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Boron carbide/*n*-silicon carbide heterojunction diodes

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The fabrication, initial structural characterization, and diode measurements are reported for a boron carbide/silicon carbide heterojunction diode. Current–voltage curves are obtained for operation at temperatures from 24 to 351 °C. Plasma-enhanced chemical-vapor deposition (PECVD) -deposited undoped boron carbide material is highly crystalline and consists of a variety of polytypes of boron carbide (BC) with crystal sizes as large as 110 nm. Crystal phases are similar to those for PECVD BC on Si but only partially match known boron and boron-rich BC phases. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1426257]

Boron carbide has long been valued as a hard, refractory, corrosion-resistant ceramic and investigated as a potential electronic material.[1,2] If combined with useful semiconducting properties, its mechanical properties make boron carbide attractive for reliable high-temperature devices that function in harsh chemical environments. In the past ten years a semiconducting form of boron carbide (BC) has been successfully grown, by plasma-enhanced chemical-vapor deposition (PECVD), and used in a variety of initial diode and transistor devices.[2–4] Not all boron-rich BC crystals are semiconducting. The crystal structures of boron-rich boron carbides share the icosahedral building block that is also found in rhombohedral boron. The structural similarities of the boron carbides imply that the energy barriers between these different structures may be small and may lead, under nonequilibrium conditions, to simultaneous formation of a number of different polytypes, as occurs, for example, in silicon carbide. The crystallinity of semiconducting BC films grown by PECVD has been questioned despite the Bragg diffraction peaks in published x-ray diffraction patterns.[5]

Here, we report the promising high-temperature electrical behavior of boron carbide/silicon carbide heterojunction diodes. We also show that the PECVD boron carbide material of these devices contains crystallites that are substantially larger than previously reported.

Boron carbide was grown on SiC substrates by PECVD using a single precursor, orthocarborane-*closo*-1,2-dicarbadodecaborane ($C_2B_{10}H_{12}$). As-received *n*-type nitrogen-doped (111) 6H–SiC wafers (SiCrystal AG, Germany) were cleaved, cleaned, and passivated immediately before insertion into a custom-designed parallel-plate radio-frequency plasma reactor. The substrate heater remained at 350 °C throughout initial plasma etching (at 200 mTorr and 10 sccm Ar for 30 min) and subsequent deposition. Orthocarborane, sublimed at ~50–70 °C, was introduced through a heated manifold by a flow of argon carrier gas. Depositions, using ~25 W of 13.56 MHz rf power for 15 min at ~200 mTorr reactor chamber pressure, were followed by cooling over 1 h to 250 °C. Coated substrates were cooled to room temperature (in one additional hour) and were stored in vacuum. The BC overlayer was ~2000 Å thick.

Gold contacts, about 1.5 mm in diameter and at least 100 nm thick, were sputtered on the BC surface and on the adjacent SiC surface rather than on the back of the SiC wafer to minimize the influence of through-wafer SiC micropipes on the electrical performance. Robust external connections were provided through electrically conductive epoxy on top of the gold contacts. Devices were heated on a hot plate while current and voltage measurements were obtained using Keithley 2400-C SourceMeter and TestPoint software.

The diode current–voltage ($I-V$) curves from the Au/BC/*n*-SiC/Au device were measured at temperatures of 24, 61, 104, 141, 187, 229, 288, and 351 °C. For clarity, only five temperature curves are shown in Fig. 1. Separate measurement of Au/SiC/Au confirmed the Ohmic behavior of the Au/SiC junctions at temperatures above 150 °C, in contrast to their well-known Schottky behavior at lower temperatures. Ideality factors, calculated by fitting of the linear portions of logarithmic plots of current as a function of applied bias, fell from ~20 at room temperature to below 2 at the highest temperature of 351 °C. We attribute this improvement in the ideality factor to the lower resistance of the BC material at higher temperatures. BC is a highly resistive material and this large resistance, which is effectively in series

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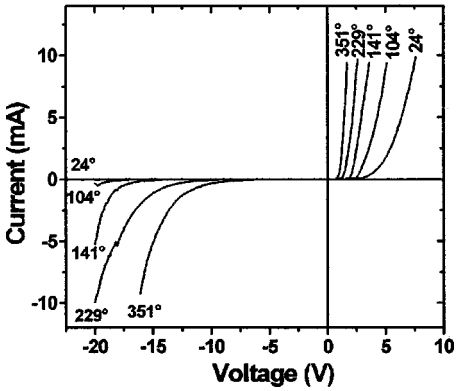

FIG. 1. Current-applied bias ($I-V$) curves of an Au/BC/n-SiC/Au device as a function of temperature. Curve labels are temperatures in °C.

with the diode, causes this marked deviation from ideality. The SiC device shows lower leakage currents and higher breakdown voltages than the Si device, under similar conditions at all temperatures (see Table I). In general, the reverse saturation current is determined primarily by the number of minority charge carriers in each material with an exponential dependence on the band gap. The band gaps of Si and SiC are 1.1 and 3.0 eV, respectively, at 300 K; this difference in band gaps of the substrate materials could account for some of the discrepancy.

X-ray diffraction was performed using a Rigaku theta-two theta diffractometer (Cu $K\alpha$ radiation) to detect BC phases present. PECVD BC on SiC shows sharp, well-defined peaks [Fig. 2(a)]. Multiple polytypes present in the SiC produced numerous peaks which were used to correct the observed BC diffraction angles, a correction that ranges from $-0.2°$ at low angles to $-0.3°$ at 65°.

The small peak widths indicate that the BC material has relatively large nanocrystallite dimensions (~30–110 nm) in contrast to previously reported PECVD BC films.[5] The peak positions, however, do not correspond to only one known boron carbide crystal type. Elemental rhombohedral boron consists of icosahedra placed at the corners of a rhombohedral unit cell. The addition of carbon leads to the formation of a chain of B and C atoms on the body diagonal of the unit cell and/or substitution of some B in the icosahedra by carbon. Small changes in the dimensions and structure of the unit cell as carbon is added to the compound often alter the main diffracting angles by only small fractions of a degree. Distinguishing between the various boron carbide compounds in a micro- or nanocrystalline material using x-ray diffraction is therefore difficult, particularly since boron and carbon differ by 1 in atomic number, and so their x-ray scattering lengths are also quite comparable.

To identify the numerous peaks, we restricted our x-ray diffraction peak search to compounds containing only boron and/or carbon, but not hydrogen. The orthocarborane molecule has a $B_{10}C_2$ icosahedral core surrounded by 12 hydrogen atoms that are readily removed in the PECVD process. On previous samples, Fourier transform infrared measurements showed little C–H or B–H bonding and atomic absorption showed less than 5% hydrogen. There are no x-ray diffraction data reported for BC compounds containing such low fractions of hydrogen.

TABLE I. Relevant diode parameters of BC deposited Si and SiC, respectively.

Temperature	Breakdown voltage		Leakage current at −4 V	
	On SiC	On Si	On SiC	On Si
24 °C	−16.7 V	−14.2 V	−66.5 nA	−71.3 nA
340 °C		<−0.1 V		−4.66 mA
351 °C	−4.3 V		−8.02 μA	

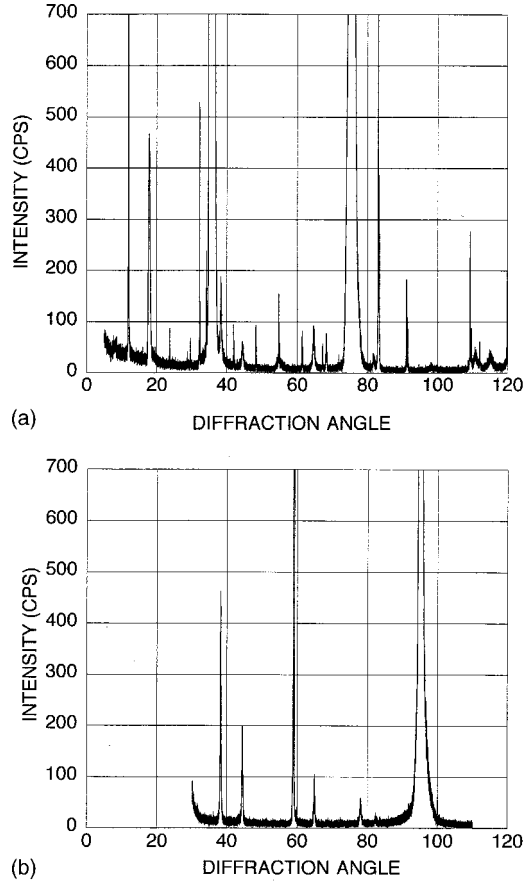

FIG. 2. Cu $K\alpha$ x-ray diffraction data for BC layers on SiC and Si substrates: (a) on SiC and (b) on Si.

The diffraction peaks (corrected for the small shift mentioned above) originating solely from the BC and not the SiC substrate are given in Table II, together with the best matches from the powder diffraction file (PDF) data files. The peaks are associated with interplanar spacings that correspond closely with some of those found in tetragonal $B_{48}(B_2C_2)$ (Ref. 6) and the rhombohedral compounds B, $B_{12}(BC_2)$, B_4C, or $B_{41.1}C_{4.45}$ but are not consistent with only one compound. For each of these possible phases, the intensities within each group of peaks do not scale according to the intensities for randomly oriented powders given in the International Crystal Diffraction Database Powder Diffraction Files, thus indicating at least some degree of preferred crystalline orientation. The large crystallite sizes, over 100 nm, indicate excellent crystallinity. One of the strongest peaks, at 31.963°, can be assigned to the (1 1 0) spacing of a variety of rhombohedral BC compounds, all very close together. The other strong peak, at 82.952° is closest to the (6 3 2) peak of $B_{48}(B_2C_2)$. Initial high-resolution electron microscopy of as-deposited BC grown on Si under slightly

TABLE II. Bragg 2θ diffraction angles and interplanar spacings obtained from Cu $K\alpha$ x-ray diffraction by BC layers on SiC substrates. Also listed are the ICDD Powder Diffraction File (PDF) data for closely matching crystalline phases and associated crystal plane indices. Bold lettering indicates the closest agreement.

2θ (degrees)	Peak height (counts)	Size (nm)	Phases (from ICDD PDF)	PDF 2θ (degrees)	PDF phase index
25.077	11.5	135.6	Rhombohedral B	25.11	(7 2 0)
28.49	15.6	154.6	Rhombohedral B	28.218	(−1 −12)
			or $B_{48}B_2C_2$	28.835	(2 1 1)
29.358	39.2	141.6			
31.963	495.2	147.5	B_4C	31.937	(1 1 0)
			or $B_{12}(BC_2)$	31.946	(1 1 0)
			$B_{6.5}C$	31.838	(1 1 0)
33.959	161	177.8	B48 B2 C2	33.982	(2 2 1)
			Rhombohedral B	34.283	(−2 2 1)
44.219	33.9	27.6	$B_{48}(B_2C_2)$	44.011	(3 3 0)
			Rhombohedral B	44.527	(4 4 1)
64.369	60	26.1	B_4C	64.374	(0 1 8)
			$B_{48}(B_2C_2)$	64.524	(3 1 3)
66.889	43.8	122.2	B_4C	66.765	(2 2 0)
			$B_{12}(BC_2)$	66.764	(2 2 0)
82.705	656	134.3	$B_{12}(BC_2)$	82.821	(6 3 2)
			B_4C	82.544	(1 2 8)
82.952	304	136.2	$B_{48}(B_2C_2)$	83.45	(6 3 2)

different conditions has revealed 3-nm-sized crystals. Lattice fringes in these crystals correspond to interplanar spacings 0.21 ± 0.01, 0.24 ± 0.01, and 0.32 ± 0.01 nm,[7] which are close to the present x-ray diffraction results.

Figure 2(b) shows the data for samples grown by us on Si under similar conditions to the growth on SiC. The peak widths correspond to crystals that are somewhat smaller (~10–100 nm) than those grown on SiC. By comparison of the x-ray diffraction pattern for growth on SiC [Fig. 2(a)] with those for growth on Si [Fig. 2(b)], it is clear that the choice of substrate influences the growth, both in the proportion of phases present and in the crystallinity Performing a similar analysis on the BC/Si x-ray peaks, the predominant phases present are tetragonal $B_{48}(B_2C_2)$ and rhombohedral B.

As pointed out earlier, the subtle differences in structure among the family of BC compounds makes a unique identification difficult. Two facts remain clear-we have more than one phase present and the material is extremely crystalline.

In summary, undoped BC/*n*-SiC devices show good semiconductor diode behavior, from room temperature to 351°C, which is superior to the BC/*n*-Si behavior previously reported.[3] The superior diode performance of the device on SiC may relate to its improved crystallinity as well as to the larger band gap of the substrate. Nanocrystalline material deposited under present PECVD reactor conditions exhibits narrow x-ray diffraction peaks at angles that correspond closely to several boron and boron–carbon phases that we have identified but not fully to any one of these phases.

The preliminary electrical assessment indicates that high-temperature operation may be successful. It is now important to identify the phase that contributes the most desirable semiconducting behavior in order that this promising semiconducting system can be better understood and used in high temperature and other applications.

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