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We have successfully nickel doped a boron carbide (B_5C) alloy film. The nickel doped boron-carbide (Ni-$B_5C_{1+\delta}$) thin films were fabricated from a single source carborane cage molecule and nickelocene $[Ni(C_5H_5)_2]$ using plasma enhanced chemical vapor deposition. Nickel doping transforms the highly resistive undoped film from a *p*-type material to an *n*-type material. This has been verified from the characteristics of diodes constructed of Ni-$B_5C_{1+\delta}$ on both *n*-type silicon and *p*-type B_5C. The homojunction diodes exhibit excellent rectifying properties over a wide range of temperatures. © *1997 American Institute of Physics.* [S0003-6951(97)00204-0]

Boron and boron-carbide devices have been sought since 1959,[1] but only recently has the fabrication of these devices been realized.[2–4] Such devices would have applicability in a wide variety of harsh conditions: they should be resistant to corrosive, high temperature, and mechanically abrasive environments. Additionally, epitaxial growth does not appear to be a prerequisite for films leading to the construction of devices such as diodes and field effect transistors.[4]

The introduction of metal dopants into boron rich films is not a trivial process. Initial attempts to dope molecular films of the precursor cluster molecule closo-1,2-dicarbadodecaborane ($C_2B_{10}H_{12}$), otherwise known as ortho-carborane, with the common dopant mercury were unsuccessful.[5] Subsequent attempts to dope molecular films of orthocarborane with Na did prove to be successful.[5,6] The above work suggests that doping of boron-rich materials may be a complex process since orthocarborane has been successfully used for the chemical vapor deposition of a B_5C films[7–10] and that the molecule is very similar to the "building block" of the semiconductor material.

Nickel, however, is a very promising dopant for the boron rich solids. A molecular nickel carborane complex has been synthesized by inorganic chemists[11] and the inclusion of nickel in other boron rich solids is well established. Nickel is a common component in the boron carbide superconductors[12] and the reactions of nickel with boron phosphide has been investigated.[13] Since both orthocarborane and nickelocene are easily sublimed from the solid, the introduction of suitable mixtures into the plasma reactor can be readily accomplished. In this letter, we present the device characteristics of diodes constructed with nickel doped boron-carbon thin films grown by plasma enhanced chemical vapor deposition (PECVD). The Ni-doped films will be identified as Ni-$B_5C_{1+\delta}$ where δ is the fractional amount of carbon introduced into the film from carbon containing fragments of nickelocene. Werheit *et al.* have previously investigated metal doping of boron-rich solids,[14–18] but to the best of our knowledge, this is the first successful demonstration of metal doping of boron-carbon films grown by PECVD. Since metals are the only known dopant to transform boron-carbon materials from *p* to *n* type, the successful incorporation of a metal dopant in a PECVD process is a significant step towards the development of boron carbon based semiconductor devices.

Deposition was carried out in a custom designed parallel plate 13.56 MHz radio-frequency plasma enhanced chemical vapor deposition reactor described previously.[3,19] During deposition, the sample was maintained at ground and the anode biased at 10 V. The plasma power was 30 W and the chamber pressure was 400 mTorr. The orthocarborane partial pressure was 100 mTorr and the nickelocene partial pressure ranged from 50 (low doping) to 150 mTorr (high doping). All films were grown on Si(111) *n*-type substrates doped to $7 \times 10^{14}/cm^3$, unless otherwise specified. They 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.

The estimate of a Ni doping concentration of $\gg 1 \times 10^{21}$ has been determined based on the observance of Ni spectral lines in Auger and x-ray emission spectroscopy (XES) spectra. Subsequently lower doping levels, i.e., lower nickelocene partial pressures, have been estimated based on the assumption that the level of Ni incorporation is proportional to the nickelocene partial pressure during deposition.

A typical diode I–V curve of B_5C/*n*-type Si is displayed in Fig. 1(a) and is similar to previously reported boron-carbide/*n*-type Si(111) heterojunctions.[2,3] The B_5C films were typically 2000–2500 Å thick. The leakage current of
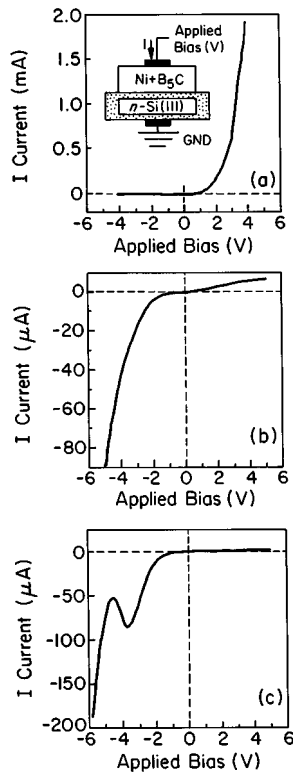
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FIG. 1. The diode I–V characteristics of (a) B_5C/n-Si(111), (b) Ni-$B_5C_{1+\delta}/n$-Si(111) with ''low'' nickel concentration, and (c) the I–V curve of a tunnel diode of Ni-$B_5C_{1+\delta}/n$-Si(111) with ''high'' nickel concentration. The inset in (a) is a schematic of the Ni-$B_5C_{1+\delta}/n$-Si(111) diode.

these devices are typically less than 5 μA at 300 K. We have previously shown that boron-carbide thin films grown on n-type Si(111) form heterojunction diodes which are insensitive to the morphology of the film.[8]

Similar diodes have been constructed with Ni-$B_5C_{1+\delta}$ on n-type Si(111). The diode characteristics of such a device with a ''low'' nickel concentration is displayed in Fig. 1(b). Upon comparison with the I–V curve for the device constructed with undoped B_5C [Fig. 1(a)], it is clear that the inclusion of Ni results in the formation of a rectifying diode with reverse bias. The observed reverse bias rectifying behavior is indicative of the n-type character of the Ni-$B_5C_{1+\delta}$ film and the formation of an $n^+ - n$ heterojunction, where Ni-$B_5C_{1+\delta}$ is more n type than the Si substrate. A crossover from p to n type has been observed for Fe doping of boron rich solids.[16,17]

With the ''higher'' nickel doping ($\geqslant 1 \times 10^{21}$), a negative differential conductivity, or a valley in the current, occurs in the effective forward bias direction for diodes formed on n-type silicon, as seen in Fig. 1(c). This behavior is characteristic of a tunnel diode[20] and is consistent with degenerative doping of pinned states, or traps, relative to the conduction band edge. Certainly at the higher doping levels, sufficient nickel from nickelocene is incorporated into the boron-carbon alloy during film growth to provide for degenerative doping.

The above behavior with ''high'' nickel concentrations suggests that the nickel states are pinned near the conduction band edge. States pinned to one band edge have been previ-
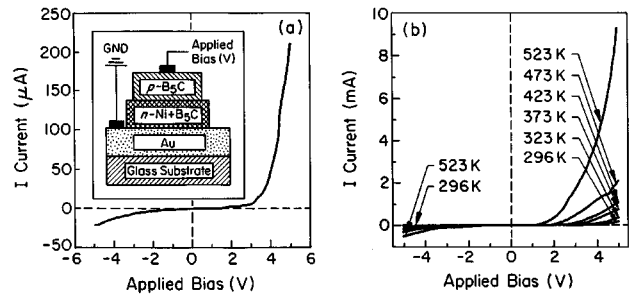

FIG. 2. (a) The I–V curve of a Ni-$B_5C_{1+\delta}/B_5C$ diode at 296 K with a ''low'' Ni concentration, and (b) the temperature dependence of the rectifying behavior of this diode. The inset in (a) is a schematic of the diode construction.

ously proposed for boron carbide and metal doped boron rich solids[2,21] and have subsequently been identified as being pinned to conduction band edge.[14,15] It may be that such states are occupied or filled through nickel doping.

The undoped B_5C films are slightly p type, i.e., essentially intrinsic. Therefore, this doped material will form a rectifying homojunction with either n- or p-type B_5C. If the junction is formed with n-type B_5C i.e., the Ni-doped material, electrons are injected into the intrinsic layer under forward bias, resulting in the diode characteristics exhibited in the I–V curve in Fig. 2(a). If the doped material was p type, injection would still be from this layer into the intrinsic layer, resulting in an I–V curve opposite to the one in Fig. 2(a). Thus the doped material is clearly n type.

The inclusion of Ni into these films dramatically increases the conductivity by approximately eight to ten orders of magnitude from 10^{-10} to 10^{-12} $(\Omega \text{ cm})^{-1}$ for undoped films. In Fig. 3, we have plotted the conductivity of Ni-$B_5C_{1+\delta}$ for a low nickel concentration ($< 1 \times 10^{19}$, as suggested by Auger electron spectroscopy and Raman spectroscopy) as a function of reciprocal temperature. At room temperature, the conductivity is 6.67×10^{-3} $(\Omega \cdot \text{cm})^{-1}$. Similar increases in the conductivity for carbon doping of boron rich solids have been observed.[14]
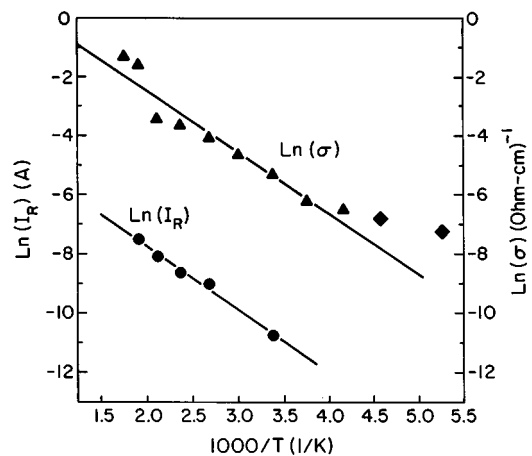

FIG. 3. (a) The natural log of the conductivity of Ni-$B_5C_{1+\delta}$ as a function of reciprocal temperature, where the line is a fit of the data, and (b) the natural log of the leakage current of a Ni-$B_5C_{1+\delta}/B_5C$ diode as a function of reciprocal temperature.
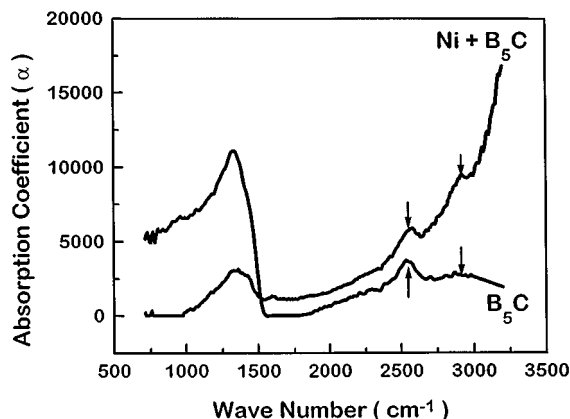
FIG. 4. IR adsorption spectra of a B_5C film and a ''low'' doped Ni-$B_5C_{1+\delta}$ film.

The linear region of the conductivity in Fig. 3 has been fit with the function,

$$\ln \sigma = \ln \sigma_0 - E_A/kT,$$

where σ_0 is the initial conductivity, E_A is the thermal activation energy, k is Boltzman's constant, and T is the temperature. This gives an apparent activation energy of 0.200 eV, which is much less than the value of 1.25 eV obtained for B_5C.[3] Werheit *et al.*[17] found evidence of states pinned approximately 200 meV below the conduction edge. Our data for the Ni-doped boron-carbon alloy also suggests the presence of donor states approximately 200 meV below the conduction band edge.

The I–V characteristics displayed in Fig. 2(a) are what we believe to be the first homojunction diode ever constructed exclusively with boron-carbon thin films. The temperature dependence of the rectifying properties of the diode are displayed in Fig. 2(b). Even at temperatures exceeding 500 K, the leakage current increase is less than 1 mA at -4 V. There is a much smaller temperature dependence of this homojunction diode than with earlier B_5C/n-type Si(111) heterojunction diodes.[2] The natural log of the leakage current (I_R) as a function of reciprocal temperature is plotted in Fig. 3. A fit of the data gives an activation barrier height of 200 meV.

In order to understand the structural changes which take place with the inclusion of Ni into the B_5C films, we have compared IR spectra of the undoped films with the low Ni-doped films. The experimental details of the IR spectroscopy measurements have been discussed in greater detail elsewhere.[22] In Fig. 4, we present the absorption spectra of B_5C and Ni-$B_5C_{1+\delta}$. For B_5C, strong vibration modes are observed between 900 and 1500 cm^{-1}. The mode at 942 cm^{-1} is attributed to B–B vibrational modes of the boron network. We have tentatively assigned the continuum of states between 1100 and 1500 cm^{-1} to B–C vibrational modes. A B–H mode is observed at 2535 cm^{-1} and is indicative of the inclusion of H into the films.

The IR absorption spectrum of the Ni-$B_5C_{1+\delta}$ film in Fig. 4 shows a dramatic decrease in the intensity of the B–B and B–C modes. Carborane-transition metal p complexes have been realized,[23] where a dicarbollyl complex forms a stable structure with a (transition metal)-(p-C_5H_5) complex.

We suggest that similar structures could form within the boron-carbon network with Ni doping. This would account for the attenuation of the B–B and C–B modes and the large increase in the C–H mode at 2916 cm^{-1} in Fig. 4. These complexes also provide the necessary defects to form the tunnel diode behavior observed in Fig. 1(c). The introduction of defects with Fe doping has been attributed to the dampening of vibrational modes of Fe doped boron carbide.[18]

In summary, we have successfully doped PECVD B_5C films with Ni to form Ni-$B_5C_{1+\delta}$ films. From the I–V curves of Ni-$B_5C_{1+\delta}$/Si heterojunction diodes, we have deduced that Ni doping transforms the normally p-type B_5C films to n-type. With high Ni concentrations we have been able to construct tunnel diodes. This work has demonstrated the feasibility of constructing boron-carbon alloy homojunctions with the incorporation of metal dopants.

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