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July 1989

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Gi Kim, Yoon; Dowben, Peter A.; Spencer, J.T.; and Ramseyer, G.O., "Chemical vapor deposition of boron and boron nitride from decaborane(I4) ^{a)}" (1989). *Peter Dowben Publications*. 134.
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Chemical vapor deposition of boron and boron nitride from decaborane(14)^a

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(Received 30 October 1988; accepted 28 January 1989)

We have investigated photoassisted, plasma enhanced chemical vapor deposition and pyrolytic deposition of boron from decaborane ($B_{10}H_{14}$) and boron nitride from decaborane combined with nitrogen or ammonia. The use of decaborane for depositing boron and boron nitride thin films is seen as a viable alternative to diborane or boron halides.

I. INTRODUCTION

The formation of cubic boron nitride has been intensively investigated,¹⁻⁹ motivated by this material's potential as a hard coating, which arises from the large cohesive energy and hardness of BN. It also has been noted that BN is not only useful in the manufacturing of hard cutting tools, but because of the excellent insulating dielectric properties and corrosion resistant nature of BN, thin films of BN could be useful for the fabrication of insulated conductors, capacitors, and providing hard protective coatings for diodes, transistors, and other monolithic devices.¹⁰⁻¹² Boron source materials useful for fabricating BN thin films may also be valuable for doping semiconductor materials with boron dopant atoms.^{13,14}

With these substantial applications for depositing BN thin films and boron dopant atoms, a number of boron source compounds have been employed including BCl_3 ,^{2,7,8,10,15-22} BF_3 ,²³ diborane (B_2H_6),^{2,3,9,11,24-29} trichloroborazole,³⁰ trimethoxyborazole,¹² trimethylboron,¹³ boric acid (H_3BO_3),³¹ HBO_2 ,^{14,32} borazine $B_3N_3H_6$ (Refs. 2, 3, 33, and 34), as well as evaporated boron.^{4,10} With the goal of the deposition of pure boron or boron nitride, many of these source compounds have serious defects, including serious safety problems due to the toxicity and/or highly inflammable nature of the source compounds. We have explored the deposition of boron and boron nitride using decaborane ($B_{10}H_{14}$) as a source material.

II. EXPERIMENTAL

Decaborane(14), $B_{10}H_{14}$, is an air-stable white crystalline solid with a vapor pressure of several Torr at room temperature.³⁵ The vapor pressure can be readily raised by heating decaborane (the vapor pressure at 100 °C is 19 Torr), since the molecule decomposes only above 170 °C.³⁶ The decaborane(14) was sublimed to separate the material from cellite (a stabilizer) and other impurities. The radio-frequency plasma deposition studies were carried out in a small 3-in., 13.56-kHz rf plasma reactor with a 1-in. plate separation. The typical power consumption of the reactor was 20 W, but could be increased to 100 W. The sample was mounted on the ground plate of the two-plate system, with the other plate connected to the rf network. The system used a commercial rf generator and impedance matcher. Argon was used as a carrier gas for pure boron deposition studies, while 300–500 μ NH_3 or N_2 was employed when boron nitride deposition was sought. The carrier gas was mixed with the $B_{10}H_{14}$ vapor prior to admission to the rf plasma reactor. The carrier gas pressures, as well as that for $B_{10}H_{14}$, were controlled by stainless-steel needle valves and monitored by thermocouple gauges. The $B_{10}H_{14}$ source vessel was heated to 80 °C to increase the decaborane(14) vapor pressure. All depositions were carried out with a constant gas flow to ensure sample purity. Typically, a $B_{10}H_{14}$ pressure of 10 to 50 μ was admitted to the rf plasma reactor (10 μ for BN and 50 μ for B_4N).

The photodeposition of boron and boron nitride was undertaken using a Quantel International Nd:YAG laser operating at 532 nm, with a pulse length of 10 ns and a peak power of 124 mJ/pulse. Pyrolysis was undertaken with a flow regime in a glass vacuum system described elsewhere.^{37,38} Temperature was determined using a Chroml-Alumel thermocouple spot welded to a resistively heated nickel foil.

III. RESULTS AND DISCUSSION

With a substantial (50μ) decaborane(14) pressure, pyrolysis of $B_{10}H_{14}$ on a nickel foil was not observed to occur below 580 °C. At 600 °C, $B_{10}H_{14}$ will pyrolyze at a sufficiently fast rate so that in a N_2 ambient atmosphere, complete nitride formation did not occur and the nitrogen concentration within the film did not exceed 3%. These pyrolysis temperatures are substantially lower than the temperatures of 600 to 1000 °C commonly used in the pyrolysis of diborane(6),^{11,24,27} 1500 to 1800 °C used with 1,3,5 trimethoxyborazole¹² and 1100 to 2300 °C with boron trichloride.^{7,22} The temperature used for pyrolysis of decaborane was comparable with the pyrolysis temperature of 300–650 °C used with borazine³⁴ and some results reported for diborane(6) and NH_3 mixtures²⁸ in the 400–700 °C temperature range.

With plasma assisted deposition processes, the thermal energies necessary for pyrolysis are substituted with electron kinetic energies (the electron kinetic energies run from 10 to 100 eV or the temperature equivalent of 10^4 to 10^5 K) and consequently, the substrate temperature can be much reduced.^{39–41} Boron deposition on GaAs substrates was observed with rf plasma assisted deposition at substrate temperature below 242 °C with the reactor operating at 20-W power.

While substrate temperatures greater than 300 °C also resulted in the deposition of boron from decaborane in the rf plasma reactor, little formation of boron nitride (either B_4N or BN) was observed with either a 400- μ ammonia or nitrogen background. The GaAs substrate temperature between 250 and 300 °C was found to be sufficient to promote the

formation of pure boron nitride with both nitrogen and ammonia as the ambient background gas.

Since decaborane contains no organic ligands or oxygen, deposition of pure boron or boron nitride is limited only by the residual impurities of the vacuum system and the source materials. As can be seen in Fig. 1, even boron–nitrogen films with high concentrations of boron are observed to contain little or no oxygen or carbon when made from the plasma assisted deposition of $B_{10}H_{14}$ in NH_3 or N_2 . Elemental analysis of boron rich plasma deposited films (B:N ratios of 5:1) did find substantial hydrogen incorporation in the film ($\sim 6.6\%$) which may be the result of the incomplete dissociation of the decaborane(14).

Ion beam assisted decomposition of borazine³³ has been successfully employed to deposit cubic boron nitride, but the use of borazine makes the film composition difficult to control. By varying the relative $B_{10}H_{14}$ to NH_3 or N_2 concentration, the composition of the film can be altered as shown in Fig. 2. To deposit the films shown, $\sim 50\mu$ decaborane and 400–600 μ of N_2 was admitted to the rf reactor chamber. Boron–nitrogen films with very low concentrations of nitrogen will, however, readily react in air, heavily oxidizing the film as seen in Fig. 1.

Since the decomposition of $B_{10}H_{14}$ can be a surface mediated reaction, as demonstrated by our pyrolytic studies, specially localized deposition of boron or boron nitride can therefore be accomplished either by photoassisted or electron assisted decomposition of the absorbed $B_{10}H_{14}$ species at substrate temperatures (for nickel) below 580 °C. To demonstrate that photoassisted patterned deposition of boron nitride and boron could be undertaken employing decaborane as a source material, we deposited boron on GaAs substrates (at room temperature) using a close contact mask technique (described in detail elsewhere^{42,43}) and radiation at 532 nm. While the feature resolution is presently poor (20 μ m) and etching of the GaAs surface occurs, patterned boron deposition can be accomplished as shown in Fig. 3. As yet, we have not determined the decomposition mechanism, and the observed deposition in Fig. 3 could be a result of photopyrolysis.

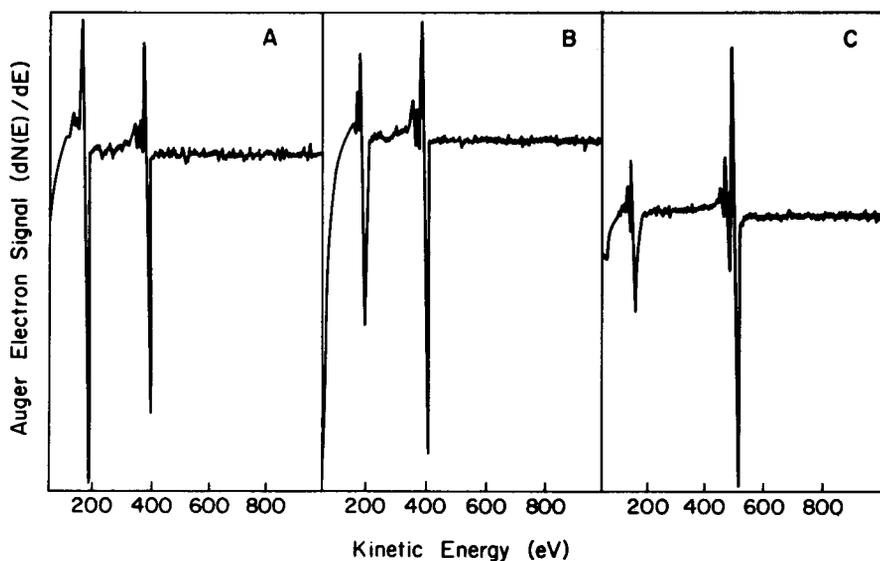


FIG. 1. Auger electron spectra of boron–nitrogen films made by the plasma assisted deposition of boron from decaborane in a nitrogen atmosphere. Films with $\sim 10\%$ (A) and 20% (B) nitrogen are formed with no impurities on GaAs substrates. Boron films will readily oxidize (C) upon exposure to air. Boron, nitrogen, and oxygen Auger electron signals are readily identified at electron kinetic energies at approximately 179, 380, and 510 eV, respectively.

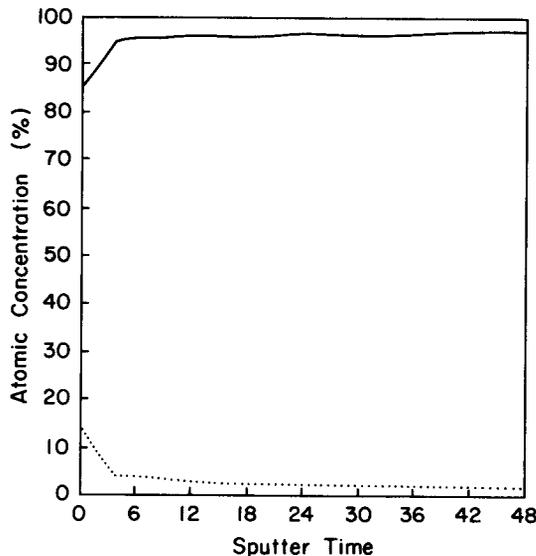


FIG. 2. The composition of boron–nitrogen films, made by plasma assisted deposition, is altered by varying the vapor pressure of $B_{10}H_{14}$ in the feed to the plasma reactor. As the $B_{10}H_{14}$ pressure is decreased from 100 to 50 μ , the nitrogen concentration in the film increases. A depth profile has been constructed from Auger electron spectra as the film is sputtered using Ar^+ ion milling. The GaAs substrate temperature is 275 $^{\circ}C$.

The “doughnut” or “volcano” shaped distribution of boron on GaAs observed in Fig. 3 is a common consequence of photoassisted organometallic chemical vapor deposition (Ref. 44 and the references therein) and indicates that our laser power may be too large. The doping and deposition of boron from decaborane(14) is clearly favorable to photoassisted deposition from trimethylboron [$B(CH_3)_3$] which has been successfully employed to dope *n*-type Si(100) to *p* type.¹³ Decaborane(14) may prove to be a more desirable photochemical doping source material since carbon contamination with $B_{10}H_{14}$ is unlikely. Some special localization of boron doping with photoassisted decomposition from decaborane followed by laser annealing is certainly conceivable. Further studies detailing the photoassisted deposition process are currently underway. The exact decomposition mechanism of decaborane(14) via pyrolysis or photoassisted deposition has not yet been determined. We postulate that

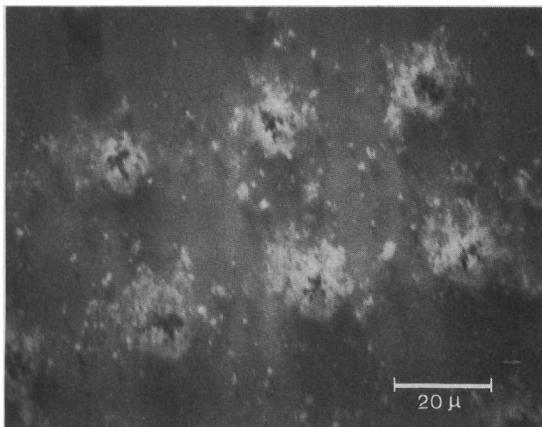


FIG. 3. Scanning electron micrographs of patterned boron deposition on GaAs formed by photolysis of $B_{10}H_{14}$. The boron is deposited into a square array of patches approximately $20 \times 20 \mu m$.

since *nido*-cage borane complexes are synthesized from diborane species,⁴⁵ decomposition also results in the formation of diborane intermediates at the surface.

In summary, we find that decaborane ($B_{10}H_{14}$) is a viable alternative to diborane(6) and other source compounds for the deposition of boron and boron nitride. We have demonstrated that we can successfully deposit boron and boron nitride from decaborane ($B_{10}H_{14}$) using photoassisted, plasma enhanced, or pyrolytic chemical deposition techniques.

ACKNOWLEDGMENTS

This work was funded by AFOSR through Contract No. F30602-88-D-0027 administered by RADC as task No. A-9-1913, the Petroleum Research Fund administered by the American Chemical Society, and IBM awards and contracts with the Center for Molecular Electronics (Research Grant No. 8074).

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Plasma chemical vapor deposition of thin platinum films

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(Received 9 November 1987; accepted 24 December 1988)

The metal organic plasma-enhanced chemical vapor deposition of platinum films using cyclopentadienyl-trimethyl-platinum as starting material is reported. Three different reactors are compared and the influence of power, substrate temperature, and temperature of the reservoir with the organometallic has been studied. Films with $\approx 100\%$ Pt and a resistivity of $46 \mu\Omega$ cm have been deposited.

I. INTRODUCTION

Thin films of platinum are used as catalysts and in microelectronics as electric contacts or as diffusion barriers. In spite of the practical importance of such films surprisingly little work has been directed at their preparation. Besides physical [physical vapor deposition (PVD)] processes¹ like evaporation and sputtering, some chemical vapor deposition (CVD) processes have been reported². Petukov *et al.*³ studied the fragments obtained by thermal decomposition of $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$ and $(\text{CH}_3)_3\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)$ at 250–350 °C, patented this process for the preparation of platinum films, but gave no further details. The only systematic study has been carried out by Rand^{4,5} who decomposed $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$, $\text{Pt}(\text{CO})_2\text{Cl}_2$, and $\text{Pt}(\text{PF}_3)_4$ thermally. The first compound at 500–600 °C yielded only films with a considerable carbon contamination. In no case could deposits with low resistivities be obtained. The second starting material resulted in bright films but was considered unsuitable for CVD processes because of its limited stability, corrosive vapor, and, most of all, because of the extremely poor adhesion of the films. The best results were obtained with $\text{Pt}(\text{PF}_3)_4$ which, under optimum conditions (200–300 °C), led to smooth adherent layers with resistivities sometimes as low as $18 \mu\Omega$ cm. However, these films showed an extremely high stress and a contamination by phosphorus which amounted to only ≈ 0.1 at. % in the total material, but was fairly severe in the top 50 Å of the films. Laser CVD of $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$ and $\text{Pt}(\text{C}_5\text{HF}_6\text{O}_2)_2$ has recently been reported by Braichotte and Van den Berg^{6(a)–6(c)} but no details have been given concerning the composition of the deposits. Also $\text{Pt}(\text{PF}_3)_4$ has been employed in laser CVD.⁷

We have report the deposition of thin platinum films from an organoplatinum precursor by plasma-enhanced CVD. The advantages of this method have already been discussed in connection with the formation of palladium⁸ and gold⁹ films.

II. EXPERIMENTAL

A. Cyclopentadienyl-trimethyl-platinum (CTMP)

There are various platinum compounds of the structural type Cp-Pt-R_3 ,¹⁰ of which CTMP was chosen because of its high vapor pressure which is reported to be ≈ 130 Pa at 70 °C.¹¹ The compound was synthesized starting from elementary platinum via the hexachloro-platinic acid and K_2PtCl_6 , which was then subjected to a Grignard reaction to yield trimethyl-iodo platinum.^{12–14} This was converted with NaCp into CTMP,¹⁵ a white, crystalline, air-stable solid of mp 104 °C (104.5 °C,¹⁶ 108.5 °C¹¹). The compound which was identified by comparison with published mass spectrometry (MS),¹¹ IR,¹⁵ and ¹H-nuclear magnetic resonance¹⁷ (NMR) data has a so-called “piano stool structure,” with 3 σ -bonded methyl groups and a π -bonded Cp group. The strength of the Pt–CH₃ bond is estimated to 160 ± 20 kJ/mol.¹¹ Appreciable decomposition starts at temperatures > 165 °C,¹¹ giving mainly elementary platinum and methane, as well as small amounts of H₂ and C₂H₆.¹¹ Photolysis¹⁸ causes dealkylation and formation of methane via homolytic cleavage of the Pt–CH₃ bond. The methyl radicals which have been detected by electron spin resonance (ESR) during photolysis abstract hydrogen from