]^{0.735}$ [7], where P is the overlap population of a bond based on Mulliken population (MP) calculations. $P = 0$ indicates a perfect ionic bond, while $P > 0$ implies increasing levels of covalency. P_c is the overlap population of a bond in a hypothetical pure covalent crystal with a special structure. For conductors, Gou et al. calculated H with f_i and metallicity f_m using the equation $H = 350\, AN_e^{2/3}\exp(-1.191 f_i - \alpha f_m^{\beta})/d^{2.5}$ [8], where A, α and β are constants, which need to be determined by experimental results. A is the contribution of d electrons to H, $N_e = n_e/v$ is the electron density expressed in number of valence electrons per Å^3, n_e is the total valence electrons per bond, and d and v are the average bond length and the bond volume. Gou et al. calculated H using other methods [9].

In conductors, free electrons fill in all interspaces, which are included partly in the MP values of the chemical bond because the MP values reflect the grade of the electrons of an atom entering into that of other atoms. $P = 0$ indicates a perfect ionic bond, while $P > 0$ implies increasing levels of covalency. Thus, P determined by MP should be divided into two parts: the covalent part P_h and the metallic part P_m:

$$P = P_h + P_m. \qquad (1)$$

It is known that the covalent bonding determines the size of H [10]. The delocalized metallic bonding in conductors has little effect on H. Taking account of the above considerations, a modification for H of conductors can be defined:

$$H = 350A(N_e')^{2/3}\exp[(1.191 f_c - 1.191)/d^{2.5}] \qquad (2)$$

where f_c is the covalency, $N_e' = (n_e - n_{free})/v$ denotes the redefinition of electron density expressed in number of valence electrons per Å^3, and n_{free} is the number of free electrons per bond. Since these free electrons do not belong to any atom, they should be deducted from N_e. The calculated N_e' values of the considered compounds are listed in Table 1. For conductors, $n_{free} > 0$, $N_e' < N_e$.

This contribution reports results of a first-principles simulation that was carried out for the electronic structures of TM carbides and nitrides using the MP technique. With some theoretical analysis, the percentage of metallic bonding in multiplex chemical bonds of the above compounds was determined. The results show that, with some improvements, the Phillips ionicity can be extended to determine the ionicity and hardness of conductors.

---

* Corresponding author. Tel.: +86 431 85095371; fax: +86 431 85095876.
E-mail addresses: ljc@jlu.edu.cn (J.C. Li), jiangq@jlu.edu.cn (Q. Jiang).

0038-1098/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ssc.2010.07.005

Table 1
Calculated bond parameters of TM carbides and nitrides, with d being the bond length, f_i the modified ionicity, f_c the covalency, f_m the metallicity, H_{calc} the calculated hardness, H_{expt} the experimental hardness, and H' the value calculated using the method in [7]. H', P' and n'_{free} are the results without using the spin-polarized and LDA + U techniques, and P'' the results without using the LDA + U technique.

Compound	Structure	d	n_e	n_{free}	n'_{free}	v	N'_e	P'	P''	P	P_m	P_h	f_i	f_c	f_m	H_{calc}	H'	H_{expt}
TiN	RS	2.123	1.500	0.183	0.173	3.190	0.413	0.360	0.360	0.350	0.052	0.298	0.311	0.529	0.160	21.7	21.6	21 [1]
	ZB	1.991	2.250	0.262	0.252	3.037	0.655	0.460	0.460	0.450	0.087	0.363	0.589	0.267	0.144	25.3		
TiC	RS	2.167	1.333	0.007	0.001	3.390	0.391	0.420	0.420	0.410	0.002	0.408	0.107	0.884	0.009	31.5	34.0	28–35 [1]
	ZB	2.047	2.000	0.000	0.000	3.303	0.606	0.550	0.550	0.540	0.000	0.540	0.435	0.565	0.000	33.2		
ZrN	RS	2.299	1.500	0.181	0.180	4.053	0.325	0.330	0.330	0.320	0.052	0.268	0.403	0.441	0.156	13.7	16.7	15.8 [1]
	ZB	2.151	2.250	0.252	0.249	3.831	0.522	0.470	0.470	0.460	0.084	0.376	0.572	0.288	0.140	18.4		
ZrC	RS	2.354	1.333	0.002	0.001	4.267	0.312	0.400	0.400	0.390	0.001	0.389	0.181	0.817	0.002	20.3	21.0	25.9 [1]
	ZB	2.203	2.000	0.000	0.000	4.117	0.486	0.580	0.580	0.570	0.000	0.570	0.383	0.617	0.000	25.4		
HfN	RS	2.324	1.500	0.182	0.181	4.185	0.315	0.360	0.360	0.350	0.052	0.298	0.311	0.530	0.159	14.4	18.0	16.3 [1]
	ZB	2.187	2.250	0.243	0.242	4.025	0.499	0.500	0.500	0.490	0.081	0.409	0.521	0.342	0.137	18.3		
HfC	RS	2.355	1.333	0.004	0.001	4.356	0.305	0.410	0.410	0.400	0.001	0.399	0.145	0.850	0.005	20.8	26.8	26.1 [1]
	ZB	2.228	2.000	0.000	0.000	4.257	0.470	0.640	0.640	0.630	0.000	0.630	0.276	0.724	0.000	27.4		
VN	RS	2.063	1.667	0.343	0.325	2.928	0.452	0.360	0.360	0.330	0.088	0.242	0.373	0.363	0.264	22.5	14.9	15.2 [1]
	ZB	1.922	2.500	0.496	0.496	2.732	0.734	0.440	0.440	0.430	0.149	0.281	0.623	0.142	0.235	28.6		
VC	RS	2.083	1.500	0.151	0.150	3.014	0.447	0.400	0.400	0.360	0.043	0.317	0.281	0.587	0.134	30.0	23.0	29 [1]
	ZB	1.954	2.250	0.000	0.000	2.970	0.758	0.500	0.500	0.480	0.000	0.480	0.538	0.462	0.000	43.1		
NbN	RS	2.208	1.667	0.286	0.285	3.586	0.385	0.290	0.290	0.270	0.074	0.196	0.553	0.234	0.213	14.7	13.6	13.3 [1]
	ZB	2.064	2.500	0.000	0.000	3.372	0.741	0.450	0.450	0.440	0.000	0.440	0.606	0.394	0.000	32.5		
NbC	RS	2.240	1.500	0.162	0.161	3.744	0.357	0.340	0.340	0.330	0.046	0.284	0.373	0.487	0.140	19.1	16.1	19.6 [1]
	ZB	2.093	2.250	0.255	0.253	3.530	0.565	0.560	0.560	0.550	0.085	0.465	0.418	0.437	0.146	28.9		
TaN	RS	2.274	1.667	0.319	0.315	3.920	0.344	0.330	0.330	0.310	0.082	0.228	0.434	0.322	0.244	14.0	20.0	11 [1]
	ZB	2.118	2.500	0.499	0.489	3.655	0.547	0.460	0.460	0.460	0.150	0.310	0.572	0.184	0.244	19.4		
TaC	RS	2.287	1.500	0.172	0.168	3.970	0.334	0.420	0.420	0.420	0.049	0.371	0.064	0.755	0.182	23.9	26.0	24.5 [15]
	ZB	2.138	2.250	0.251	0.250	3.760	0.532	0.610	0.610	0.600	0.084	0.516	0.330	0.524	0.146	29.2		

2. Simulations and calculations

Calculations of the density of states (DOS), electron density difference diagrams (EDFDs) and MPs of TM carbides and nitrides with the rock salt (RS) and zinc blende (ZB) structure were carried out by using first-principles simulations. The calculations were based on density functional theory (DFT) with the Perdew–Burke–Ernzerhof (PBE) functional of the generalized gradient approximation (GGA) and with norm-conserving pseudopotentials [11], as implemented in the CASTEP code. Geometry optimizations of all materials were made on conventional unit cells using ultra-fine cut-off energies for the plane-wave expansion. The k-point sampling set was $10 \times 10 \times 10$ division of the reciprocal unit cell based on the Monkhorst–Pack scheme [12]. The convergence tolerance of energy 5.0×10^{-6} eV/atom, maximum force 0.01 eV/Å, and maximum displacement 5.0×10^{-4} Å were used. Both spin-polarized and LDA + U techniques [13] were used. In the LDA + U method, the strong correlation between localized d electrons is explicitly taken into account through the screened effective electron–electron interaction parameter U. $U = 2$ eV for Ti, Zr and Hf, and $U = 3$ eV for V, Nb and Ta, respectively [14].

Based on the definition of ionicity, the modified f_i, f_c, and f_m are defined as

$$f_i = C^2/(C^2 + E_h^2 + E_m^2) = [1 - \exp(-|P_c - P|/P)]^{0.735}, \tag{3a}$$

$$f_c = 1 - [1 - \exp(-|P_c - P_h|/P_h)]^{0.735}, \tag{3b}$$

$$f_m = 1 - f_i - f_c, \tag{3c}$$

where E_m is the metallic part in a multiplex chemical bond. The MP values of the simulated TM carbides and nitrides are listed in Table 1, with $P_c \approx 0.43$ for the considered RS structure [8] and $P_c \approx 0.75$ for the considered ZB structure [7].

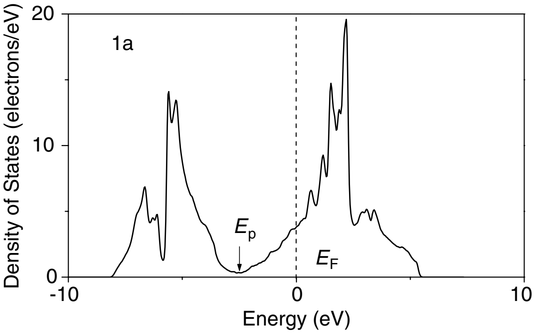

Fig. 1. DOS diagram of TiN.

3. Results and discussions

The DOS of TiN is shown in Fig. 1, where the vertical broken line is the Fermi level, E_F. There is a deep valley E_p at the left of the E_F, which is named the pseudo-gap. Thus, the electrons occupying the levels above E_p become delocalized and the corresponding materials with such electrons are metalized. All simulated compounds have a similar DOS. The integral of the area between E_p and E_F in the DOS is denoted as the number of free electrons in each bond n_{free}; the values are listed in Table 1. $n_{free}/n_e > 10\%$ for the most compounds. Since, when $P = P_c$, a material is purely covalent, we define P_m as

$$P_m = P_c n_{free}/n_e. \tag{4}$$

The corresponding values of f_i, f_c and f_m are calculated in terms of Eqs. (3) and (4) and are listed in Table 1.

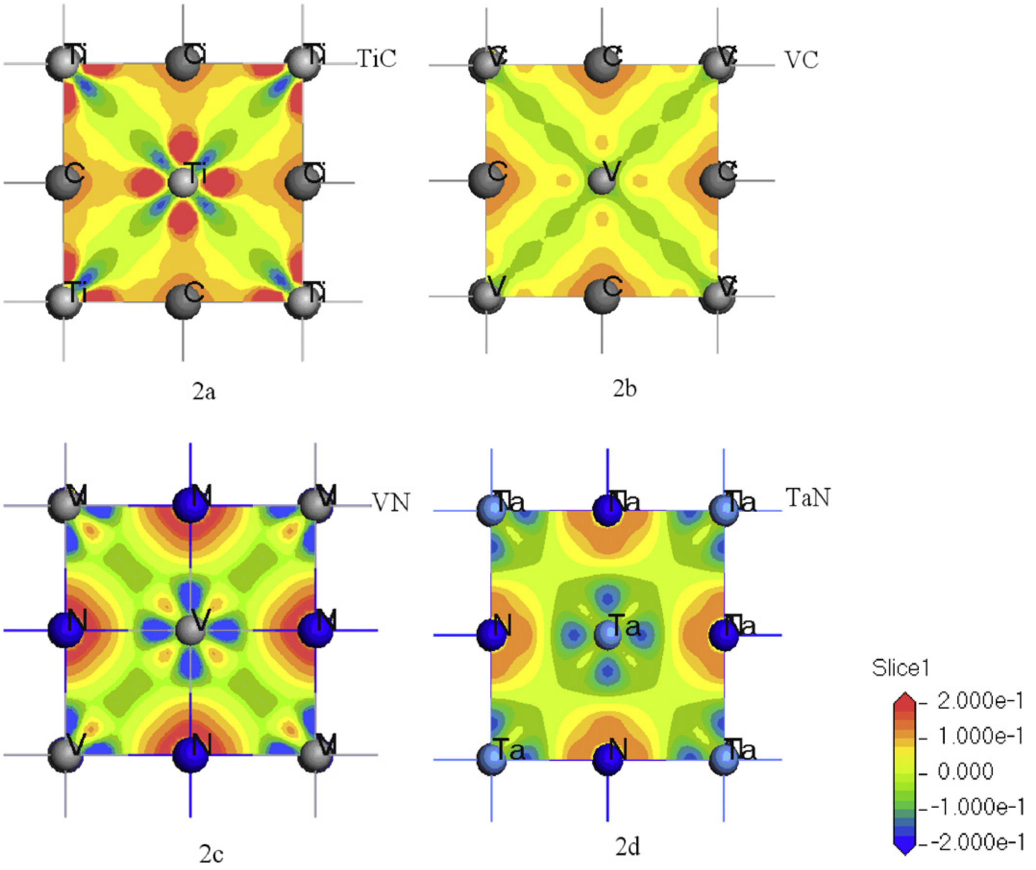

Fig. 2. The electron density difference diagrams of TiC, TiN, VC and VN. The red and yellow regions show the electron accumulation and the blue and green regions show the electron loss. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In Table 1, $P'' > P$ implies that if the LDA + U correction has not been used the results for H will be overestimated. The LDA + U correction guarantees that the electronic structures of these materials are consistent with those of experiments. $P' = P''$ and $n_{free} = n'_{free}$ imply that the spin polarization has little effect on the overlap population and the number of free electrons, because they have small magnetic moments in our considered systems [5]. Thus, spin polarizations have little effect on the hardness of these materials.

Four typical EDFDs of TM carbides and nitrides (TiC, VC, TiN and VN with the RS structure) are shown in Fig. 2. The red and yellow regions show the electron accumulation and the blue and green regions show the electron loss. Between the TM and C or N, there are red or yellow regions in the compounds, denoting their covalent bonding characteristics. The electron density difference values are 0.093, 0.058, 0.022 and 0.018 for TiC, VC, TiN and VN, respectively, which are related to their f_c values of 0.884, 0.587, 0.363 and 0.322, respectively. The above results support our definitions for f_c and f_m.

Since s–p–d hybridization is present where the bond strength of the s–p–d hybridization is larger than that of s–p hybridization [8], the contributions of the d valence electrons in TM carbides and nitrides to H should be considered, which leads to the definition for A in Eq. (2):

$$A = n_e/(n_e - n_d), \tag{5}$$

where n_d is the number of d electrons per bond. $A > 1$ implies that there is a higher directionality and a larger orbital strength for s–p–d bonds than for s–p bonds [10]. Based on Eqs. (2)–(5) and the data in Table 1, the H values of 12 compounds were determined, and they are shown in Table 1; the H values for the RS structures are in good agreement with Gou's results [8] and experimental data. Moreover, the corresponding H values for the ZB structures are larger than those for the RS structures, since the RS structure is the equilibrium structure at ambient pressure while ZB structure is the equilibrium structure only under tensile strain [5]. Hence, tensile strain will enhance the hardness of the materials.

4. Conclusion

In summary, DOS and MP values of several TM carbides and nitrides were calculated by using the LDA + U technique and theoretical considerations. The results show that the percentage of metallic bonding in multiplex chemical bonds is large for most of the compounds. The redefinition of Phillips ionicity results in good correspondence for the hardness calculation of TM carbides and nitrides. The additional contribution of s–p–d hybridization in TM carbides and nitrides to the hardness of materials has been quantitatively determined. In addition, materials with the ZB structure are harder than those with the RS structure.

Acknowledgements

The authors acknowledge the financial support from NNSFC (Grant No. 50571040), National Key Basic Research and Development Program (Grant No. 2010CB631001) and the Program for Changjiang Scholars and Innovative Research Team in University.

References

[1] H.O. Pierson, Handbook of Refractory Carbides and Nitrides, Noyes, Westwood, NJ, 1996.
[2] L.C. Leu, D.P. Norton, L. McElwee-White, T.J. Anderson, Appl. Phys. Lett. 92 (2008) 111917.
[3] F.M. Gao, J.L. He, E.D. Wu, S.M. Liu, D.L. Yu, D.C. Li, S.Y. Zhang, Y.J. Tian, Phys. Rev. Lett. 91 (2003) 015502.

[4] K. Sarasamak, A.J. Kulkarni, M. Zhou, S. Limpijumnong, Phys. Rev. B 77 (2008) 024104.
[5] W.R.L. Lambrecht, M.S. Miao, P. Lukashev, J. Appl. Phys. 97 (2005) 10D306.
[6] J.C. Phillips, Rev. Modern Phys. 42 (1970) 317–356.
[7] J.L. He, E.D. Wu, H.T. Wang, R.P. Liu, Y.J. Tian, Phys. Rev. Lett. 94 (2005) 015504.
[8] X.J. Gou, L. Li, Z.Y. Liu, D.L. Yu, J.L. He, R.P. Liu, B. Xu, Y.J. Tian, H.T. Wang, J. Appl. Phys. 104 (2008) 023503.
[9] H.Y. Gou, L. Hou, J.W. Zhang, F.M. Gao, Appl. Phys. Lett. 92 (2008) 241901.
[10] J.H. Westbrook, et al., The Science of Hardness Testing and Its Research Applications, ASM, Metals Park, Ohio, 1973.
[11] D.R. Hamann, M. Schluter, C. Chiang, Phys. Rev. Lett. (1979) 1494–1497.
[12] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188–5192.
[13] I.V. Solovyev, P.H. Dederichs, V.I. Anisimov, Phys. Rev. B 50 (1994) 16861–16871.
[14] W.E. Pickett, S.C. Erwin, E.C. Ethridge, Phys. Rev. B 58 (1998) 1201–1209.
[15] http://www.ultramet.com/ceramic_protective_coatings.html.