Strong binding at the gold (Au) boron carbide interface

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Abstract

We have investigated the interaction of gold (Au) with the semiconductor boron carbide through X-ray photoemission. Hydrogenated semiconducting boron carbide films, deposited by plasma enhanced chemical vapor deposition (PECVD) of *closo*-1,7-dicarbadoodecaborane (metacarborane, *m*-B₁₀C₂H₁₂), show a shift in the binding energies of the core level photoemission features when gold is deposited on the surface. The shifting of the B 1s level is smaller than for the C 1s level and the non-uniform nature of the shifts indicates a strong, complex and reversible Au chemical interaction with the surface, particularly with the C sites. Capacitance versus voltage, C(V) and current versus voltage, I(V), results for the film deposited on p-type Si(100) yield a carrier scattering time of 50 ns, significantly smaller than the 35 μs for the PECVD orthocarborane boron carbide films.

Keywords

Boron Carbide; metal contact; electrical properties; carrier lifetimes

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I. Introduction

Semiconductor boron carbides have been shown to be suitable for semiconducting devices [1-21] and solid state neutron detection [11-23]. Essential to any semiconductor device is the metal contact and the chemical interactions or band bending that may occur at the metal/semiconductor interface, so increasingly there has been investigation of the interface of various boron carbides to various metals [24-27]. Understanding the metal contacts on the surface of these semiconductors presents a number of important challenges. Such interface characteristics could lead to either rectifying or non-rectifying junctions [28,29], affecting device functionality. While semiconducting boron carbides are generally p-type, in the absence of transition metal doping [1,4-6], hydrogenated semiconducting boron carbides made by the plasma enhanced chemical vapor deposition (PECVD) from metacarborene (the *closo*-1,7-dicarbadoodecaborane isomer of the icosahedral *closo*-carboranes, $C_2B_{10}H_{12}$) are generally n-type [11,13,30]. As such, a fairly unreactive large work function metal contact, such as Au (with a work function in the range of 5.3 to 5.5 eV [31-33]) or Pt (with a work function in the range of 5.6 to 5.9 eV [33,34]), would be expected to form a Schottky barrier contact. Low work function metals have attracted much attention, but are often seen to be quite reactive at the interface with boron carbide [24]. A less reactive metal, with high work function, is an important juxtaposition, and may afford insight as to whether the formation of Schottky barrier contacts with PECVD hydrogenated semiconducting boron carbide is facile. Schottky barrier contacts, while increasing the complexity of a heterojunction diode device's performance, and while likely leading to increases in device capacitance, have the potential advantage of reducing leakage and some parasitic currents that would hamper pulse counting in neutron detection. The investigation of the interaction of gold with hydrogenated semiconducting boron carbide is therefore a natural

extension of efforts to understand how to optimize the contacts to PECVD boron carbide devices.

II. Experimental

The boron carbide film was formed by plasma enhanced chemical vapor deposition (PECVD), as described in prior work [27], using *closo*-1,7-dicarbadoodecaborane (metacarborane, $m\text{-B}_{10}\text{C}_2\text{H}_{12}$) in a 20 mTorr Ar inductively coupled plasma (20 W), and deposited on atomically clean p-type Si(100). This isomer of the icosahedral *closo*-carboranes, $\text{C}_2\text{B}_{10}\text{H}_{12}$, has been successfully used as a PECVD source compound for forming a hydrogenated n-type semiconducting boron carbide [11,13,17,30], $\text{B}_{10}\text{C}_2\text{H}_{12-x}$, thus making the fabrication of an all boron carbide semiconductor diode device possible [11,13]. During PECVD, the partial vapor pressure of metacarborane in the PECVD chamber was ~ 1 mTorr, created by sublimation through annealing the source compound and gas lines to 70-80° C. The partial vapor pressure of metacarborane was controlled by a mass flow controller at 5 sccm (standard cubic centimeters per minute).

X-ray photoemission spectroscopy (XPS) was used to characterize the Au interface with semiconducting boron carbide. Experiments were carried out in an ultrahigh vacuum (UHV) system, to prevent impurity scattering events. The XPS spectra were acquired with a dual anode X-ray lamp and a hemispherical angle resolved electron energy analyzer (detector). The X-ray source used the Mg-K α line at 1253.6 eV, with data taken at normal emission. Data were acquired with the analyzer in constant pass energy mode (50 eV). Core level spectra were analyzed using CASAXPS [35], and a Shirley background [36] was used for all spectra.

Prior to Au deposition, the film was cleaned by Ar^+ bombardment at $\sim 9.5 \times 10^{-5}$ Torr at 1.0 kV for 15 min. To maximize the uniformity of the reduced surface layer, the sample was rotated $\pm 40^\circ$ off normal, with respect to the incident ion beam. Following the initial sputter cleaning of the sample surface, no oxygen was evident in XPS (i.e. no O(1s) core level photoemission peak above the background noise). Gold(Au) was deposited via thermal evaporation from a tungsten(W) filament at a pressure of 10^{-7} Torr. Different Au coverages ranging from 4 Å to 21 Å average thickness, as determined by XPS, were investigated. After deposition of Au on the PECVD hydrogenated boron carbide film, the sample was transferred to the photoemission chamber, *in vacuo*, without exposure to ambient conditions. The core level B(1s), C(1s) and Au(4f) binding energies were obtained from the XPS spectra before and after each Au deposition experiment.

Ar^+ bombardment was also used to remove deposited Au from the boron carbide surface to determine the reversibility of Au-boron carbide surface interactions. During the sputtering process, the same Ar pressure and beam voltage conditions were used as for initial surface cleaning. Different Ar ion sputtering times, however, running from 15 min to 1 hour, were selected in order to eliminate more Au layers.

The capacitance versus voltage, C(V) and current versus voltage, I(V), measurements were used to extract estimates of the carrier diffusion lifetime, as was done elsewhere [37,38]. The procedure followed here is as in [37]. Corresponding transistor and Hall measurements are certainly indicated, but because of the high resistivity of the PECVD hydrogenated semiconducting boron carbide (10^{10} to 10^{12} Ohm-cm), these supporting measurements are beyond the scope of this work.

III. Results and Discussion

III.1 Evidence of Strong Gold-Boron Carbide Interactions

Fig. 1 shows the evolution of B(1s), and C(1s) spectra with deposition and subsequent removal of a Au overlayer. The measured XPS binding energies for boron and carbon are summarized in table 1. Some oxygen was observed before sample cleaning, but its intensity decreased after Ar^+ bombardment (and its concentration did not change appreciably with Au deposition; therefore it is not shown in this work). Spectra **a** and **e** in Fig. 1 refer to the sample after cleaning. As expected no oxygen bonds are present. The B(1s) spectra are deconvoluted into two peaks: one at low binding energy corresponding to the B-B bond, and the second one at higher binding energy representing the B-C bond. For the samples Ar^+ ion sputtered free of contamination, values for binding energies representing these peaks are in good agreement with previous results [24-27,39-40]. Unlike in other work on orthocarborane-derived films, there is a single C(1s) core level feature as there is no C-C carbene bond in the metacarborane icosahedra, making core level shifts far easier to identify. The main C(1s) core level peak in these spectra is attributed to C-B bonding environments.

As Au is deposited on the sample, the B(1s) core level XPS spectra exhibit a small feature at higher binding energy, 191.5 to 192.1 eV, while the main B(1s) core level XPS feature is seen to shift about 0.5 eV to higher binding energy (Fig. 1**b**, and 1**c** and table 1). The shift is substantially more dramatic for the C(1s) core level.

The C(1s) XPS spectra show a gradual increase in C(1s) binding energy and the addition of a satellite feature near 289 eV binding energy (Fig. 1**e-g** and Table 1). This growth of a significant satellite feature, accompanied by the large increase in binding energy of the main

C(1s) peak with increasing of Au overlayer coverages, indicates that carbon reacts with Au forming C-Au bonds at the semiconductor-metal interface. This increase in core level binding energy is significantly larger than observed for the B(1s) spectra, indicating that this effect cannot be ascribed to simple Au-induced band bending. This also suggests that Au-C interactions are stronger than Au-B interactions. As expected, the high binding energy B(1s) and C(1s) features disappear once Au is completely removed with Ar⁺ bombardment (Fig. 1d, and Fig. 1h). The core level energies of the main peaks are also largely restored.

Fig. 2 plots the evolution of the B(1s) core level binding energy as the gold overlayer is added and then removed. The B(1s) core level shifts to higher binding energies as Au coverage increases (Fig. 2, * black stars), but is reversible upon removal of the gold overlayer (Fig. 2, ◀ red triangles). This indicates that if band bending is induced at the metal/semiconductor interface, the shift is to higher binding energies. This cannot be a photovoltaic charging effect, as the binding energy increases as the surface is metallized, which would lead to a decrease in binding energy if there was significant suppression of photovoltaic charging.

While such an increase in binding energy has been seen with the addition of a copper overlayer on various boron carbides [24-27], there are some subtle differences. Metacarborane (*closo*-1,7-dicarbadoodecaborane) is unusual in that it is generally regarded as a n-type material [11,13,17,30]. As gold has a large work function (in the range of 5.3 to 5.5 eV [31-33], as noted above), this means that Schottky barrier formation should be favored as it is for many semiconductors, and the apparent binding energy should decrease with increasing gold coverage. Increasing binding energy indicates strong interfacial interaction where gold exchanges charge with the semiconductor through the C-Au bonds. While gold is generally considered unreactive, interfaces with gold can be quite complex. Electron charge abstraction from graphene, at the gold

interface, is known and predicted [41-44] and boron carbide is more reactive than graphene. A sputtered semiconducting boron carbide, as is the case here, may have a number of dangling bonds and may be even more reactive than a boron carbide whose surface has not been damaged by Ar^+ ion sputtering.

Previous results reported a metal oxide layer in the case of Cr, Ti and Al metals, which could lead to increased Schottky barrier heights [24]. Here, no metal oxide layers were found, and no oxygen diffusion from the bulk was observed. As a result, low device resistance at the metal-semiconductor interface is predicted. This study was limited to thin layers of Au, but no evidence of Au diffusion into the bulk was found. The gold adlayer could be almost completely removed with modest Ar^+ ion sputtering. If gold diffused into the bulk of the PECVD hydrogenated semiconducting boron carbide, then a persistent gold signal would be present, even after significant Ar^+ sputtering, and the facile removal of the Au overlayer would be hindered. Furthermore, we find that the concentration of oxygen at the surface and bulk can be minimized.

III.2 Electrical measurements

To demonstrate that n-type PECVD hydrogenate semiconducting boron carbide is formed from the decomposition of metacarborene ($\text{m-B}_{10}\text{C}_2\text{H}_{12}$), heterojunction diodes were fabricated with p-type silicon, and electrical measurements were taken. Figure 3 shows the current-voltage, $I(V)$ and capacitance-voltage, $C(V)$ curves for the resulting diodes. As expected, $\text{m-B}_{10}\text{C}_2\text{H}_{12}$ makes an excellent p - n diode when deposited on p -type silicon, showing a very small leakage current in the reverse bias region, and less than 1 nA in the region of zero bias. The very large turn-on voltage in forward bias is similar to, but not quite as extreme, as that seen for the all boron carbide heterojunction diodes [30], that included an n-type boron carbide. The $I(V)$ and

C(V) data provide no indication of any Schottky barrier formation. On the other hand, the capacitance changes significantly with the frequency (Fig. 3b), indicating that there are some charge carriers that can no longer respond to the perturbation signal as the frequency increases.

The carrier lifetime value varies the height and slope of the small forward bias rise in the C(V) curve. We have modeled the device capacitance, as seen in Figure 4, and found a good fit using a carrier lifetime of about 50 ns. This would be a very short lifetime, roughly 10^3 shorter than the 35 μ s indicated by I(V) and C(V) data for the PECVD orthocarborane boron carbide film on silicon [39], and far smaller than suggested by the findings of Bao *et al.* [38] for sputter-deposited boron carbide films which indicated carrier lifetimes of 0.91 to 0.98 ms.

IV. Summary

X-ray photoemission spectroscopy was used to identify the core level binding energy shifts seen with Au adlayer film on a hydrogenated semiconducting boron carbide film formed from the plasma enhanced chemical vapor deposition (PECVD) of boron carbide from closo-1,7-dicarbadoodecaborane (metacarborane, $m\text{-B}_{10}\text{C}_2\text{H}_{12}$). The characteristic B(1s) and C(1s) core levels of boron carbide were observed to increase, as the Au the gold overlayer concentration increased. This was especially significant for the C (1s) core level, suggesting gold interaction with the carbon was significant. The absence of the typical signatures of Schottky barrier formation, yet the strong interactions evident in the core level shifts and addition of a core level satellite features suggests that at least some extrinsic interface doping of the boron carbide by gold or formation of a metal-induced gap state at the interface. The facile manner in which gold can be removed from this boron carbide surface does suggest that diffusion of gold into the boron carbide surface region does not occur at room temperature.

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Table Caption

Table 1. Summary of the X-ray photoemission derived boron and carbon components, the B 1s and C 1s core levels respectively, as a function of the addition (deposition) and removal (Ar^+ bombardment or sputtering) of a gold overlayer.

Figures Caption

Figure 1. Evolution of the XPS core level spectra of the B(1s) (left), and C(1s) (right) as a function of Au exposure; **a** and **e** cleaned sample, **b** and **f** first Au deposition, **c** and **g** last Au deposition, and **d** and **h** after 2 hours and 45 min sputtering.

Figure 2. Shift in the binding energy of the B(1s) peak with increasing Au overlayer thickness deposition (black stars), and after Ar^+ bombardment to remove the gold overlayer (red triangles ◀).

Figure 3. (a) Current versus voltage of the n-type boron carbide film on p-type Silicon ($\text{m-B}_{10}\text{C}_2\text{H}_x/\text{Si}$), and (b) Capacitance versus voltage as a function of frequency (blue 10 MHz, red 10 kHz, and black 1 kHz). Inset in (b) shows an expanded scale plot for the for 10 MHz capacitance data.

Figure 4. A model of diffusion capacitance, C_D , overlaid on $C(V)$ data at 10 kHz. The calculated C_D indicates an effective carrier lifetime of about 50 ns.

Table

	B(1s) B – B bond		B(1s) B – C bond		C(1s) C – B bond		C(1s) C – Au bond	
	BE (eV)	atomic % B	BE (eV)	atomic % B	BE (eV)	atomic % C	BE (eV)	atomic % C
Clean Sample	188.3	45	189.2	55	283.6	100	-	-
1st Au deposition	188.7	80	191.5	20	284.6	95	289.3	5
2nd Au deposition	188.8	83	191.9	17	284.8	95	288.7	5
3rd Au deposition	188.8	77	192.1	23	284.8	87	288.3	13
1st sputtering (15 min)	188.7	89	191.0	11	283.3	74	285.1	26
2nd sputtering (30 min)	188.6	81	189.8	19	283.4	100	-	-
3rd sputtering (30 min)	188.4	58	189.3	42	283.4	100	-	-
4th sputtering (1 hour)	188.3	45	189.2	55	283.5	100	-	-

Table 1

Figures

Figure 1

Figure 2

Figure 3

Figure 4