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Chemical and electronic structure of composite films deposited by plasma-enhanced chemical vapor deposition from orthocarborane and pyridine source compounds

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ABSTRACT

Semiconducting boron carbide films, with aromatic moieties, were formed by plasma-enhanced chemical vapor deposition (PECVD) using pyridine (C_5H_5N) and *closo*-1,2 dicarbadodecaborane (1,2-$B_{10}C_2H_{12}$; *ortho*-carborane) as source compounds. X-ray photoelectron spectroscopy (XPS), in conjunction with pyridine/orthcarborane cluster density functional theory (DFT) calculations, indicates that such films consist of partially dehydrogenated orthocarboranes coordinated to pyridine moieties at icosahedral B sites. The XPS data also suggest a constant average coordination number of 3–4 pyridines per icosahedral carborane, indicating that higher pyridine content in the film results in greater areas of plasma-polymerized pyridine. Ultraviolet photoelectron spectroscopy (UPS) results and DFT cluster calculations indicate that electronic states near the valence band maximum are associated with pyridine moieties, while states near the conduction band minimum are associated with either carborane or pyridine moieties. Variable angle spectroscopic ellipsometry (VASE), the UPS data and theoretical results also indicate only gradual changes in indirect band gap energies with changing pyridine/orthocarborane stoichiometry, in agreement with previously reported results. The results presented here are consistent with and provide additional insight regarding recent neutron voltaic and photoluminescence results for these materials.

1. Introduction

Semiconducting boron carbide films are of long-standing interest for neutron detection applications due to the high thermal neutron capture cross section of ^{10}B [1–14]. A type of semiconducting boron carbide composite film, with significantly better charge extraction in zero-bias neutron voltaic measurements, has now been fabricated through the plasma-enhanced chemical vapor (PECVD) co-deposition of pyridine (C_5H_5N) and 1,2 dicarbadodecaborane, 1,2-$B_{10}C_2H_{12}$ (orthocarborane) [12,14]. There are indications that the improved charge collection may be related to enhanced electron-hole separation [12–14] in these materials, as well as to significant increases in the drift carrier lifetime [14]. Importantly, even more significant increases in carrier lifetimes (up to roughly 2.5 msec) have been observed in the semiconducting boron carbides made from (PECVD) co-deposition of benzene and orthocarborane [15]. To understand better these improved boron carbides, there needs to be a better characterization of the electronic structure and local chemical bonding interactions between pyridine and carborane moieties, and how these interactions affect band gaps and dielectric constants. While there have been some efforts at modeling the possible local configurations of carboranes and aromatics [14,16], a more complete assessment of the isomers possible has been, so far, absent. Preliminary X-ray photoelectron spectroscopy (XPS) and Fourier transform infra-red absorption (FTIR) measurements indicate that such PECVD boron carbide films consist of partly dehydrogenated, but otherwise intact pyridine and

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orthocarborane moieties [17]. Because the composition and morphology of the semiconducting boron carbide composite has such a profound impact on the resulting electronic properties, the detailed pyridine/carborane chemical bonding interactions in such films are therefore of significant practical as well as fundamental interest.

Here we present core and valence band photoemission, density functional theory (DFT) cluster calculations, and VASE-determined band gaps for a series of semiconducting boron carbide composite films deposited by PECVD with a combination of pyridine and orthocarborane source compounds, for pyridine/orthocarborane ratios ranging from 2:1 to 10:1. Of additional practical interest, the data also indicate that such properties should vary relatively slowly with variations in pyridine/orthocarborane relative stoichiometry.

2. Methods

2.1. Experimental methods

The boron carbide film depositions and subsequent characterization were undertaken in a system described previously [17,18]. Briefly, the system consisted of a sample introduction and plasma deposition chamber (with a base pressure 1×10^{-7} Torr), and an analytical chamber (base pressure 2×10^{-10} Torr) with capabilities for XPS and UPS. The two chambers were isolated by manual gate valves. Sample transfer between chambers occurred without sample exposure to ambient.

The XPS spectra were acquired using unmonochromatized Al Kα radiation from a non-monochromatic source operated at 300 W, 15 kV, and with a 140 mm mean radius hemispherical analyzer operated in constant pass energy mode (23.5 eV). Ultraviolet photoelectron spectra (valence band photoemission, or UPS) spectra were acquired with a differentially pumped discharge source, using He I excitation (21.2 eV) and a constant analyzer pass energy of 2.95 eV.

The XPS and UPS spectra were analyzed by standard methods [19]. The core level spectra were modified by using a Shirley background subtraction [19,20]. Binding energies were corrected for sample charging by setting the Si (2p) peak energy level at 99.3 eV [21,22]. No additional charging effects were observed as increased film thickness obscured photoelectrons from the Si substrate. High resolution core level photoelectron spectra of B (1s), C (1s) and N(1s) features were deconvoluted by fitting with full width at half maximum (FWHM) values of 1.5 eV, 1.4 eV and 1.8 eV, respectively, as indicated by previous studies with this instrument [17,18,23].

The hydrogenated boron carbide films, with pyridine moieties, were deposited on n-doped 1 cm × 1 cm Si (100) substrates. The Si substrates were cleaned prior to film deposition by 1000 eV Ar+ ion sputtering. The *closo*-1,2 dicarbadodecaborane, i.e. 1,2-$B_{10}C_2H_{12}$ (orthocarborane) and pyridine (C_5H_5N) precursors were obtained from commercial sources, purified by freeze-pump-thaw procedures, and introduced into the deposition chamber via separate mass flow controllers. For orthocarborane, the container vial, stainless steel gas lines, and manual control valve were all heated to 330 K, and the mass flow controller was maintained at 373 K to prevent condensation of precursor vapor and ensure reliable operation of the mass flow controller. For pyridine, the mass flow controller was kept at ~363 K, while the precursor was kept at room temperature. The films were fabricated in the custom-built deposition chamber by using an inductively-coupled Ar^+ plasma (20 W, 50–70 mTorr total pressure). For convenience, these PECVD semiconducting boron carbide films, fabricated from the pyridine and orthocarborane source compounds, will be referred to as "PECVD pyridine/orthocarborane" films, with the stoichiometric ratio of pyridine to orthocarborane given. PECVD films of orthocarborane without pyridine will be referred to as "PECVD orthocarborane" films.

The relative pyridine and orthocarborane contributions were obtained from the XPS B 1s and N 1s core level intensities, by methods discussed previously [14,17,18]. This method assumes that pyridine and carborane precursors remain basically intact during the PECVD process, an assumption recently verified by experiment [17]. Films with pyridine/orthocarborane ratios from 2:1 to 10:1 were formed by controlling the pyridine flow rate from 5 sccm (standard cubic centimeter per minute) to 35 sccm and maintaining orthocarborane at 5 sccm. All of these films with specific pyridine/orthocarborane ratios were formed reproducibly.

In order to analyze the composition of relatively thick (~300 nm or more) films by XPS, spectra were acquired at various intermediate stages of the deposition process. While the results reported here represent averages of such data at various deposition times, the film stoichiometry showed little variation with deposition times, in agreement with previous results [14,18].

The variable angle spectroscopic ellipsometry (VASE) measurements were used to determine the film band gaps and dielectric constant. Film thicknesses were not determined but pyridine/orthocarborane films of similar compositions and deposited by identical methods exhibited film thicknesses of ~350–500 nm [14]. The ellipsometry data were acquired on multiple instruments, but primarily on a J. A. Woollam RC2 VASE ellipsometer in ambient conditions. Data were acquired from films deposited on n-Si(100) substrates, over a range of photon energies in the visible to ultraviolet range (0.73 eV–6.4 eV (1690 nm–193 nm)), in increments of 1 nm (1000 nm–1690 nm) and 2.5 nm (1000 nm–193 nm), respectively. The angles of incidence were varied from 45° to 75°, in 5°increments. Data were fit by standard methods [24,25], using commercially available software. Standard spectroscopic ellipsometry determines the ratio (ρ) of the complex-valued Fresnel reflection coefficients r_p and r_s and is commonly presented by parameters ψ and Δ where $\rho = r_p/r_s = \tan(\psi)e^{i\Delta}$. The parameters ψ and Δ have been used to plot the real and imaginary part of the dielectric response, so that the band gap could be ascertained from the cutoff of the imaginary part of the dielectric response [14]. Plots of absorption coefficient $(\alpha)^n$ were fitted so as to extract both the indirect ($n = 1/3$) and direct ($n = 2$) band gaps of PECVD co-deposited pyridine and orthocarborane semiconducting hydrogenated boron carbide films and were found to be in agreement with the cutoff of the dielectric response [14].

2.2. Theoretical methods

First-principles DFT calculations were carried out to gain further insight into XPS and UPS experimental results. Two different packaged codes were used. In both cases, the DFT calculations were carried out within the Generalized Gradient Approximation (GGA). One set of DFT calculations were performed using the Gaussian 09 software [26], with the B3LYP hybrid functional and 6–31++G 2d 2p basis set. Complementary first-principles calculations were performed in the framework of density functional theory (DFT), as implemented in the DMol^3 code [27,28]. The generalized gradient approximation (GGA) was used, in the form of Perdew-Burke-Ernzerhof (PBE) [29]. All the electrons were considered equally, and the double numerical plus polarization (DNP) basis set, which is comparable to the 6-31G** basis set, was used. The convergence tolerance for the self-consistent field is 2.72×10^{-5} eV, and the molecular structures were optimized until the maximum force was below 0.054 eV/Å.

For simplicity, the clusters considered, for modeling, involved 1–4 pyridine rings bonded via ring N or C sites to icosahedral B atoms in a single orthocarborane icosahedron and a single pyridine bridging two carborane icosahedra via ring N or C sites bonded to icosahedral B or C atoms. Population analyses were then carried out based on the fully relaxed structures using the minimal basis