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National Research Council
CAST (Cooperation in Applied Science and Technology)
PROGRAM

PROJECT RESEARCH REPORT

on "Investigation and modeling of metastable structures and states in superhard carbon and boron nitride based films formed by CVD and pulsed plasma fluxes deposition methods"

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ABSTRACT

"Investigation and modeling of metastable structures and states in superhard carbon and boron nitride based films formed by CVD and pulsed plasma fluxes deposition methods"

The interest to boron nitride - carbon ternary films is based on the suggestion that this compound may have new intermediate physical properties between those either for graphite (semimetal) and hBN (insulator) or for diamond and cBN The main goal of this project was to investigate the formation of the ternary boron-carbon-nitrogen based materials by the plasma assisted deposition processes The chemical vapor deposition (CVD) permits to deposit diamond coatings Our main efforts during the project covering the period from 06/13/96 to 06/13/97 were concentrated on the microwave plasma assisted CVD process in an attempt to grow any B/N/C ternary phases

A number of coatings with $B_xC_yN_z$ compositions was prepared using a tube type microwave CVD reactor The coatings have mostly nanocrystalline structure (grain size less than 20 nm) and electric properties from a dielectic to a conductor in dependence on the deposition conditions Some coatings have high microhardness A variety of the non-equilibrium chemical reactions in the plasma results in multiphase materials It was found that even small changes in the process parameters and experiment geometry lead to a significant difference in the coating properties, chemical and phase composition The coating were characterized by electron microscopy, infrared and Raman spectroscopy, microprobe analysis, photoelectron spectroscopy and X-ray diffraction Results of the coatings investigation in some cases indicate the presence of microcrystalline diamond, graphitic boron nitride, boron carbide and some unidentified phases

Inspite of the number of experimental results which do not correspond to that for graphite-like structure of B/C/N, it is to early to make conclusion about the formation of a new hard metastable B/C/N phases

As the result of this project, a systematic study of the boron-carbon-nitrogen (B/C/N) ternary coatings formation by microwave CVD process was started As a particular benefit for the project participants, a new research direction on the synthesis of hard ternary compounds was initiated We intend to develop this research and consider the following joint tasks for the future cooperation

- Optimization of the CVD equipment and process parameters with the aim to increase the yield of the a single phase B/C/N ternary metastable material
- Modeling of the vibrational spectra of ternary B/C/N compounds what is very important for the proper interpretation of the experimental data
- Development of an alternative approaches to grow ternary B/C/N films, for example, by sputtering or ion-beam depositon techniques
- Investigation of electronic and mechanical properties of B/C/N ternary thin films, important for industrial application

These tasks are thought to be realized in the close cooperation with other scientific organizations in U S and Europe

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PROJECT TITLE "Investigation and modeling of metastable structures and states in superhard carbon and boron nitride based films formed by CVD and pulsed plasma fluxes deposition methods"

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SUMMARY OF THE PROJECT

Project tasks

The main goal of this project is to investigate the formation of the ternary boron-carbon-nitrogen based materials at the plasma assisted chemical vapor deposition process

Two other subtasks relating to the main goal of the project were considered

- Development and improvment of pulsed plasma, CVD and combined methods to grow metastable carbon, boron nitride and related films with controlled structure and properties
- Development of characterization techniques of metastable state in hard films by surface and volume sensitive methods and structure modeling

Introduction

Diamond and diamond-like carbon, carbon nitride and boron nitride coatings prepared by the plasma methods represent significant interest because of their unique optical, mechanical and electrical properties The particular interest to boron nitride - carbon ternary films is based on the suggestion that this compound may have new intermediate physical properties between those either for graphite (semimetal) and hBN (insulator) or for diamond and cBN To present time, however, not too many papers were published in comparison with the publications on diamond and boron nitride films Detailed overview of the published experimental data shows, that the most of the reported B/C/N materials prepared by the plasma-chemical methods have rather

graphite-like amorphous structure Some evidence for hard diamond-like B/C/N phases formation was provided only for high temperature/ high pressure proceeses

Our main efforts were concentrated on the microwave plasma assisted CVD process in an attempt to grow B/N/C ternary coatings having non-graphitic structure

The present state of research shows that the results received can be summarized in two groups

1 State of art

1 1 CVD processes

Inspite of the number of publication, there is little evidence for non-graphitic B-N-C phases in CVD prepared films Instead, most of the films had a turbostratic graphite-like structure A proposition about the presence of true B-N-C solid solution with cubic strusture is also not proved yet There are two typical models for the structure of turbostratic materials In one case, the structure is presented as alterating layers consisting of carbon and BN sheets In the other case, all three atoms are presented within each layer in various configuration [Ref 1-4]

Some evidence for a cubic phase was presented only once [Ref 5] It was noticed, that this cubic phase was unstable to the electron beam irradiation in TEM Besides, composition of those cubic nanocrystals is still unknown

1 2 High Temperature/High Pressure synthesis

Most of the prepared materials were mixes of at least cBN and diamond However, there were some signatures of a new phases They appeared in distinct peaks in Raman (1323 cm^{-1}) and IR (1000-1120) spectra, some new interplanar distances in X-ray diffractogramms Nevertheless, no single phase cubic material with well-defined crystallites was prepared Thus, it is difficult to say, if there is a new phase or some distorted known phases [Ref 6]

Only few papers give more reliable evidence for the formation of a new cubic phase with composition $BNC_{2\ 5}$ and $BN_{1\ 1}C_{2\ 2}$ [Ref 7,8]

2 Method

2 1 Coatings preparation

A microwave plasma assisted CVD method was chosen All experiments were performed using a 2 45 GHz microwave tube type CVD reactor This reactor was modernized to provide facilities for simultaneous use of at least four gases A sketch of the experimental system is shown in Fig 2 1 The silicon, silcon with pulsed-arc predeposited carbon layer, molibdenium, graphite or diamond substrates were placed into the discharge cavity on boron nitride holder Gas mixes of $B_2H_6/CH_4/N_2/H_2$ and $B_2H_6/CH_4/NH_3/H_2$ were used in all experiments The microwave discharge power in the range of 400-600 W, substrate temperature of 900-1350 ^oC, gas pressure of 5-90 Torr and gas flow rate of 100-200 sccm were varied to study growth of B/C/N coatings A number of samples at the different atomic ratios of the components in the gas flow within B-N-C composition triangle (Fig 2 2) have been prepared

2 2 Characterization

Characteristics of the coatings such as chemical and phase composition, morphology and bonding configuration were examined by infrared and raman spectroscopy, scanning and transmission electron microscopy, X-ray photoelectron spectroscopy, electron microprobe analysis, X-ray diffraction

3 Results and discussion

3 1 Chemical and phase composition

All three elements - boron, carbon and nitrogen were presented in the samples Some examples of the coatings composition defined by microprobe and XPS analysis are given in the Table 3 1

Table 3 1 Some examples of CVD deposited B/C/N coatings chemical composition

Sample	Ratio B/N/C in the gas flow	Ratio B/N/C in the film	Composition
BNC55	1 0/0 5/0 5	1 0/0 58/0 38	$B_{0\ 51}C_{0\ 19}N_{0\ 3}$
BNC61	carbon	1 0/00/21 8	$B_{0\ 04}C_{0\ 96}$
BNC64	1/1 38/1 1	1 0/0 80/0 67	$B_{0\ 4}C_{0\ 27}N_{0\ 33}$
BNC65	1/1 93/1 54	1 0/0 33/0/36	$B_{0\ 59}C_{0\ 21}N_{0\ 2}$
BNC66	1/1/3	1 0/0 0/3 49	$B_{0\ 22}C_{0\ 78}$
BNC23	1/10/0 11	1 0/0 89/0 17	$B_{0\ 49}C_{0\ 08}N_{0\ 43}$
BNC28	1/40/0 7	1 0/0 84/0 13	$B_{0\ 51}C_{0\ 06}N_{0\ 43}$
BNC29	1/40/0 7	1 0/0 89/0 13	$B_{0\ 5}C_{0\ 06}N_{0\ 44}$
BNC30	1/10/0 2	1 0/0 86/0 09	$B_{0\ 51}C_{0\ 05}N_{0\ 44}$

Comparison of the atomic ratio of B/C/N in the gas flow and coating clearly shows that reactions between carbon and nitrogen which form volatile HCN and/or C_2N_2 compounds are responsible for the reduction of these elements in the coatings

TEM data show that most of the B/C/N samples posesses quaziamorphous or nanocrystalline (5-20 nm) predominantly graphite-like structure Boron carbide B_4C crystallites were also found in the coatings prepared in the nitrogen corner of the compositional triangle At the same time coatings show electric conductivity in the range from dielectric to conductor in dependence on the deposition conditions Some coatings have high microhardness compatible with cubic boron nitride This indicates a difference in both chemical composition and structure of the coatings on the nanoatomic level

Surface morphology of the coatings is crystalline-like in many cases as shown in Fig 3 1 and 3 2 This diagreemnet between TEM and SEM data require more detailed analysis and corrections for the samples preparation techniques

3 2 Microprobe and XPS analysis

Only few B/C/N coatings were investigated using XPS An example of XPS spectrum for the sample prepared in nitrogen corner (BNC29) is shown in Fig 3 3 The data for B1s, C1s and N1s levels were interpeted taking into consideration charge shift of the levels of 3 eV This sample contains few percent of carbon Some contamination with oxygen, probably due to after the process oxidation is presented too The observed peaks positions idicates the following bonding types in this sample

C1s core level peak can be described with four gaussians at the - 282 84 eV (B-C bond in B_4C is at 281 8 eV), 284 6 (C-C in graphite), 286 24(C-N sp^2 single bond), and 287 9 eV(C-O)
B1s core level peak - 187 87 (B-C bond in something intermediate between B_4C and B_2C, or in C_2-B-N structural element), 190 2 (B-N in hBN is at 189 8 eV)
N1s core level peak - 398 0 (B-N in hBN is at 397 5 eV)

Taking into consideration the peaks intensity, we can conclude that B-C and B-N chemical bonds are formed in the coatings rather than C-N

EELS spectra for B1s and N1s both show p-plasmon peaks Thus, we have sp^2 states of these atoms, and it confirms the presence of a graphite-like structure

3 3 Infrared and Raman spectroscopy

The results of the infrared and Raman spectroscopy show multiphase composition of B/C/N films and the formation of possible new chemical compounds

FTIR spectra of a number of samples show some general features There is sharp absorbtion peak varying from 802 to 822 cm^{-1}, broad band from 1506-1653 cm^{-1} Some examples are presented in Fig 3 4 As it is known, graphitic boron nitride has absorbtion at 1380 and 780 cm^{-1} Thus, this shift may correspond to substitution of BN with carbon within of a graphite-like structure A small absorbtion peaks at 1086 and 950 cm^{-1} in Fig 3 4b may be due to cubic BN, while shoulder at 1179 cm^{-1} in Fig 3 4c was not identified However, some samples show different features For example, BNC61 doesn't show any features, while BNC66 has only very weak peaks at 1500, 1320 and 800 cm^{-1} Nitrogen was not found in these samples No absorbtion connected with N-H, C-H, and C-C, C-N triple bonds was noticed The peaks in the range 1200-1300 observed for some samples are probably due to B-C bonding, and shift to lower wavenumbers with increase of boron content. At the same time Knittle [8] indicated peaks 1000-1120 for $C_{0\ 33}(BN)_{0\ 67}$ cubic solid solution, while range of 1000-1260 is for reststrahlen band in cBN Loeffler [5] assigned 1210 and 1260 peaks for BNC films to C-N σ–bonds and noticed that they are presented only when cubic nanocrystals are present in film

MicroRaman shows high non-uniformity of film structure on the substrate However, there is some general tendency for all B/C/N samples Raman spectra of the samples prepared in carbon corner of the compositional diagram show the signatures of microcrystalline diamond or heavy doped diamond (Fig 3 5) Raman spectra of the boron corner are typically complex and show possible signatures of boron carbide and luminescence The similar situation is observed for nitrogen corner and the center part of the diagram All these spectra are difficult to interprete Distinct Raman peaks which could be related to the known phases were found in several cases only for hBN, diamond and boron carbide In some cases Raman scattering at 1400-1450 cm-1

was mentioned It corresponds to theoretical prediction for graphitic B/C/N solid solution A questionable peak at 1323 cm^{-1} appeared in several cases as shown in Fig 3 6 The peaks 1323+/-2 and 1053 cm^{-1} were indicated by Knittle [8] for $C_{0\ 33}(BN)_{0\ 67}$ cubic solid solution However, in the sample BNC66 (Table 3 1) there is no nitrogen Raman spectrum shows peaks which could be related to boron carbide (scattering below 1000 cm^{-1}), heavy doped diamond (1200-1300 cm^{-1}) and graphite-like amorphous and/or boron substituted carbon (1350-1600 cm^{-1}) In some cases luminescence background was presented in Raman spectra Compexity of raman spectra hinder the proper phases definition As a part of the characterization task, Raman spectra of hydrogen-free carbon and nitrogenated carbon films were studied [Publ 1]

4 Conclusion

4 1 Microwave CVD of B-N-C coatings from B_2H_6-NH_3(or N_2)-CH_4-H_2 gas mixture results in non-uniform multiphase material Its chemical and phase composition, structure and surface morphology depend very strongly on deposition condition, especially the flow rate ratio of gas components

4 2 The reactions in the plasma provide predominantly B-N and B-C bonds rather than C-N bonds in resulting coatings

4 3 Coatings have predominantly nanocrystalline structure with mostly graphite-like features Some results indicate the presence of non-graphitic phases, however, more experiments are necessary to prepare non-graphitic crystalline B/C/N material with controllable properties

5 Project benefits and future development

As the result of this project, systematic study of B/C/N ternary coatings prepared by microwave CVD method has been started The possible benefit of this project for both participating countries is the development of a new material with perspectives in electronics We intend to continue this research and propose several future tasks

- Optimization of the CVD equipment and process parameters with the aim to increase the yield of a single phase B/C/N ternary metastable material
- Modeling of the vibrational spectra of ternary B/C/N compounds what is very important for the proper interpretation of the experimental data
- Development of an alternative approaches to grow ternary B/C/N films, for example, by sputtering or ion-beam depositon techniques
- Investigation of electronic and mechanical properties of B/C/N ternary thin films, important for industrial application

6 Influence on other fields

It is difficult to predict now which areas can be affected by the results of this project We expect that B/C/N materials developed in the framework of this research can be important for high power electronics because of their high termo- and radiation stability

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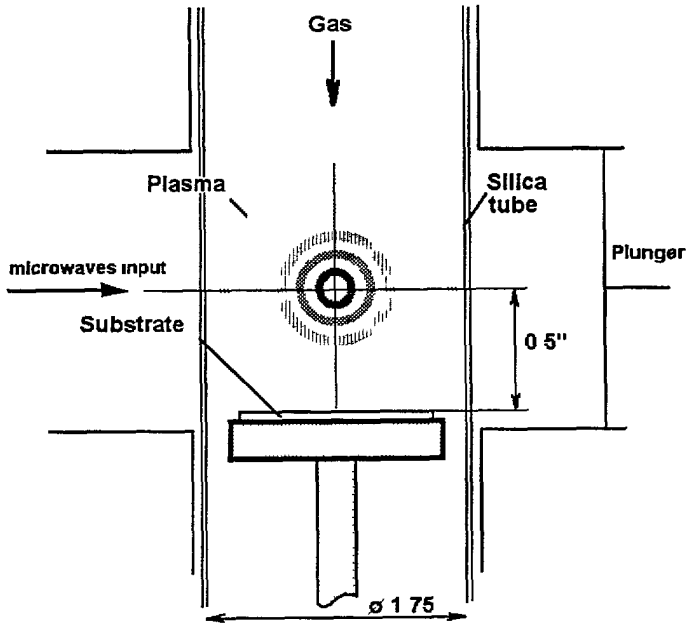


Fig.2 1 A sketch of the experimental procedure

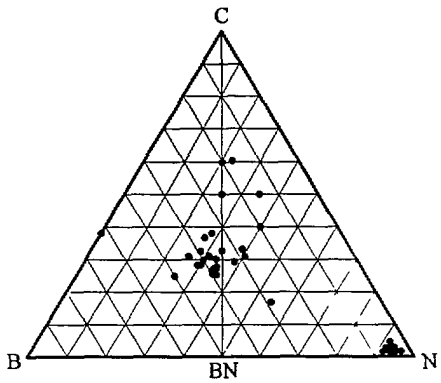


Fig.2.2 The investigated range of B/N/C atomic ratio in the gas flow during BCN film deposition

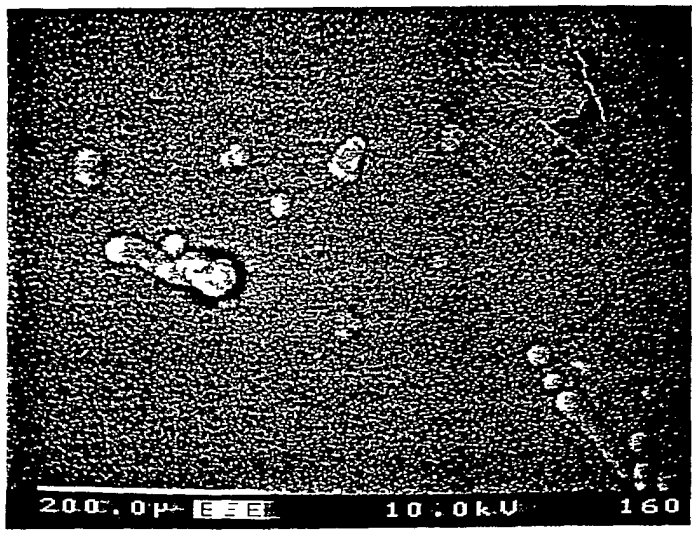


Fig 3 1 Typical SEM image of the amorphous BCN film surface

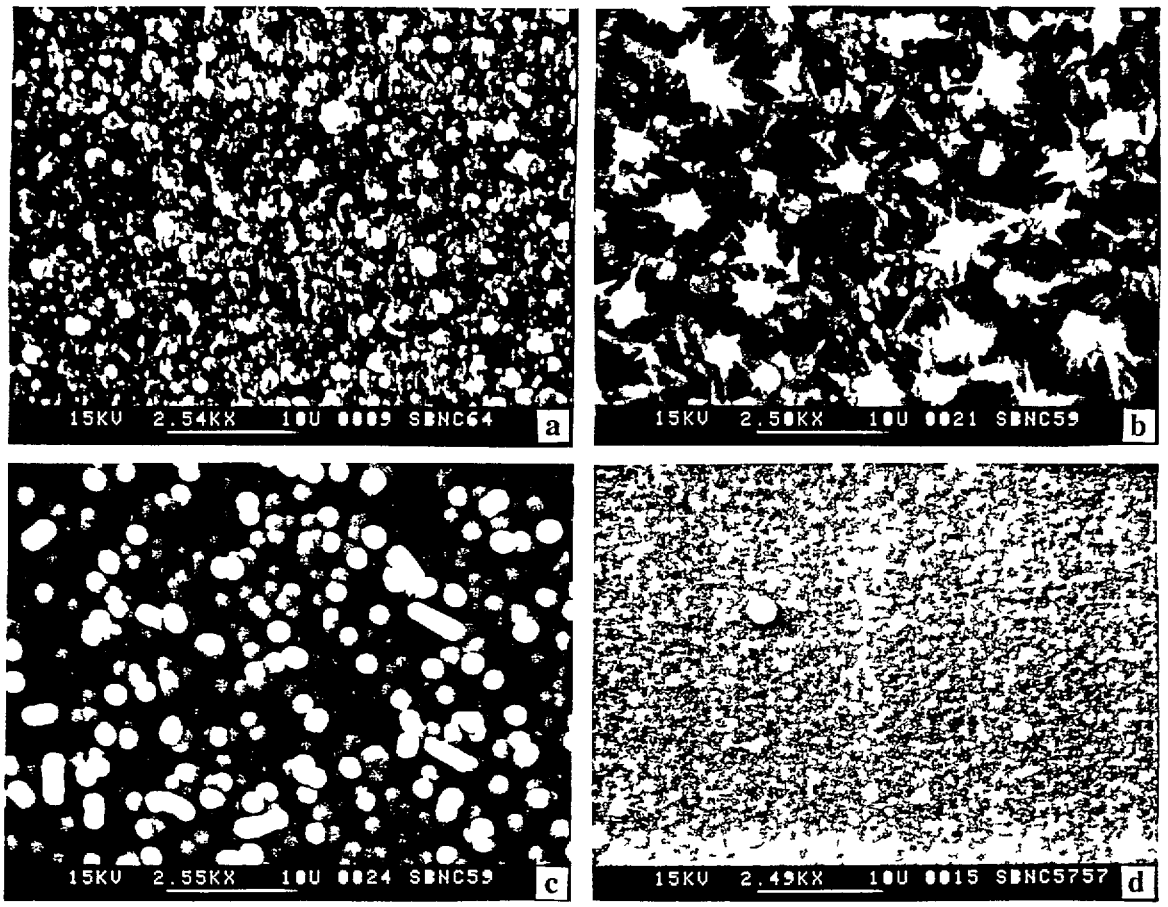


Fig 3 2 Surface morphology of B/C/N coatings prepared under different conditions of microwave CVD process and gas pressure of 85 torr
a - 1070 °C, 600 W, atomic ratio of B/N/C in the gas flow 1 0/1 38/1 1
b - 970 °C, 450 W, atomic ratio of B/N/C in the gas flow 1 0/0 8/0 64
c - 1030 °C, 485 W, atomic ratio of B/N/C in the gas flow 1 0/0 85/0 75
d - 980 °C, 450 W, atomic ratio of B/N/C in the gas flow 1 0/0 9/0 67

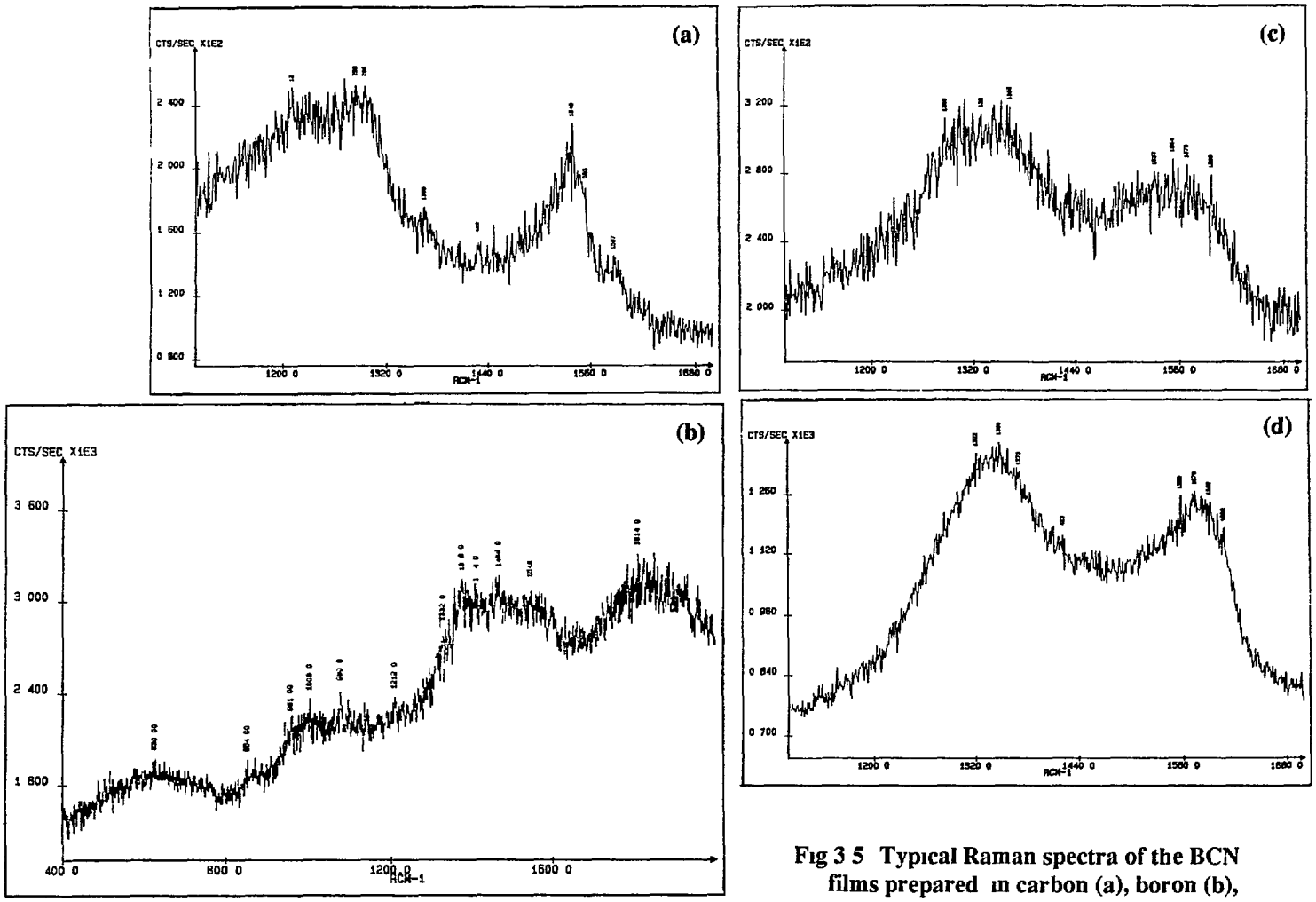


Fig 3 5 Typical Raman spectra of the BCN films prepared in carbon (a), boron (b), nitrogen (c) corners and the center (d) of the B-C-N composition diagram

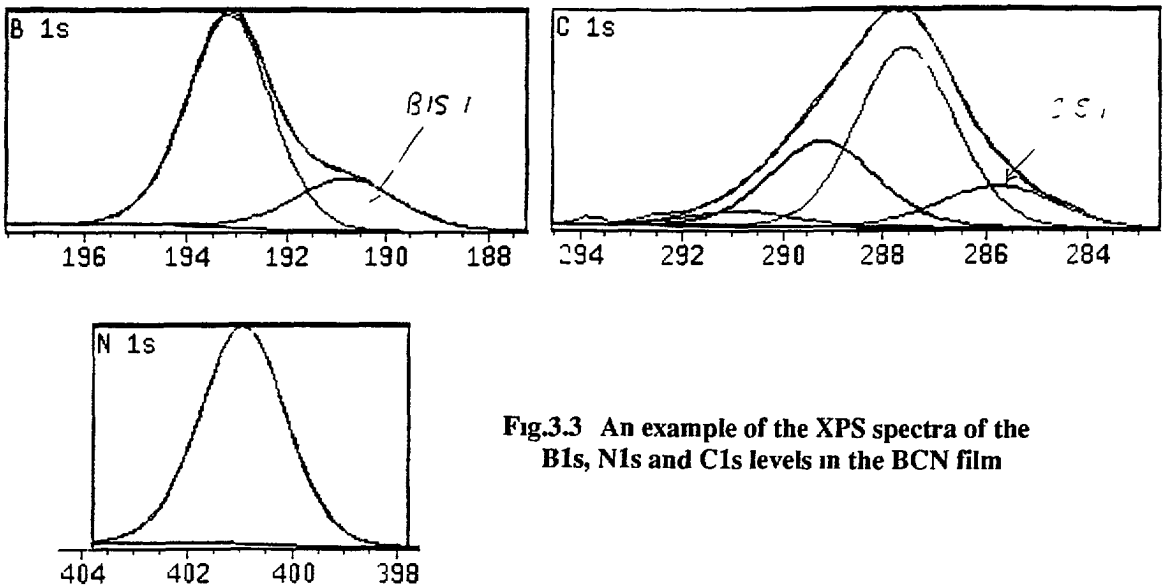
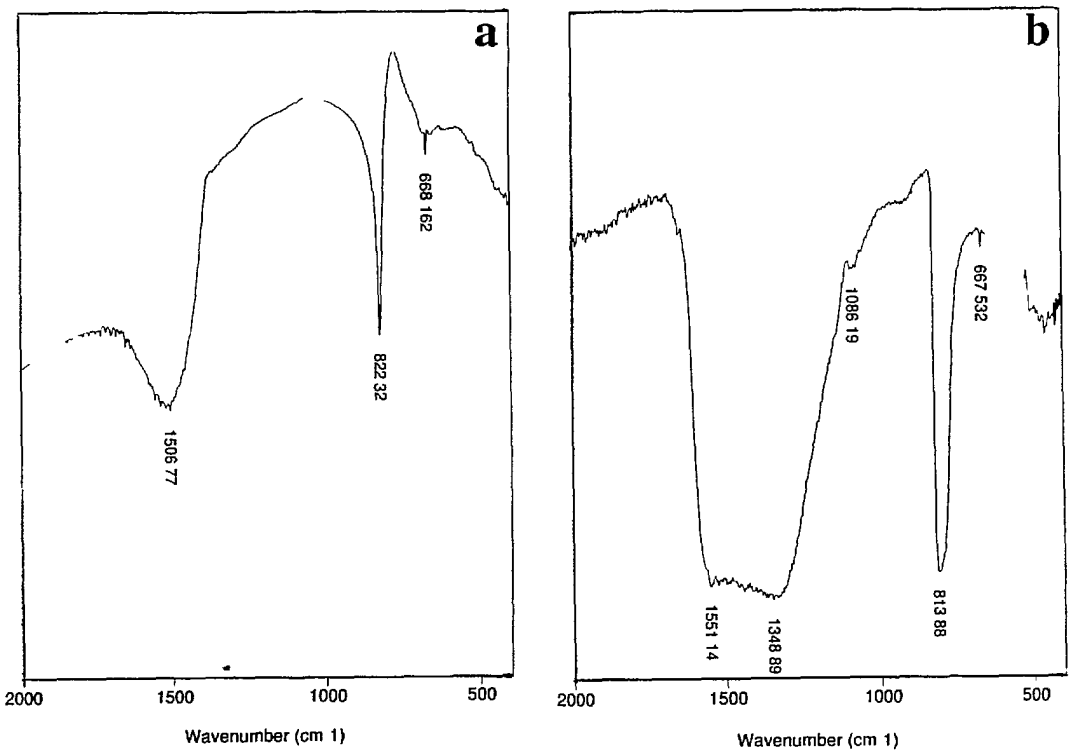


Fig.3.3 An example of the XPS spectra of the B1s, N1s and C1s levels in the BCN film



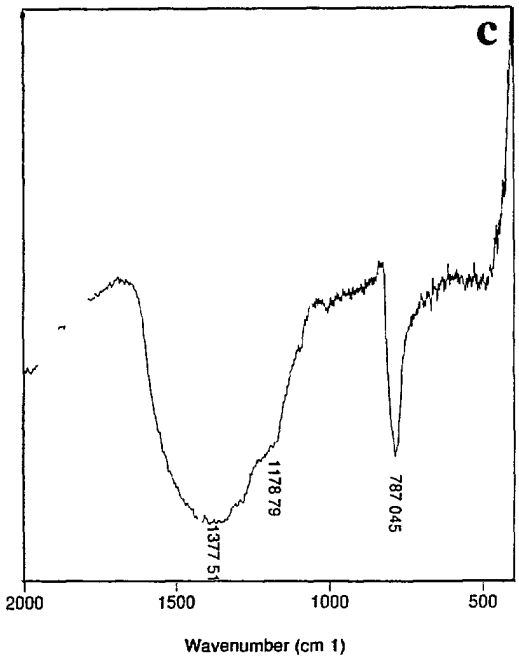


Fig.3 4 FTIR spectra of B/C/N coatings
a - 1070 °C, 600 W, atomic ratio of B/N/C in the gas flow 1 0/1 38/1 1
b - 1030 °C, 480 W, atomic ratio of B/N/C in the gas flow 1 0/1 0/1 0
c - 1030 °C, 500 W, atomic ratio of B/N/C in the gas flow 1 0/0 9/0 8

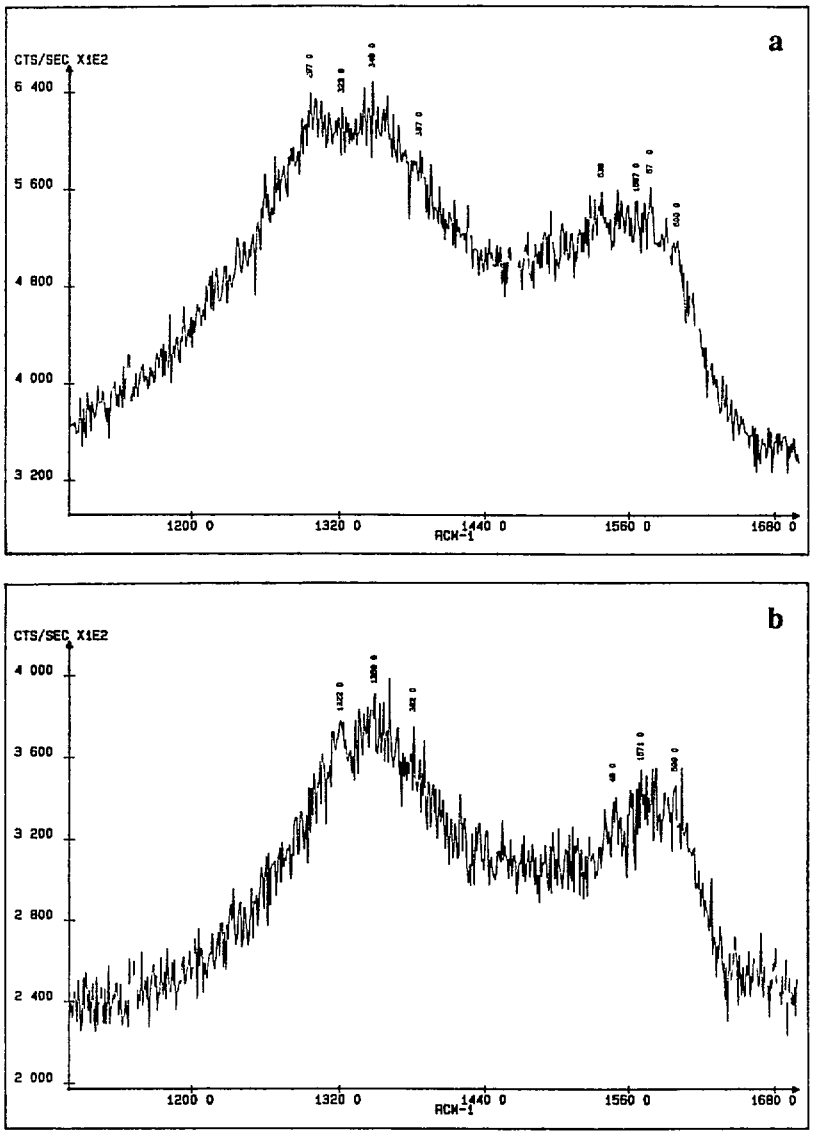


Fig.3 6 Raman spectra of the samples showing 1322 cm ^{1} peak
a - 1050 °C, 600 W, atomic ratio of B/N/C
in the gas flow 1 0/1 0/3 0, in the film 1 0/0 00/3 49
b - 1090 °C, 600 W, atomic ratio of B/N/C
in the gas flow 1 0/1 93/1 54, in the film 1 0/0 33/0 36

FINANCIAL REPORT

on the NRC CAST Program project "Investigation and modeling of metastable structures and states in superhard carbon and boron nitride based films formed by CVD and pulsed plasma fluxes deposition methods"

1 Support provided by NRC
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- Correspondence - $ 220 00

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2 2 ONR/BMDO, # N00014-95-I-0905 "Wide Band Gap Semiconductor Electron Emitters"

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