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**Boron-Carbide and Boron Rich Rhobohedral Based Transistors and Tunnel Diodes**

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BORON-CARBIDE AND BORON RICH RHOBOHEDRAL BASED TRANSISTORS AND TUNNEL DIODES

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Related U.S. Application Data

Continuation of application No. 08/1933,962, filed on Sep. 19, 1997, now Pat. No. 6,025,611.

Provisional application No. 60/026,972, filed on Sep. 20, 1996.

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U.S. Cl. .................. 438/183; 438/167; 438/180; 438/478
Field of Search ........................................ 438/183, 181, 438/180, 167, 478

References Cited

U.S. PATENT DOCUMENTS

3,224,913 A 12/1965 Ruehrwein ............... 148/175
3,364,084 A 1/1968 Ruehrwein ............... 148/175
4,348,428 A 9/1982 Rockey .................. 427/54.1
4,362,766 A 12/1982 Damhueser et al. ........... 427/39
4,766,482 A 8/1988 Smeltzer et al. ........... 357/23.7
4,957,773 A 9/1990 Spencer et al. ........... 427/39
5,061,322 A 10/1991 Assano ................... 136/258
5,070,027 A 12/1991 Mito et al. ............... 437/15
5,468,978 A 11/1995 Dowben .................. 257/258
5,632,699 A 5/1997 Azarian .................. 451/54
5,658,834 A * 8/1997 Dowben

ABSTRACT

The present invention relates to the fabrication of a boron carbide/boron semiconductor devices. The results suggest that with respect to the approximately 2 eV band gap pure boron material, 0.9 eV band gap boron carbide (B5C) acts as a p-type material. Both boron and boron carbide (B5C) thin films were fabricated from single source borane cage molecules using plasma enhanced chemical vapor deposition (PECVD). Epitaxial growth does not appear to be a requirement. We have doped boron carbide grown by plasma enhanced chemical vapor deposition. The source gas close-1,2-dicarbadecaborane (orthocarborane) was used to grow the boron carbide while nickelocene (Ni(C5H5)2) was used to introduce nickel into the growing film. The doping of nickel transformed a B5C material p-type relative to lightly doped n-type silicon to an n-type material. Both p-n heterojunction diodes and n-p heterojunction diodes with n- and p-type Si [1,1,1] respectively. With sufficient partial pressures of nickelocene in the plasma reactor diodes with characteristic tunnel diode behavior can be successfully fabricated.

23 Claims, 8 Drawing Sheets
OTHER PUBLICATIONS


Dowben et al., “Nickel doping of boron carbide and Fermi level shifts,” pp. 1–6, unpublished manuscript.


* cited by examiner
FIG. 4b
FIG. 5a

Applied Bias (V)

Current (mA)

FIG. 5b

Applied Bias (V)

Current (mA)
FIG. 6
BORON-CARBIDE AND BORON RICH RHOBODHIERAL BASED TRANSISTORS AND TUNNEL DIODES

RELATED APPLICATIONS

This application is a continuation in part of U.S. application Ser. No. 08/933,962, filed Sep. 19, 1997, now U.S. Pat. No. 6,025,611, which claims priority under 35 U.S.C. §119(e) to provisional application Ser. No. 60/026,972, filed Sep. 20, 1996. Each of said applications is incorporated herein by reference in its entirety.

GOVERNMENT RIGHTS

This work resulted in part from research conducted under U.S. Air Force grant AFOSR F49620-94-1-0433. The government has certain rights in this invention.

BACKGROUND OF THE INVENTION

The present invention relates to a process for the deposition of boron carbide semiconductor material, and also to semiconductor devices formed by deposition of a boron carbide film. The invention is more particularly directed to a technique for creating a layer of boron carbide with a boron-to-carbon ratio of about 5. The invention is also particularly directed to semiconductor devices produced by this technique.

Boron and boron carbide devices have been sought since 1959 [1] but only recently has the fabrication of these devices been realized [2, 3]. Such devices would have applicability in a wide number of harsh conditions. For example, they should be resistant to corrosive, high temperature, and mechanically abrasive environments.

Because of the large neutron capture cross-section, these materials could be used in devices in radioactive environments as well [4].

Techniques are known for forming boron-rich carbides. These techniques may employ alkanes and heavy boron cage molecules to deposit boron carbide thin films. Plasma-enhanced chemical vapor deposition (PECVD) can be employed to fabricate boron carbide films without resort to high temperatures or high pressures. These techniques typically employ a halide of boron, e.g., BCl3, BB3 or BF3. Most recently boranes, such as nido-decaborane and nido-pentaborane have gained interest, because these compounds are safe and stable, yet produce a vapor pressure of several Torr at room temperature. However, until very recently, only low-resistivity boron carbide materials could be produced, i.e., materials with resistivities on the order of about ten ohm-cm at room temperature. Boron carbide material of this type has an extremely low band gap, and is not suited as a semiconductor material.

At the same time, boron carbide has become an attractive material because of its inherent hardness and durability. Boron carbide, like other boron-containing materials, has been considered for high temperature electronic devices because it retains its useful characteristics at elevated temperatures. For example, boron carbide is known to have a melting temperature of 2350°C, a strength of 50 ksi, a hardness of 2800 kg/mm², and a thermal conductivity of 0.22 cal/cm/sec°C C/cm. Diamond and silicon carbide have been investigated because of their good thermal and mechanical characteristics, and because of their wide band gaps. However, these materials have not yet proven cost effective.

Recent successes in construction of boron carbide/n-Si [1,1,1] heterojunction diodes [5, 6] have demonstrated that boron carbide/Si [1,1,1] heterojunction diodes can be fabricated from close-1,2-dicarbadodecaborane (C2,B12H22) by using synchrotron radiation induced chemical vapor deposition (SR-CVD) [5, 6], and plasma enhanced chemical vapor deposition (PECVD) [2, 3, 5–7].

SUMMARY OF THE INVENTION

It is an object of the present invention to provide boron/ boron carbide and doped boron carbide semiconductor devices and techniques to fabricate same.

It is another object of the present invention to provide a semiconductor device suited for use in high temperature, corrosive, mechanically abrasive, or radioactive environments.

Another object of the present invention is to provide boron carbide semiconductor devices and fabrication techniques which do not require a silicon interface.

Yet another object of the present invention is to provide boron carbide semiconductor devices and fabrication techniques to fabricate same which do not depend on epitaxial growth or crystallite size.

Still another object of the present invention is to provide doped boron carbide semiconductor devices and fabrication techniques for making same. In one embodiment, the doped boron carbide appears as n-type relative to an n-type silicon substrate.

The objects of the present invention are provided by the boron/boron carbide heterojunction devices and the doped boron carbide/silicon semiconductor devices and fabrication techniques as disclosed herein.

The fabrication of several working boron/boron carbide semiconductor devices is described herein. In an effort to fabricate a more sophisticated device, a transistor was made in a PECVD system. A diode was made directly on an aluminum substrate to demonstrate that a silicon interface is not essential for fabrication of a boron carbide device.

The use of plasma enhanced chemical vapor deposition (PECVD) provides a means for fabricating boron and boron carbide thin films successfully in a high resistivity form [2, 3]. The present invention addresses some of the issues associated with making devices of increasing complexity from boron carbide.

The aluminum substrates were polycrystalline, and the silicon substrates were [1,1,1], n-type. Both were chemically etched and cleaned prior to insertion in vacuo and set on the lower electrode. The substrates were further cleaned by Ar+ bombardment at 300 mTorr, 40 W and annealed at 400°C in the vacuum system. Deposition was carried out in a custom designed parallel plate 13.56 MHz radio-frequency plasma enhanced chemical vapor deposition (PECVD) reactor described previously [3, 7]. A suitable plasma chamber in which this technique can be carried out is shown and described in U.S. Pat. No. 4,957,773, hereby incorporated by reference in its entirety.

The above, and many other objects and advantages of the present invention will become apparent from the ensuing detailed description of the invention, to be read in conjunction with the accompanying drawings.

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It is another object of the present invention to provide a semiconductor device suited for use in high temperature, corrosive, mechanically abrasive, or radioactive environments.

Another object of the present invention is to provide boron carbide semiconductor devices and fabrication techniques which do not require a silicon interface.

Yet another object of the present invention is to provide boron carbide semiconductor devices and fabrication techniques to fabricate same which do not depend on epitaxial growth or crystallite size.

Still another object of the present invention is to provide doped boron carbide semiconductor devices and fabrication techniques for making same. In one embodiment, the doped boron carbide appears as n-type relative to an n-type silicon substrate.

The objects of the present invention are provided by the boron/boron carbide heterojunction devices and the doped boron carbide/silicon semiconductor devices and fabrication techniques as disclosed herein.

The fabrication of several working boron/boron carbide semiconductor devices is described herein. In an effort to fabricate a more sophisticated device, a transistor was made in a PECVD system. A diode was made directly on an aluminum substrate to demonstrate that a silicon interface is not essential for fabrication of a boron carbide device.

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The above, and many other objects and advantages of the present invention will become apparent from the ensuing detailed description of the invention, to be read in conjunction with the accompanying drawings.
BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1a is a graph of diode I-V characteristics of a boron carbide/boron/aluminum device according to the present invention with a schematic cross-sectional view of the diode structure and wire connections for characteristics shown in the inset.

FIG. 1b is a graph of diode I-V characteristics of a boron carbide/boron/n-Si [1,1,1] device according to the present invention with a schematic cross-sectional view of the diode structure and electrical wire connections for characteristics shown in the inset.

FIG. 2a shows the schematic cross-sectional geometry of fabricated boron carbide junction field-effect transistor (JFET) according to the present invention. The schematic also illustrates electrical wire connections as well as polarities of each applied bias.

FIG. 2b shows transistor characteristics of I_D (drain current) vs. V_DS for the device shown in FIG. 2a. Gate voltage, V_G, was applied from 0 V to 10 V by the step of 2 V.

FIG. 3 shows the transistor characteristics of I_D (gate current) vs. V_DS for the device shown in FIG. 2a. Note that, relative to FIG. 2, the currents are small.

FIG. 4a shows the schematic cross-sectional geometry of a boron carbide/n-Si [1,1,1] heterojunction and a graph of diode I-V characteristics for the device shown.

FIG. 4b shows the schematic cross-sectional geometry of the high nickel doped boron carbide/n-Si [1,1,1] heterojunction according to the present invention and a graph of diode I-V characteristics for the device shown.

FIG. 4c shows the schematic cross-sectional geometry of the low nickel doped boron carbide/n-Si [1,1,1] heterojunction according to the present invention and a graph of diode I-V characteristics for the device.

FIG. 5a shows a graph of I-V diode characteristics a nickel doped boron carbide heterojunction diode, with low nickel doping concentrations, according to the present invention.

FIG. 5b shows a graph of I-V diode characteristics a nickel doped boron carbide heterojunction diode, with high nickel doping concentrations, according to the present invention.

FIG. 6 is a graph of diode I-V characteristics of a boron rich semiconductor homojunction diode according to the present invention with the schematic cross-sectional geometry of the diode shown in the inset.

DETAILED DESCRIPTION OF THE INVENTION

Using CVD sources, boron carbide/boron multilayers were deposited on aluminum and silicon. FIG. 1a shows the schematic cross-sectional view of the fabricated multilayer devices. Decaborane was used to form a pure boron film on the substrates. Boron carbide (B₄C) films were then deposited on the pure boron layer from orthocarbaborane. The purity of the orthocarbaborane and decaborane was determined by infrared (IR), nuclear magnetic resonance (NMR) and mass spectral measurements (purity 98%) and compared with literature values [10]. Less than 1% of the metacarbaborane and paracarborane isomers were found to be present. The decaborane was sublimed to separate the source material from cellite (a stabilizer) and other impurities [10].

The diode I-V characteristics of a B₄C/boron/aluminum structure are seen in FIG. 1a. Although not shown here, a boron/aluminum structure exhibits an ohmic characteristic, which leads to the conclusion that a junction exists between the B₄C and boron with the B₄C acting as the p-type material. The I-V diode characteristics of a B₄C/boron/n-type silicon structure are seen in FIG. 1b. In this case the boron/n-type silicon structure, which is not shown, exhibits a diode characteristic with the boron acting as a p-layer with respect to the n-type silicon. This result, combined with results of FIG. 1a and the boron/aluminum structure indicate the B₄C/boron/n-type silicon structure consists of two diodes in series oriented in the same direction. This is borne out by the observed diode curve in FIG. 1b. Furthermore, neither structure exhibits the classical exponential diode behavior in the forward direction. This type of behavior is similar to the previously reported boron carbide/n-type Si [1,1,1] heterojunction [2, 3]. It has been demonstrated that boron carbide thin film on n-type Si [1,1,1] heterojunction diodes are insensitive to the morphology of the film [6]. The semiconductor properties of the material do not appear to depend upon crystal size and the extent of long range order, and similar material can be grown on other substrates such as silver, Si [1,1,1], and titanium.

The fabricated boron carbide/boron/silicon multilayer device can be employed as a junction field effect transistors (JFET). FIG. 2a shows the schematic diagram of the measurement circuit, while FIG. 2b shows the drain current vs. drain voltage, with the source at ground, as a function of the gate voltage. Based on the characteristics of FIG. 1b, the gate is biased positive, while the drain is swept through negative voltages, each with respect to the grounded source. As the gate voltage is increased, the magnitude of the drain current decreases for any given value of drain voltage, which is the expected behavior for a JFET. It should be pointed out that the device does not saturate, nor does it completely cut off. This is probably a result of the fact that this is a single junction device, and the junction is relatively far removed from the source and drain region.

FIG. 3 is the gate current vs. drain voltage as a function of gate voltage. When combined with FIG. 2b, this clearly indicates the leakage current is less than 10% of the drain current.

Diodes fabricated from boron carbide with crystallites of different sizes (30 Å, 100 Å and 240–340 Å) have been compared [6]. While the ideality factors of these diodes do differ, similar rectifying diodes were fabricated [6] to the ones shown in this work. It is believed that this insensitivity to crystal grain size and the clear evidence that devices can be fabricated on very different substrates provides some evidence that epitaxial growth is not a determining issue in the fabrication of devices made with this microcrystalline or polycrystalline semiconductor material.

The fabrication of heterojunction devices from plasma enhanced [11–14] and synchrotron radiation [14, 15] chemical vapor deposition is possible from decomposition of cluster borane molecules. In fact, not only have diodes been fabricated, but a field effect transistor as well [13]. Nonetheless, no intentional doping of this material grown by plasma enhanced chemical vapor deposition (PECVD) has been attempted successfully prior to this work.

Attempts to dope films of the molecular icosahedra closo-1,2-dicarbadoxodecaborane (orthocarbaborane) have not been uniformly successful. Such molecular films can be doped with sodium [16, 17], but not the more common dopant mercury [16]. Since the suitability of orthocarbaborane (C₃B₁₃H₂₅) for the chemical vapor deposition of a boron carbide film suitable for making devices has been stab-
phosphide have been investigated for boron rich solids. A molecular nickel carborane complex has been synthesized in inorganic chemists [18] and the inclusion of nickel in other boron rich solids is well established. Nickel is a common component in the boron carbide superconductors [19] and the reactions of nickel with boron phosphide have been investigated [20, 21]. Nickelocene, Ni(C5H5)2, has been shown to be a suitable source compound for the deposition of nickel containing thin films [22]. Nickelocene is volatile and far less toxic than nickel carbonyl, though a number of other nickel containing organometallic compounds may be suitable [23]. Since both orthocarobane and nickelocene are easily sublimed from the solid, introduction of suitable mixtures into the plasma reactor can be readily accomplished.

The p-n and n-p heterojunctions were formed by depositing boron carbide thin films on n-type and p-type Si(111) substrates respectively, doped to 7x10^14/cm^2, following procedures described in detail elsewhere [11, 12]. The Si(111) substrates were prepared by Ar+ ion sputtering in the plasma reactor. Deposition of the films was performed in a custom designed parallel plate 13.56 MHz radio-frequency PECVD reactor used in previous studies [11-12]. The source molecule gas closo-1,2-dicarbadecaborane (ortho-carborane) was used to grow the boron carbide while nickelocene (Ni(C5H5)2) was used to introduce nickel into the growing film. Other dopants can be introduced using other metalloccenes, including, for example, chromium (chromocene), manganese (manganocene), iron (ferrocene), cobalt (cobalocene), and ruthenium (ruthenocene). Like organometallic compounds can be used to extend the range of dopants even further.

In still further embodiments, the boron carbide layer is doped with phosphorous. In one embodiment, phosphorous doped boron carbon alloy films were made by chemical vapor deposition from a single source compound, dimeric chloro-phospha(III)carborane ([C3B11H10]2(PhCl)2), and the resulting phosphorous doped B,C materials exhibited increases in the band gap from 0.9 eV to 2.6 eV. Other methods of phosphorous inclusion may also be employed, and will also increase the band gap substantially.

Typical boron carbide/n-type silicon heterojunctions have been routinely formed by this technique [11-14] as seen in FIG. 4a. With inclusion of nickelocene as an additional source gas, nickel was included in the growing boron carbide thin film. The presence of nickel at high doping levels was established by Auger electron spectroscopy employing a cylindrical mirror analyzer (Perkin Elmer double pass CMA) as the electron energy analyzer. Several different partial pressures of nickelocene were employed. Low relative partial pressures of nickelocene to orthocarbone during film growth (<0.1) resulted in the heterojunction diode shown in FIG. 4b while higher partial pressure ratios (about 9) resulted in the heterojunction diode shown in FIG. 4c.

The consequence of inclusion of nickelocene with orthocarbone as a source gas, the normally p-type boron carbide, relative to the n-type silicon, results in the formation of rectifying diodes with reverse bias. Thus the nickel doped boron carbide heterojunction diodes appears n-type relative to the lightly doped n-type silicon substrate. This is consistent with the fabrication of n-p heterojunctions diodes on p-type silicon, again by including nickelocene with the orthocarbone as an additional source gas, as seen in FIG. 5a.
for use in radar. The semiconductor devices prepared in accordance with the present invention are robust and operate at high temperatures and thus are well suited to high power applications of this type.

The boron/boron carbide devices in accordance with this teaching may also be used as sensors in automobile engines. Sensors in car engines currently do not exceed 100°C, however, direct control of the engine, transmission, antilock braking system, and manifold absolute pressure is expected to increase the temperature requirements.

The boron/boron carbide devices in accordance with the present invention may also be used as “throw-away” sensors in forms used in the fabrication of steel parts. The problem with steel form sensors is that molten steel is very corrosive and as a result very few sensors work in contact with molten steel. Such sensors are used to make sure the molten steel fills all parts of the form, in particular parts where vapor tends to get trapped as the molten steel is poured into the form.

The description above should not be construed as limiting the scope of the invention, but as merely providing illustrations to some of the presently preferred embodiments of this invention. In light of the above description and examples, various other modifications and variations will now become apparent to those skilled in the art without departing from the spirit and scope of the present invention as defined by the appended claims. Accordingly, the scope of the invention should be determined solely by the appended claims and their legal equivalents.

All references cited herein are expressly incorporated by reference in their entireties.

REFERENCES


What is claimed is:
1. A process for preparing a semiconductor device comprising the steps of:
A process according to claim 1, wherein said dopant is phosphorous.  

12. A process according to claim 11, wherein said dopant is phosphorous.  

13. A process according to claim 12, wherein said second layer is formed by chemical vapor deposition from dimeric chloro-phospha(II1)carborane.  

14. A process according to claim 11, wherein said dopant is selected from the group consisting of nickel, chromium, manganese, iron, cobalt, and ruthenium.  

15. A process according to claim 11, wherein said dopant is nickel.  

16. A process according to claim 15, wherein said second layer comprises silicon [1,1,1].  

17. A process according to claim 15, wherein said substrate material comprises aluminum.  

18. A process for introducing a metal as a dopant in a boron carbide layer deposited onto a suitable substrate comprising the steps of:  

- supplying into a chamber that contains the substrate a gaseous mixture of orthocarborane and an organometallic compound comprising the metal;  
- energizing the gaseous mixture in the chamber sufficiently to dissociate boron and carbon atoms and metal atoms which combine to form a metal doped boron carbide layer on said substrate.  

19. A process according to claim 18, wherein said organometallic compound is a metalloocene.  

20. A process according to claim 18, wherein said organometallic compound is selected from the group consisting of nickelocene, nickel carbonyl, chromocene, manganocene, ferrocene, cobalticene, and ruthenocene.  

21. A process according to claim 18, wherein said organometallic compound is nickelocene.  

22. A process according to claim 21, wherein nickelocene and orthocarborane are supplied to provide a partial pressure ratio of nickelocene to orthocarborane of from about 0.1 to about 10.  

23. A process for introducing a phosphorous as a dopant in a boron carbide layer deposited onto a suitable substrate comprising the steps of:  

- supplying gaseous dimeric chloro-phospha(III)carborane into a chamber that contains the substrate;  
- energizing the gaseous mixture in the chamber sufficiently to dissociate boron, carbon, and phosphorous atoms which combine to form a phosphorous doped boron carbide layer on said substrate.