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Structural changes of boron carbide induced by Zr incorporation

C. H. LIU, C. HUANG
Department of Physics, Tsinghua University, Beijing 100084, People's Republic of China

Zr doped boron carbide ($B_{4.3}C$) semiconductor was prepared by hot pressing of mixture of boron carbide powder ($B_{4.3}C$) and Zr nanocrystals (0.5 at %), to investigate influence of impurity incorporation on the subtle structure of B_4C crystals. XRD analyses indicated that the hot-pressed sample was composed of $B_{4.3}C$, (BN)4H, and (ZrB_2)3H. Zr introduction does have modified the $B_{4.3}C$ structure. Especially, remarkable vacancies were led into on the B(3) sites of the C–B–C chain centre. The effect of Zr incorporation seems to be unique because similar structural change was not observed by the same experimental procedure with Ni doping. XPS studies revealed that the Zr atoms existed in a state with unsaturated bonding. $B_{4.3}C$ with interstitial Zr atoms is speculated. © *2000 Kluwer Academic Publishers*

1. Introduction

Boron-rich solids have shown to be the most promising materials to achieve high-efficiency direct thermoelectric energy conversion [1]. Among them boron carbides are the mostly investigated. Their superior properties on some aspects (such as stability) also make them of potential use as the semiconductors on some special applications [2, 3]. However, up to now, only p-type boron carbide with its $R\bar{3}m$ structural features can be obtained. Some efforts have been made by doping or forming ternary compound to invert the conductivity type of boron carbides [3–5]. Results indicated that even though some transport parameters such as the electronic conductivity and Seebeck coefficients can be varied somewhat from that of the boron carbide, all the doped boron carbides were still p-type semiconductors. It seems that the exact locations that dopants might incorporate in the lattice and its roll to influence the electronic properties need to make clear. In fact, till now even the detailed structure of boron carbides and their conduction mechanism herewith are still ambiguous. Subtle structural investigations are still necessary in order to solve such problems as the possibility or in which way to invert the conductivity type of the boron carbides. Structural variation caused by the changes of B/C stoichiometry have been studied over the years in order to better understand the structural feature of the boron carbides [6–9]. Our purpose of this study is to carefully examine the structural modification when different dopants are introduced into the boron carbides. Some structural investigations on the ternary compounds of Si [4], Al [5] with boron carbide have been taken by some authors. In this paper, we report the subtle structural changes of the boron carbide ($B_{4.3}C$) induced by zirconium incorporation. The selection of Zr dopant was based on the consideration that the radius of Zr ions was very compatible with that of boron (or carbon) atoms.

2. Experimental

The boron carbide powder was commercially purchased as boron 77.78 wt %, carbon 20.49 wt %. The free boron and free carbon weight percentages were 0.046 and 0.6%, respectively. The stoichiometry of the boron carbide phase was $B_{4.3}C$ ($B_{4.34}C$), i.e., the carbon-rich limit for the boron carbides. By the energy-dispersive x-ray analysis (EDXA) no detectable impurity (for atomic number ≥ 11) was found. Zirconium addition was nanocrystals of 99.995% purity. The boron carbide powder and 0.5 at % Zr were mixed sufficiently to obtain the homogeneous mixture. Then the mixture was hot pressed at 2000 °C and 44 MPa for 1 h in a graphite die under nitrogen atmosphere. About 1 mm thick from the surface of the prepared material was cut out in order to reach the homogeneous region of the sample.

Scanning electron microscopy (SEM) and EDXA (Hitachi S-450) were used to check the general ceramic feature of the sample. The detectable element by this EDXA was in the range of atomic number $Z \geq 11$. X-ray diffraction (XRD) was performed in a Rigaku D/max-RB diffractometer with Cu K_α radiation. Scanning angle 2θ was increased in a step of 0.02°.

X-ray photoelectron spectroscopy (PHI 5300, Al K_α radiation 400 W) analyses were carried out to determine the chemical surrounding of atoms in the sample. The background of the chamber was 1×10^{-10} torr. The total energy resolution was 0.8 eV. The effective thickness that contributed to XPS signals was 3 nm.

3. Results and discussion

The SEM micrograph of the prepared sample is shown in Fig. 1. The morphology shows the ceramic feature that is usually seen after hot-pressing process. The microstructure appearance was dense and homogeneous for different region. EDXA confirmed that the

TABLE I Spacing and intensity for each XRD peak and (*hkl*) identification results for the Zr doped sample and the original $B_{4.3}C$ powder

No.	Spacing (Å)	Intensity	Spacing[a] (Å)	Intensity[a]	(*hkl*)	BN (*hkl*)	ZrB_2 (*hkl*)
1	4.026	19	4.052	20	003		
2	3.779	52	3.805	49	012		
3	3.525	9					001
4	3.336	110				002	
5	2.798	15	2.813	12	110		
6	2.741	10					100
7	2.561	59	2.574	57	104		
8	2.377	100	2.387	100	021		
9	2.300	7	2.308	6	113		
10			2.025	4	006		
11	2.166	21				100	101
12	2.063	5				101	
13	1.815	10	1.818	5	211	102	
14	1.763	3					002
15	1.710	11	1.716	9	205		
16	1.668	6				004	
17	1.625	3	1.630	3	107		
18	1.583	3					110
19			1.570	2	214		
20	1.499	13	1.503	9	303		
21	1.483	4					102
22	1.460	14	1.463	12	125		
23	1.442	11	1.444	9	018		111
24	1.400	16	1.403	12	220		
25	1.337	9	1.339	7	131		
26	1.323	9	1.324	8	223	104	
27	1.313	11	1.315	8	312		200
28	1.281	4	1.283	3	208		
29			1.263	4	306		
30	1.257	9	1.260	6	217	110	
31	1.207	3	1.209	3	119		

[a] Denotes the original $B_{4.3}C$ powder.

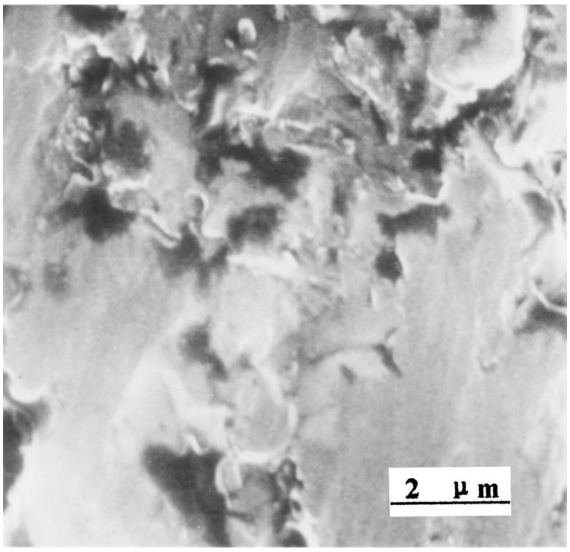

Figure 1 SEM micrograph of the Zr doped boron carbide.

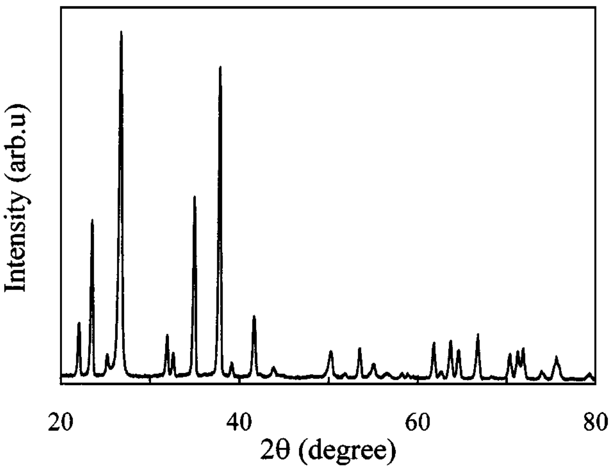

Figure 2 XRD pattern of Zr doped boron carbide fabricated by hot pressing at 2000 °C under N_2 atmosphere.

zirconium was distributed in the sample, and no other impurity was found.

Fig. 2 illustrates the XRD pattern of the sample. The corresponding spacing and intensity for each peak and (*hkl*) identification results are listed in Table I. In comparison, the XRD results for the original boron carbide powder are also presented. The identification results reach a conclusion that three phases were formed in the sample, i.e., ($B_{4.3}C$), (ZrB_2)3H and (BN)4H. Unexpectedly, the peak (002) of BN was so intense as to be comparable to the (021) of $B_{4.3}C$, even though some BN was anticipated in the surface of sample because the graphite die was under N2 atmosphere. The stable BN coating is used industrially on the inner mold surfaces to prevent reaction with the mold [10]. In some literature BN material was used as crucibles to synthesize boron carbides at high temperature [11]. The unique structural variation for ($B_{4.3}C$) itself after doping was that its (006) peak disappeared. We use this term "unique" because the variation was not found by the same experimental procedure with Ni doping. The lattice parameters were also a little smaller ($a = 5.600$ Å, $c = 12.08$ Å) than that of the original $B_{4.3}C$ ($a = 5.612$ Å, $c = 12.15$ Å). In addition, relative intensity increased a little for most peaks. However, the outstanding increase of intensity at 1.816 and 1.257 Å was due to superposition of (211) and (217) peaks of $B_{4.3}C$ with (102) and (110) peaks of BN, respectively.

The general structural feature of boron carbides has been described as consisting of 12-atom icosahedra on the corners of a rhombohedral unit cell and an intericosahedral three-atoms chain along the long diagonal. The constitution of the icosahedra and chains varies with the boron and carbon stoichiometry. According to the Emin's model [12], the idealized (B_4C)15R cells contain $B_{11}C$ icosahedrons and C—B—C chains. As the composition becomes more boron rich, the $B_{11}C$ icosahedra initially retain its carbon while C—B—C chains are gradually replaced by C—B—B. With further carbon reduction from $B_{13}C_2$ some of $B_{11}C$ are replaced by B_{12} icosahedra while the chains remain C—B—B. However, many experiments indicated that the carbon-rich limit is $B_{4.3}C$, and carbon atoms are always deficient to reach B_4C. Studies by Kuhlmann and Werheit [13, 9] indicated that the boron carbide structure consists of mixtures of B_{12} and $B_{11}C$ icosahedra and CBC and CBB chains. Moreover, with decreasing carbon content a growing proportion of unit cells without three-atom chains develops, whose concentration is zero at the carbon-rich limit and about 50% close to the boron-rich limit. In the carbon-rich limit $B_{4.3}C$, there are statistically 81% CBC and 19% CBB chains and exactly $B_{11}C$ icosahedra. Both models hold that in the stoichiometry range from B_4C to $B_{13}C_2$ the structural difference is mainly on the chain structure. Chains of CBC are predominant near the carbon-rich limit. Viewing from crystallography, the chain-center atoms B(3) [B(m) Kwei's notation] in the $(B_4C)15R$ cells pile up the (006) plane. In contrast, in the $B_{13}C_2$ cells chain-free and predominantly CBB chains result in B(3) atoms displacing from (006) plane owing to destruction of the symmetry of chains. This structural difference was reflected by their XRD patterns [14], i.e., the (006) peak is not presented in the $B_{13}C_2$ pattern. Another illustrative evidence is (303) peak. For $(B_4C)15R$ the C(4) atoms pile up the (303) plane. The absent of (303) peak for $B_{13}C_2$ can be interpreted by the displacement of atoms at the chain ends.

It is necessary to indicate that in this study the structure of the original $B_{4.3}C$ powder is of difference from that of $(B_4C)15R$ (or $B_{13}C_2$) in view of XRD difference for (009) and (312) peaks. The unit cells were also a little larger than the $(B_4C)15R$. We notice that B_4C or $B_{13}C_2$ with other diffraction patterns have also been obtained by some authors [15]. The difference of these patterns of boron carbide with same stoichiometry can be attributed to the multiple replacement of B atoms at the icosahedra or chains. In brief, the general feature of the $B_{4.3}C$ powder is more close to the $(B_4C)15R$ attribute. Especially, its B(3) atoms were in the centre of the chains. For the doped sample the (006) peak absence revealed the atoms at the B(3) sites were displaced by vacancies. And yet (303) peak reveals the symmetry of the chains still remained.

The view of soft and weak binding of the B(3) has been envisioned by the structural models. Early work by Tucker and Senio [16] provided the experimental evidence supporting this view. Their study showed that heavily irradiation introduced a large number of vacancies in the chain center of B_4C single crystals. Neutron powder diffraction studies by Kwei and Morosin [17] suggested an apparent large vacancy concentration at the central atom position of the chains for ceramic boron carbide powder. However, as to our knowledge this is the first time showing that by impurity incorporation remarkable vacancies are introduced in ceramic boron carbide $B_{4.3}C$. The impurity element seems selective because such result was not obtained with similar experiment by Ni doping.

The XPS studies revealed the chemical surroundings of atoms located. The binding energy of atoms was usually calibrated by that of the absorbed graphite (284.5 eV) which is attached in most of XPS studies. In this study a calibration of $\Delta E = 0.9$ eV is deduced for the binding energy data. The XPS spectra were obtained as received without ion etching in order to avoid energy shift. Fig. 3 illustrates the XPS spectra of the B 1s, C 1s and Zr 3d of the sample. The C 1s spectrum was deconvoluted into four peaks, with binding energy 281.3, 284.5, 286.6, and 288.1 eV, respectively. The predominant signal at 284.5 eV is due to graphite (or hydrocarbons) contamination on the surface of the sample. The signal at 288.1 eV was also usually observed in XPS studies and therefore was attributed to contamination (C—O bonding). The component 281.3 eV corresponds to C—B bonding from the $B_{4.3}C$. This value is consistent with the criterion that the binding energy difference $\Delta = E_b\,(\mathrm{C\ 1s}) - E_b\,(\mathrm{B\ 1s}) = 94.5$ eV for polycrystalline B_4C [18]. The nature of peak at 286.6 eV is not clear yet. In some literature similar binding energy was attributed to C—O bonding [19].

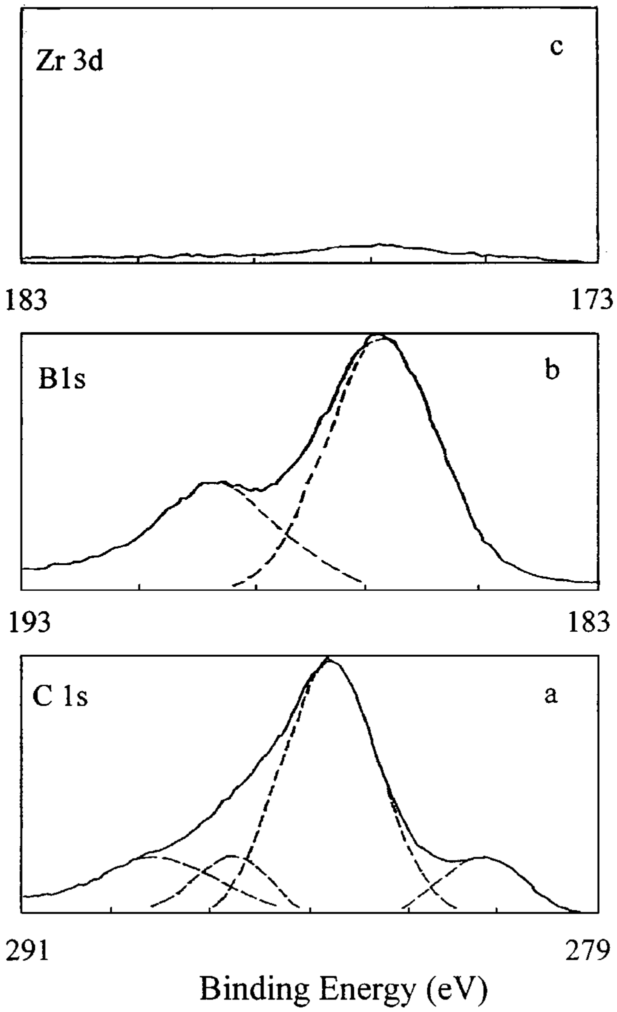

Figure 3 XPS spectra of the B 1s, C 1s and Zr 3d of the Zr doped boron carbide.

The B 1s spectrum consisted two peaks. The stronger peak at 186.7 eV is attributed to B atoms from the $B_{4.3}C$ (186.5 eV) [20]. The binding energy at 189.7 eV is close to but a little greater than that of B simple substance, exactly speaking the B—B bonding of B_{12} icosahedra (189.4 eV) [20]. However, in literature the B1s photopeak from BN departs from 189.8 to 190.3 eV by different authors [20]. Therefore, it can not exclude that the 189.7 eV corresponds to the B atoms from BN. From the relative intensity of the peaks at 189.7 and 186.7 eV in B 1s the amount of boron carbide $B_{4.3}C$ in the sample is deduced as nearly 70%.

The Zr 3d spectrum consisted a broad peak centered at 176.9 eV. From its relative intensity to the B 1s and taking into account the sensitivity factors of Zr (1.00) and B (0.088) atoms, the Zr content in the sample was evaluated as 0.45 at%. This value is essentially consistent with the composition of the original mixture. In order to demarcate the binding energy of Zr in ZrB_2,

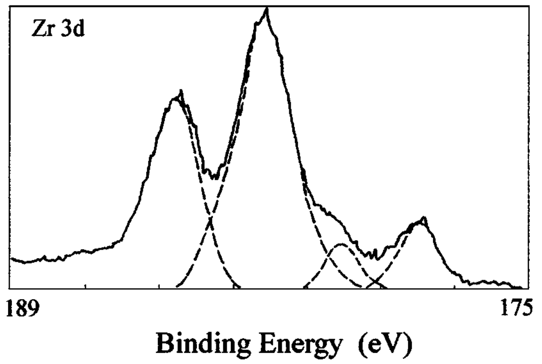

Figure 4 Zr 3d spectrum of ZrB_2 film with B deficiency.

the zirconium compound detected in the sample, a zirconium boride film specimen was prepared by Ar ion beam assisted sputtering deposition of ZrB_2. XRD studies confirmed that (ZrB_2) 3H was the only crystal phase formed in the film. However, the composition analyses by Auger electron spectroscopy (AES) indicated that the atomic ratio B/Zr was 1.43, i.e., boron atoms were deficient in the specimen. The Zr 3d XPS spectrum of this zirconium boride film is shown in Fig. 4. Synthesizing the XRD and AES results, the binding energy at 182.1 and 184.5 eV correspond to Zr $3d_{5/2}$ and Zr $3d_{3/2}$ with saturated Zr-B bonding. The other two peaks at 178.0 and 180.1 eV, close to $3d_{5/2}$ (178.9 eV) and $3d_{3/2}$ (181 eV) from metal Zr, are attributed to Zr atoms with unsaturated bonding owing to B deficiency. In Fig. 3 it can be seen that there is no clear peak around 184 or 182 eV. In view of the binding energy 176.9 eV of this peak the Zr state in the sample is similar to the situation of Zr atoms with unsaturated bonding. It is merely that the binding energy in Fig. 3c is even less than that in Fig. 4. Obviously, providing sufficient B atoms was not problem in the doped sample. Therefore, it is difficult to attribute all these Zr atoms existing in the form ZrB_2 with B deficiency. It is reasonable to suspect that Zr atoms in interstitial sites of B_4C may also exhibit similar binding situation with unsaturated bonding. Studies by Yakel [6] have revealed that the interstitial site B(6) in boron carbide was of sufficient size to accommodate a boron atom. That Al atoms can be accommodated at similar sites in boron carbide have also been proposed [5]. In view of the XPS results and the effects of Zr atoms on the structural modification of the $B_{4.3}C$, a feasible interpretation is that most Zr atoms were incorporated in the $B_{4.3}C$ chains, in addition to a part of Zr atoms in the ZrB_2 phase.

Further investigations are still needed to determine the definite sites of Zr atoms.

4. Conclusions

This study confirms that the subtle structure of boron carbides can be modified by introducing proper dopants with the experimental procedure hereof. The structural variation can be characterized by the XRD analyses. Our results indicate that the three-atoms chains are more easily to be modified. Chains with vacancies in the center, or two-atoms chains in other words, were led into by Zr atom introduction. The result suggests that some impurity atoms may also squeeze into the chain center by inverse action. The XPS analyses revealed that the Zr atoms existed in a state with unsaturated bonding. Synthesizing the XRD results, most doping Zr atoms might incorporate in the $B_{4.3}C$ lattice in interstitial sites. The electronic properties of the Zr doped boron carbide are under investigation.

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