PECVD of Boron Carbide/Aromatic Composite Films: Precursor Stability and Resonance Stabilization Energy

Bin Dong, Robinson James, and Jeffry A. Kelber
Department of Chemistry, University of North Texas, Denton, TX

Abstract

Recently developed composite films formed by PECVD from orthocarbaborane and aromatic precursors exhibit exciting potentials in areas such as neutron detection and photocatalysis. An important factor in determining the electronic properties of these materials is the existence of an intact π system in the deposited film, indicating deposition of a (more or less) intact aromatic precursor. X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR) data for films formed by co-deposition of ortho-carborane and pyrimidine, pyridine, aniline, indicate that the integrity or decomposition of the aromatic π electron network correlates closely with aromatic resonance stabilization energy. The resonance stabilization energy of pyrimidine is low (8 kcal/mole), and the resulting films exhibit no evidence of a π network. Pyridine and aniline have resonance stabilization energies of 24.2 and 39.5 kcal/mole, respectively, and both exhibit FTIR and XPS core level shakeup features indicating intact π networks. This trend permits the prediction of film properties for a broad variety of aromatic precursors in such films.

Introduction

Semiconducting boron carbide films formed from carbaborane precursors have been of long-standing interest in areas such as neutron detection [1], drug delivery [2], and photocatalysis [3]. Such applications have been limited, however, by the generally poor and inconsistent semiconducting properties of such films, including low charge carrier mobility [4]. Novel semiconducting boron carbide/ aromatic composites have been recently developed by plasma enhanced chemical vapor deposition (PECVD), and have been applied in the fabrication of neutron detectors. These composite materials are co-deposited with carbonanes (ortho-carborane) and an aromatic precursor by PECVD. The molecular structures of three such precursors discussed here—pyrimidine, pyridine, and aniline—are shown in Figure 1. Such films have exhibited dramatically improved sensitivities in neutron voltaic experiments [4], at least in part due to improved charge carrier properties. Since charge mobilities and other electronic characteristics can be significantly impacted by the presence or absence of a delocalized π electron network in the deposited film [5], the stability of the aromatic precursor during PECVD is of obvious importance. XPS and FTIR data presented here demonstrate that precursor stability—and therefore the presence or absence of an intact π network in the deposited film—is directly correlated with the precursor resonance stabilization energy (shown in Figure 1), which equals the difference between the calculated heat of formation for the most stable valence bond structure of molecule and the experimental value [6,7].

XPS and FTIR data were acquired for PECVD films of pyrimidine/orthocarborane, pyridine/orthocarborane, and aniline/orthocarborane. XPS π→π* shakeup features were observed for the pyridine/orthocarborane and aniline/orthocarborane films, but not for the pyrimidine/orthocarborane film. Similarly, FTIR data indicated a high intensity for the C-H aromatic stretching mode and other relevant vibrational modes for the pyridine/orthocarborane and aniline/orthocarborane films, but not for the pyrimidine/orthocarborane film, in excellent agreement with the XPS shakeup features. The experimental data therefore demonstrate that preservation of precursor aromatic character in the deposited film correlates with aromatic resonance stabilization energy.

Experiment

The aromatics/ortho-carborane films were grown in a deposition chamber with a base pressure of 1×10⁻⁷ Torr by PECVD. The plasma setup has been described previously in detail [8]. Briefly, the heated precursors in the vapor state were introduced into the chamber using a mass flow controller (MKS). The ratio of aromatics/orthocarborane was controlled through setting the flow rates of the precursors. Flow rate of aromatic precursors (pyrimidine, pyridine, aniline) and ortho-carborane were maintained at 5sccm to achieve a fixed ratio (≈2-3) of aromatics/ortho-carborane. Then, Ar was introduced into the deposition chamber via a leak valve and the total pressure was maintained ~70 mTorr by adjusting the Ar pressure level. The composite films were deposited in inductively coupled plasma generated using a 13.56 MHz RF generator, a coil and a matching network, with a typical plasma power of 20W, although lower settings were used in some depositions of pyrimidine. After deposition, the sample was transferred into an ultrahigh vacuum (UHV) analysis chamber with a base pressure of 3×8×10⁻¹⁰ Torr using a transfer arm. XPS spectra were acquired with an unmonochromatized AlKa X-ray source operated at 15 kV, 300W and a hemispherical analyzer with a constant analyzer pass energy of 23.5 eV in the UHV analysis chamber. After the films
were characterized by XPS, FTIR spectra were acquired ex-situ using a Brucker, Vector 22 spectrometer in transmission mode, as described previously [9].

**Results**

Core level spectra for composite films containing pyrimidine, pyridine or aniline with orthocarborane are shown in Figure 2. The binding energies shown have been corrected for charging according to previously described methods [8, 10]. A more detailed analysis of these spectra will be published elsewhere. The B 1s, C 1s and N 1s XPS spectra for a pyrimidine/orthocarborane film are shown in Figure 2 a-c, respectively. Corresponding data for a pyridine/orthocarborane film are displayed in Figure 2 d-f, and corresponding data for an aniline/orthocarborane film are shown in Figure 2 g-i. B 1s and C 1s data for a pure B,C film are shown for comparison in Figure 2j and k, respectively. From a comparison of N 1s/ B 1s intensities [10], the pyrimidine/orthocarborane ratio is ~ 2:1, the pyridine/orthocarborane is also ~ 2:1, and the aniline/orthocarborane ratio is ~ 3:1.

A comparison of the B 1s spectra for the composite films (Figure 2a, d, g) to that of the pure B,C film (Figure 2j) shows that the B 1s spectrum for the aniline film is shifted to higher binding energy compared to the pure B,C film, and the B 1s spectra for the pyrimidine and pyridine films exhibit even larger shifts in this direction. Such shifts to a higher binding energy reflect B bond formation with a more electronegative species, i.e., C or N instead of B [8, 11, 12]. This is evidence that in the aromatic/orthocarborane composite films, the orthocarborane moieties are bonded to the aromatic species primarily through the icosahedral B sites. That the shift is greater in the pyrimidine and pyridine films indicates that in these films, B bonding occurs with the more electronegative N, but that the N site in the aniline films is not involved in such bonding. These findings are also consistent with the corresponding N 1s spectra (Figure 2c, f, i). The N 1s spectrum for the pyrimidine/orthocarborane film (Figure 2c) and for the pyridine/orthocarborane film (Figure 2f) exhibit two significant features, indicating two different N bonding environments, consistent with both N-B bonding and with N unbonded to B. In contrast, the N 1s spectrum for the aniline film exhibits only one prominent feature, consistent with unreacted N in polyaniline with a binding energy ~399.5 eV [13]. A N 1s feature with a binding energy near 401.3 eV is shown in pyridine/orthocarborane (Figure 2f). This binding energy is higher than observed for either the pyrimidine/orthocarborane film (Figure 2c) or the aniline/orthocarborane film (Figure 2i). Such a high binding energy is attributable to N cationic radical formation, (essentially, N⁺) [13], indicating formation of tetrahedrally-coordinated B−N(−C)₃ (in pyridine) and consistent with B bond formation to the N site in an intact pyridine entity. Analysis of C(1s) spectra in Figure 2b, e, h for composite films indicates that incorporation of aromatic moieties and orthocarborane inhibits the formation of interstitial carbon atoms, with an absence of the feature centered at 282.8 eV in pure B,C shown in Figure 2k [14]. In summary, the spectra displayed in Figure 2 indicate composite films consisting of orthocarborane moieties embedded in and bonded to a polymerized pyrimidine, pyridine or aniline matrix.
PECVD of Boron Carbide/Aromatic Composite Films: Precursor Stability and Resonance Stabilization Energy

continued from page 31

XPS spectra of the C 1s and N 1s π→π* shakeup regions for aromatic/orthocarborane film are shown in Figure 3. The XPS spectra of pyridine/orthocarborane (Figure 3c, d) and aniline/orthocarborane (Figure 3e, f) exhibit a shakeup peak with a binding energy ~6 eV higher than the main C 1s, N 1s lines. These shakeup peaks are a sign of a π network system in deposited film—indicating essentially intact aromatic species within the polymerized films. In contrast, there is no shakeup peak in pyridine/orthocarborane films (Figure 3a, b). This indicates that no intact aromatic network exists in this film, and that the aromatic nature of the pyridine precursor does not survive the PECVD process. These results are consistent with trend of decreasing resonance stabilization energy from aniline (39.5 kcal/mole), to pyridine (24.2 kcal/mole), and to pyrimidine (8 kcal/mole) [6,7] in Figure 1. The evidence of intact π systems observed for the pyridine/orthocarborane and aniline/orthocarborane films but not for the pyrimidine/orthocarborane film indicates that the stability of the aromatic precursor under these conditions correlates closely with the resonance stabilization energy. Indeed, the pyridine precursor failed to remain intact ring even at very low plasma power levels (5 W).

Further evidence for the stability/dissociation of aromatic precursors under PECVD conditions is shown by FTIR spectra (Figure 4). For comparing the relative absorbance of stretch mode peaks, B-H stretch [15] intensities are normalized to that of the pure B$_2$C film (Figure 4a), with other mode intensities increased or decreased accordingly. The aromatic C-H stretch peak in pyrimidine/B$_2$C (Figure 4b) [16] exhibits a lower absorbance intensity compared to pyridine/B$_2$C and aniline/B$_2$C, indicating more extensive ring opening in the pyrimidine/B$_2$C composite film. Additionally, due to a lower resonance stabilization energy of pyrimidine, a higher absorbance value is observed for C-C triple bond or C-N triple bond stretch mode in pyrimidine/B$_2$C (Figure 4c) also consistent with aromatic ring breaking during PECVD. In contrast, the FTIR spectra for the pyridine/orthocarborane and aniline/orthocarborane films are consistent with aromatic character, in exact agreement with the XPS shakeup data (Figure 3).

Summary and Conclusions

Composite films of pyrimidine/B$_2$C, pyridine/B$_2$C and aniline/B$_2$C have been fabricated using PECVD and characterized by XPS and FTIR. XPS data show that significant N-B bond formation is observed for the pyridine/orthocarborane and pyridine/orthocarborane films, but the N in aniline is largely uninvolved in bond formation. XPS π→π* shakeup features are observed for the pyridine/orthocarborane and aniline/orthocarborane films, but not for the pyrimidine/orthocarborane film. FTIR spectra indicate reduced aromatic C-H bond stretch intensity and enhanced C=N/C≡C intensity for pyrimidine/B$_2$C films relative to pyridine/B$_2$C and aniline/B$_2$C films, consistent with dissociation of the pyrimidine, but not for the pyridine or aniline precursors, during PECVD. These trends are in direct correspondence with increasing resonance stabilization energies for pyrimidine-pyridine-aniline [6,7], with the dissociation of pyrimidine observed even under very low power plasma conditions. The XPS and FTIR data presented here therefore indicate that the resonance stabilization energy of an aromatic precursor can be used to predict the relative stability of the precursor during the PECVD process. The resonance stabilization energy is therefore an excellent predictor for which aromatic precursors will result in intact π networks in PECVD films, with important consequences for the electronic properties of such films in areas such as neutron detection and photocatalysis.

Acknowledgement: This work was supported by the US Defense Threat Reduction Agency under Grant. No: HDTRA1-14-1-0041

References

Dycor LC-D RGA
Full-featured functionality, right out of the box. And the price is amazing, too!

The Dycor LC-D Residual Gas analyzer offers the kind of performance and features that you would only expect on high-priced units. With mass ranges out to 300 amu and several ion source choices, the LC-D is ready to work—from vacuum system pump-down characterization to reaction end-point monitoring of multiple ions with data transfer back to your control system. Visit our website for your local representative.

ametekpi.com

© 2014 by AMETEK Inc. All rights reserved.