

LETTERS

New Phase of sp^3 -Bonded BN: The 5H Polytype

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A new phase of sp^3 -bonded BN, that is, 5H polytype, has been found. The representative lattice parameters a and c were determined to be 2.528 and 10.407 Å, respectively. The new BN phase was prepared by chemical vapor deposition assisted with 193 nm laser irradiation of the surface. Source gases were diborane and ammonia diluted in argon and hydrogen. The substrate temperature was 850 °C.

Introduction

Materials with covalent bonds of tetrahedral coordination, i.e., sp^3 bond, may show polytypism as is well-known in silicon carbide (SiC), because of variations in the stacking of the densely packed layers.¹ Boron nitride (BN) with this bonding has excellent physical and chemical properties that are almost equivalent to and in some cases superior to those of diamond.² Until now, however, only two sp^3 -bonded phases of BN have been registered in JCPDS-ICDD,³ i.e., wurtzite^{4,5} and cubic forms;^{6,7} these are classified into 2H and 3C, respectively, according to the Ramsdell notation.¹ Sp^3 -bonded BN, carbon, and SiC are picked up from JCPDS-ICDD³ and classified from this point of view in Table 1. This paper introduces a new phase of 5H polytypic BN with sp^3 bonds.

Experimental Section

The films were deposited on mirror-polished silicon (100) substrates of 1 in. diameter by chemical vapor deposition (CVD) which was assisted with simultaneous irradiation of the surface with an ArF excimer laser at 193 nm. The repetition frequency and energy density of the laser were 10 Hz and 6 W/cm², respectively; photochemical effects on the surface reactions are supposed to be dominant over thermal ones at this energy

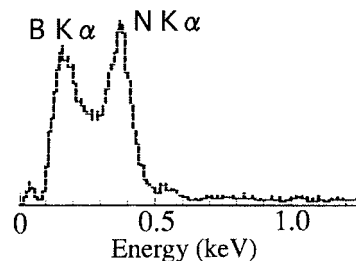


Figure 1. 1. Energy-dispersive X-ray spectrum (EDX) of a CVD film. X-ray intensity peaks from B ($K\alpha$) and N ($K\alpha$) are found at around 0.18 and 0.39 keV, respectively.

density. The depositions were carried out for 90 min from the source gases of diborane (B_2H_6) and ammonia (NH_3) diluted with the mixture of argon and hydrogen gases. The flow rates of the gases were as follows: 50 sccm (standard cubic centimeters per minute) of 5% diborane diluted in argon, 10 sccm of ammonia, 100 sccm of hydrogen, and additional 3 SLM (standard liters per minute) of argon. The total pressure was 20 Torr. The substrate temperature was kept constant at about 850 °C.

Results and Discussion

Compositional analysis (Figure 1) performed by energy-dispersive X-ray spectroscopy (EDX) at an acceleration voltage

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TABLE 1: Classification of sp^3 -Bonded Materials from the Point of View of Polytypism^a

Ramsdell notation	BN		C		SiC	
	JCPDS-ICDD	<i>D</i> (%)	JCPDS-ICDD	<i>D</i> (%)	JCPDS-ICDD	<i>D</i> (%)
2H	26-0773	1.41	19-0268	0.12	29-1126	-0.01
	20-0174	0.86			29-1130	0.49
	this report (70805)	-1.88				
3C	35-1365	0.00	6-0675	0.00	29-1129	0.00
			26-1078	0.00	29-1127	-0.01
4H					22-1317	0.17
5H	this report	0.82			42-1360	-0.77
6H			26-1082	0.00	29-1131	0.17
8H			26-1075	0.00		
10H			26-1081	0.00		
bond distance (Å)	1.5657		1.5444		1.8875	
distance between planes along <i>c</i> axis (Å)	2.0876		2.05923		2.5166	

^a The bond distance and the interplane distance are represented by those of 3C (cubic) polytypic forms. *D* is defined as the deviation of $c/(na)$ from 0.816 where *n* is the number in the Ramsdell notation.

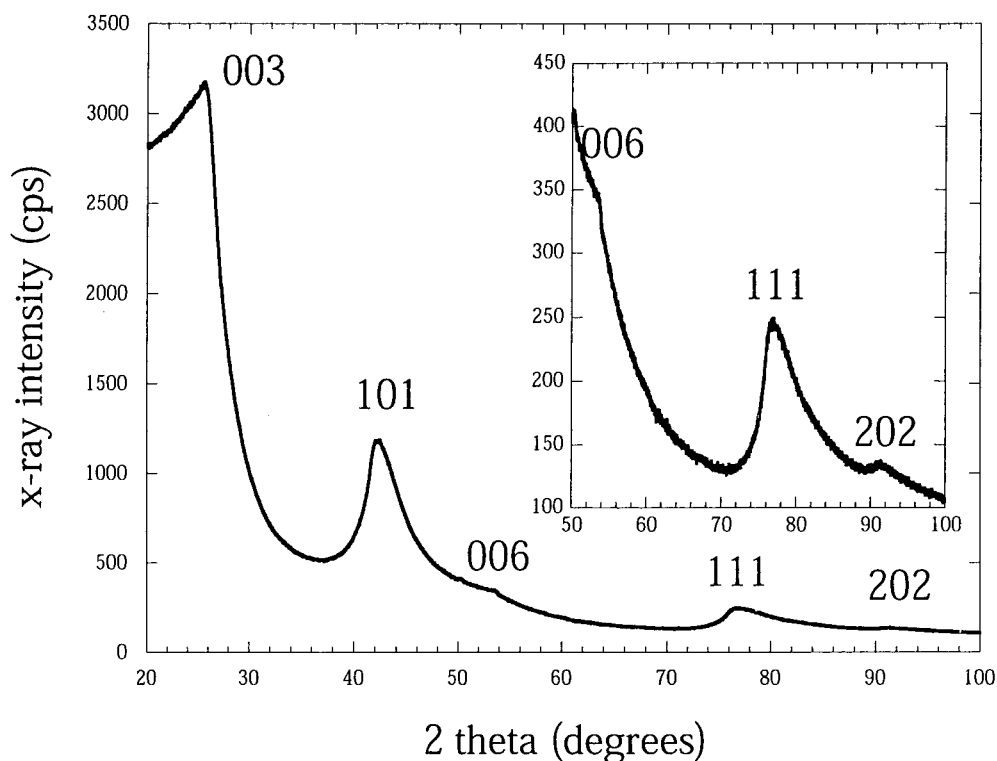


Figure 2. X-ray diffraction pattern of the sample of Figure 1. Weak peaks in the high 2θ region are made distinguishable in the inset. This is the raw data with no computer processing such as smoothing and background reduction.

of 3.0 keV indicated stoichiometric composition with no detectable impurities. A high-purity sintered pyrolytic BN disk (N1 grade BN commercially available from DENKA Co., Inc., Japan) was used as a standard. X-ray intensity peaks from B ($K\alpha$) and N ($K\alpha$) are found at around 0.18 and 0.39 keV, respectively.

An X-ray diffraction pattern for the sample of Figure 1 was obtained as shown in Figure 2 by using a fully computerized film X-ray diffraction system (RIGAKU RINT 2500) in which the incident X-ray angle was fixed at 0.3° and the voltage and current applied at the rotating Cu target were 40 kV and 400 mA, respectively. The scanning rate and step in the detector were 0.02 deg/min and 0.02° , respectively. This pattern proved to be consistent with a hexagonal lattice where the lattice parameters *a* and *c* were 2.528 and 10.407 Å, respectively, as shown in Table 2. The crystallite size is estimated to be very

TABLE 2: Analysis of the X-ray Diffraction Pattern Shown in Figure 2 in Terms of the sp^3 -Bonded 5H Structure of BN in Which the Lattice Parameters *a* and *c* Are 2.528 and 10.407 Å, Respectively

<i>h k l</i>	<i>d</i> (Å)	<i>d</i> (observed)	error (%)	comment
0 0 3	3.4690	3.469	0.01	very strong
0 0 6	1.7345	1.757	-1.30	weak, broad
1 0 1	2.1425	2.143	0.00	medium
1 1 1	1.2548	1.244	0.87	medium weak
0 0 9	1.1563	1.1512	0.44	weak, broad, observed only after smoothing and background reduction
2 0 2	1.0712	1.0708	0.04	weak

fine, about 100 Å, from the broadness of the XRD peaks by using the Scherrer's equation.

This hexagonal lattice is best understood in terms of a 5H polytypic form of sp^3 -bonded BN. The deviations of *a* from

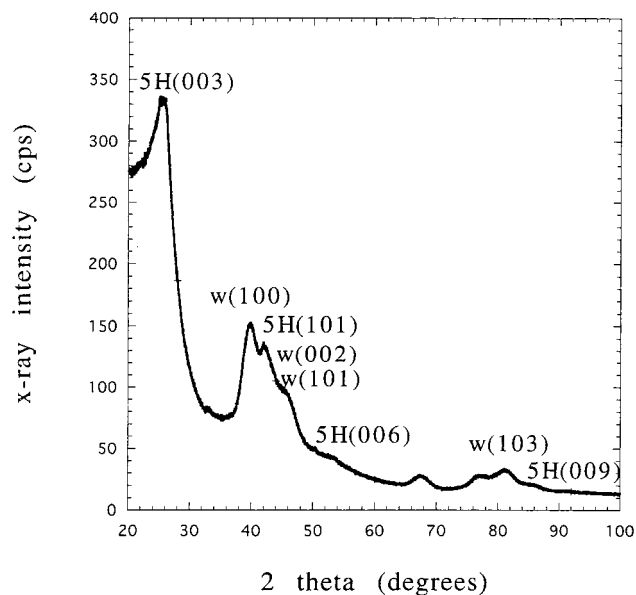


Figure 3. X-ray diffraction pattern of a sample indicating the growth of wBN together with the 5H polytypic BN.

TABLE 3: Analysis of the X-ray Diffraction Pattern Shown in Figure 3 in Terms of the Wurtzite Structure (2H) of BN in Which the Lattice Parameters a and c Are 2.6069 and 4.1771 Å, Respectively

h	k	l	d (Å)	d (observed)	error (%)	comment
1	0	0	2.2576	2.258	0.00	medium strong, broad
0	0	2	2.0886	2.103	-0.69	medium strong, broad
1	0	1	1.9861	1.988	-0.08	medium, broad
1	0	3	1.1851	1.185	0.00	weak, broad

the ideal a , which is based on the bond distance of cubic BN (JCPDS-ICDD 35-1365), in this sample and wurtzite form (JCPDS-ICDD 26-0773) are -1.1% and -0.15%, respectively. On the other hand, the deviations in c in this sample and the wurtzite form are +0.67% and +1.27%, respectively. The deviations in our sample may be considered to be within the allowed values suggested by the data of the wurtzite form.

In an ideal close-packed structure, the ratio of interplane distance ($c/5$ in our case) to a is $\sqrt{2/3}$, i.e., 0.8165 (ref 1). The deviation from this value is regarded as an indicator of the degree of elongation (compression) of the bond along the c axis if the sign is plus (minus). These data are also summarized in Table 1. We at first notice that the bonds in the wurtzite BN are not isotropic but elongated along the c axis. This seems to support the data in our sample, +0.82%, in comparison with those for the wurtzite form, 0.86 and 1.41%. The deviation in 5H polytypic SiC, 0.77%, is also very close to that of our sample. We found these indications of the 5H polytypes in at least 15 samples. We further notice that "diamond" polytypes, which have no stoichiometric polarity, show ideally close-packed structures, on the other hand.

We briefly refer to another sample, which was prepared under almost the same conditions as above, indicating the growth of wurtzite BN (wBN). The deposition duration was 60 min in this case. The XRD pattern (Figure 3) is best understood in terms of the mixture of sp^3 -bonded 5H BN and wBN as shown in Tables 3 and 4. It is noteworthy that the intensity ratio of the XRD peaks is in good agreement with those for the powder XRD data (JCPDS-ICDD 26-0773) as seen from Table 5. The critical condition to determine which phase should dominantly grow is still not clear. It should be also noted that the depositions

TABLE 4: Analysis of the X-ray Diffraction Pattern Shown in Figure 3 in Terms of the sp^3 -Bonded 5H Polytypic Form of BN in Which the Lattice Parameters a and c Are 2.5431 and 10.3668 Å, Respectively

h	k	l	d (Å)	d (observed)	error (%)	comment
0	0	3	3.4556	3.456	0.00	very strong
0	0	6	1.7278	1.724	0.23	very weak, broad
0	0	9	1.1519	1.151	0.06	very weak, broad
1	0	1	2.1543	2.154	0.00	medium strong

TABLE 5: Comparison of JCPDS-ICDD 26-0773 (Wurtzite BN) with the Sample of Figure 3

h	k	l	JCPDS-ICDD 26-0773		70805	
			d (Å)	intensity	d (Å)	intensity
1	0	0	2.211	100	2.26	100
0	0	2	2.114	70	2.10	84
1	0	1	1.959	45	1.99	46
1	0	2	1.528	18		
1	0	3	1.188	16	1.19	15
1	1	0	1.277	25		
1	1	2	1.980	12		
2	0	2	0.980	<1		
2	0	3	0.870	<1		
			0.840	<1		

under the same condition, but for the laser irradiation, yielded only amorphous films.

The enhancement of the growth of sp^3 -bonded BN by 193 nm laser irradiation was previously discussed using the molecular orbital method, where the photochemical depassivation of the nitrogen (100) surface of cubic BN under CVD conditions was predicted.⁸ The passivation of that surface by atomic hydrogen is regarded as one of the major obstacles to the CVD growth of sp^3 -bonded BN.² Further reviews on the growth of the cubic form of sp^3 -bonded BN from the vapor phase by various techniques are found in the literature,^{9,10} while technical aspects of BN preparation methods are reviewed in a recent volume.¹¹

Summary

A new phase of sp^3 -bonded BN of the 5H polytypic form was found. It was grown under CVD conditions with the assistance of 193 nm laser irradiation on the surface.

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