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A New Generation, Promising Engineering Material: Cubic Boron Nitride (c-BN)

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ABSTRACT

In order to meet the design requirements and expanding demands in various engineering fields, it is essential to incorporate new technological improvements in material sciences into existing processes and applications. This involves engineering new material systems and improving existing ones towards higher strength, toughness and wear resistance. In this context, cubic boron nitride (c-BN), which is a special polymorph of boron nitride, seems to be a high-potential candidate for engineering solutions due to its great mechanical and chemical properties. In this article, advantages and disadvantages of c-BN material system are presented with respect to our ongoing research efforts. The preliminary results about the characterization study of thin film c-BN coatings with Raman spectroscopy are also presented.

Key Words:
Cubic Boron Nitride; Wear Resistance; Raman Spectroscopy.

INTRODUCTION

Because of its high mechanical, chemical and tribological properties and its potential on improving tool parts, c-BN material system attracts major research interest. c-BN has a very high hardness value (45 GPa Knoop) and has a potential to exceed that of diamond if it is understood and engineered at the microstructural level. It does not react with ferrous metal and oxygen even at high temperatures besides of its high thermal conductance and electrical resistance. Chemical stability towards ferrous metals and oxygen at high temperatures such as 1300°C, is a field that c-BN surpasses the diamond [1-3]. It was observed that when a fragment of c-BN was twice heated over 2000°C in vacuum, the material was not attacked by any of the usual acids and was only slowly oxidized in air at 2000°C [4]. By means of its great properties, c-BN is being used in production of tool steels with powder metallurgy or coating of them by PVD, coating of die steels in sheet metal forming or direct applications to final product where high wear resistance is needed [5-6]. Furthermore its antibacterial behavior creates opportunities for biomedical applications [7].

Polymorphs of BN

BN exists in nature with different polymorphs. Due to the specific bonding behavior of boron and nitrogen atoms, BN exists in many different structures. The well-known four polymorphs of BN are cubic (c-BN), hexagonal (h-BN), rhombohedral (r-BN) and wurtzite (w-BN). The variety of interesting properties of boron-nitrogen materials are closely related to their crystal structures. For example c-BN is a hard material, and its mechanical, thermal, and electronic properties are similar to diamond. On the contrary, h-BN is a soft material, whose softness comes from its layered hexagonal crystal structure, similar to graphite; therefore, h-BN is known also as "white graphite" [8-9]. Crystal structure information for the primary crystalline boron nitride phases are given in Table 1 [10].

As it is discussed, different polymorphs of BN such as c-BN and h-BN exhibit different mechanical properties. In comparison of both polymorphs, c-BN coatings have higher hardness while h-BN coatings yield better self-lubricating properties.

Table 1. Structural Data for Boron Nitride Phases

Phase	a (A°) [18]	c (A°) [18]	Space Group	Atom Positions
h-BN [19]	2.5043	6.6562	$P6_3/mmc$ (194)	B: (0,0,0), (2/3,1/3,1/2) N: (2/3,1/3,0), (0,0,1/2)
r-BN [20]	2.5042	9.99	R3m (160)	B: (0,0,0), (2/3,1/3,1/3), (1/2,2/3,1/3) N: (2/3,1/3,0), (1/3,2/3,1/3), (0,0,2/3)
c-BN [1,21]	3.6153		F43m (216)	B: (0,0,0), (1/2,1/2,0), (0,0,1/2), (1/2,0,1/2) N: (1/4,1/4,1/4), (3/4,3/4,1/4), (1/4,3/4/,1/4), (3/4,1/4,3/4)
w-BN [21,22]	2.5505	4.210	$P6_3/mmc$ (186)	B: (0,0,0), (1/3,2/3,1/2) N: (0,0,3/8), (1/3,2/3,7/8)

Therefore, c-BN is better solution in case of tool steel coating while h-BN is better choice where lubrication is an issue. This necessitates improved control over polymorph compositions for the specific purpose. In other words, it is a crucial issue for deposition of film coating to assure the content of desired polymorph and make the necessary characterization operations in order to evaluate the results. Volumetric percentage of c-BN, h-BN and others polymorphs in the resultant coating may alter hugely by small changes in deposition process parameters or material combinations. The higher is the c-BN content, the harder the resultant coating will be. It is not that much easy but possible to obtain BN coatings whose c-BN content is nearly %90. On the other hand, it should be taken into account that, adhesion is also a crucial subject. The most performant coating is not the one which has the highest c-BN content, i.e. strength and hardness. For instance, a coating with high hardness but low adhesion may not result in high machining performance [11]. In order to reach the most performant point, c-BN content and adhesion should be sufficiently good at the same time. Existence of high intrinsic stress in coating has a high potential in perturbing the adhesion of thin film.

Intrinsic Stress Problem of c-BN

The major disadvantage of c-BN is the high intrinsic stress values if a standard PVD (Physical Vapor Deposition) process is applied and a critical thickness (approximately 500 nanometer) is exceeded. This intrinsic stress which occurs between the substrate and thin film could reach up to very high levels such as 20 GPa. This huge amount of stress may lead to crack formation or peeling-off of the thin film [12]. One of the basic reasons for formation of intrinsic stress is the epitaxial interactions and different coefficients of thermal expansion of the substrate and coating material [13]. In the literature, it is proven that by means of special methods and processes like sequential growth, ion reduced stress relief, annealing, sputter cleaning, etc., c-BN films could be created with a 0,5 GPa intrinsic stress and a 1,3μm thickness [14]. In Figure 1, intrinsic stress – time graphs for medium energy simultaneous implantation technique is illustrated as example.

Utilization of complex cyclic process of sputter cleaning, growth, ion radiation induced stress relaxation and annealing might also give good and low-stress results. This process is illustrated in Figure 2 using the transverse optical (TO) Fourier transform infrared (FTIR) line position of c-BN as an indicator for the averaged stress in the growing film [15].

A very good alternative for the creation of stress-free c-BN films is the fluorine based CVD (Chemical Vapor

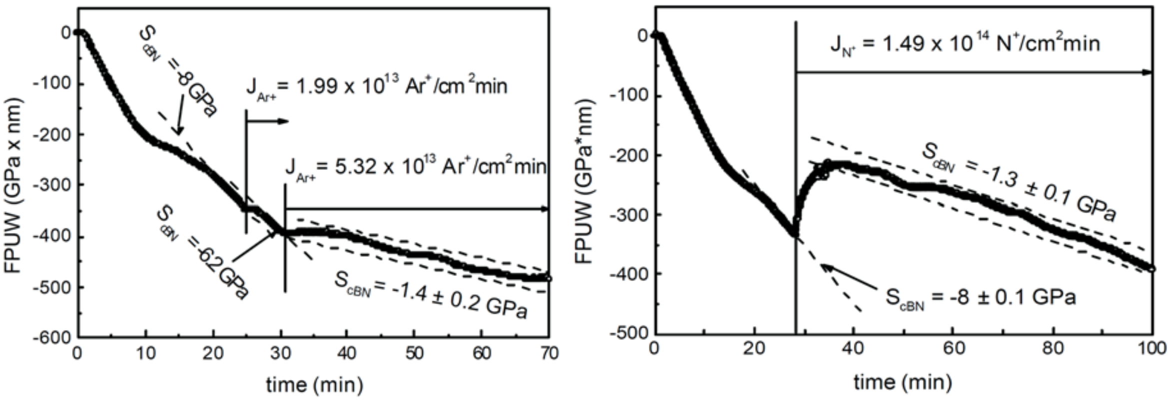

Figure 1. a) Stress-relief of c-BN by simultaneous Argon implantation during deposition, b) Stress-relief of c-BN by simultaneous Nitrogen implantation during deposition [11].

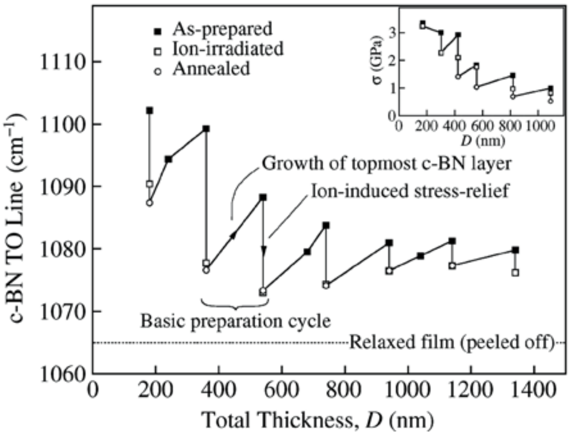

Figure 2. Cyclic PVD deposition process of c-BN

Deposition) application. With this special process, the critical ion energy level which is needed for the nucleation of c-BN can be decreased reasonably. As a result of the lower ion-bombardment energy, intrinsic stress might be reduced to ~1-2 GPa and the films show good adhesion with substrate and long-term stability [15]. However, CVD has also an important disadvantage of high operating temperatures. This high temperatures may cause some thermal softening or recrystallization of the substrate which can highly effect its hardness and toughness. Therefore, some optimization should be made among the deposition methods and also the operating parameters in order to obtain a c-BN coating which is desired.

Characterization of BN Coatings

There are several methods in the characterization of thin films such as FTIR spectrometry, Raman spectroscopy, X-Ray diffraction, and etc. Performing characterization tests is essential for deposition process since the final content of the film is barely dependent to operation parameter, substrate material, and etc. In order to assure the repeatability of the deposition or create any correlation between the operating parameters and content of the resultant film, it would be better to make characterization with minimum two methods. With the characterizations of thin films, deposition processes should be verified.

The characterization of c-BN is a challenging task because c-BN films could be very small-grained and highly defective [10]. It should also be noted that while working with very thin films like 40-50 nanometer, the penetration depth in other words the wavelength of the input light is very important. When the penetration depth goes superior to coating thickness, the spectroscopy analysis would also give information not only about the coating s but also about the substrate material.

Raman spectroscopy is a non-destructive testing method that is used to determine chemical composition and molecular strain in materials by utilizing photon vibration frequencies. Raman spectroscopy with its small wavelength (~532 nm) has a great advantage in thin film characterization with proper optical penetration depth. If the characteristic Raman shift values of a specific molecule is defined previously, then it can easily be detected by measurements.

In the field of BN coatings, the standard frequency shifts (Raman peaks) of the polymorphs are designated in the literature in a detailed manner. Therefore, the volumetric composition of any BN coating could be determined or computed by means of confirm Raman spectroscopy analysis.

There is a collaborative study between Atilim University, Nanoscopy Laboratory and FNSS Defense Systems Inc. which focuses on micro and nano characterization of BN

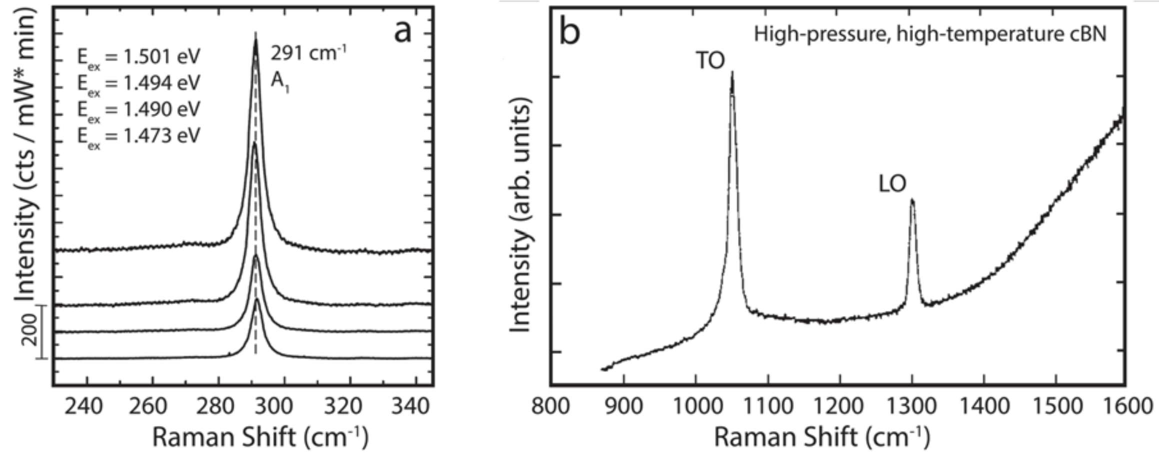

Figure 3. a) Raman spectra of a Cu-rich prepared $CuInS_2$ sample [16], b) Raman spectra of commercial sintered c-BN HTHP [10].

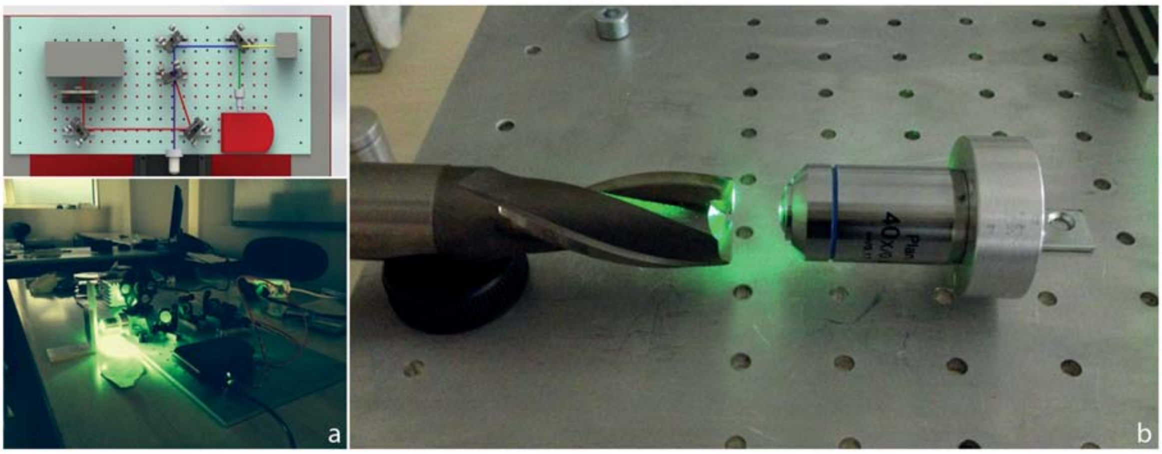

Figure 4. a) Design and prototype of the BN Raman spectrometer at the Atilim University Nanoscopy Lab., b) Raman measurement on the BN coated cutting tool.

coatings on tool parts. A novel Raman spectrometer has been designed specializing only on analysis of BN coated tool parts. As software and hardware development of the system still continues, the preliminary results on BN coated cutting tools (end mill cutters) using Raman spectroscopy is shown in the Figure 4. The end mill cutter studied here was made from high speed steel (HSS) and it was coated with BN using RF magnetron sputtering technique after ultrasonic cleaning process.

In Figure 4a, design and prototype of the BN Raman spectrometer is shown. Optical and mechanical design has been completed and the measurements have been initiated as shown in Figure 4b. The preliminary results on a cutting tool using Raman spectroscopy is shown in the Figure 5 with the calibration data. In Figure 5.a, PDMS polymer was measured using 532 nm excitation wavelength. The calibration data shows proper calibration of the spectrometer with clear signatures matching with the standards. In Figure 5b, the first measurement on a cutting tool coated with BN is shown. The first results show that possible fluorescent background should be eliminated by changing c-BN coating parameters in order to obtain better signal to noise ratio to study phonon signatures shadowed. While main phonon modes for BN system are known from the literature, many others relating to interfacial and chemical phases are also needed to be investigated in order to understand the mechanisms contributing to fluorescent background and low signal to noise ratio. We expect they might originate to multiple reasons including chemical phases on the interface, metal oxides and material defects. Further studies are ongoing in order to elucidate their real behavior on the coated systems.

CONCLUSIONS

c-BN systems promise high potential on improving mechanical and thermal properties of the tool parts as well as the wear resistance. In order to unleash its true potentials there are many challenges to overcome its growth where understanding of its microstructural properties becomes rather important. In this study, we have developed a custom Raman spectrometer specially designed for BN coating characterization in order to understand behavior of its molecular level dynamics in relation to macro scale properties. The calibration data shows proper calibration of the Raman spectrometer system with clear standard signatures obtained from the test sample. Our first result on a cutting tool shows not only phonon signatures may be present but also fluorescent background is observed which may be attributed to many origins including interfacial effects, chemical phases and material defects. Further studies are ongoing in order to understand the real behavior relating to micro scale dynamics of the BN coatings on tool parts.

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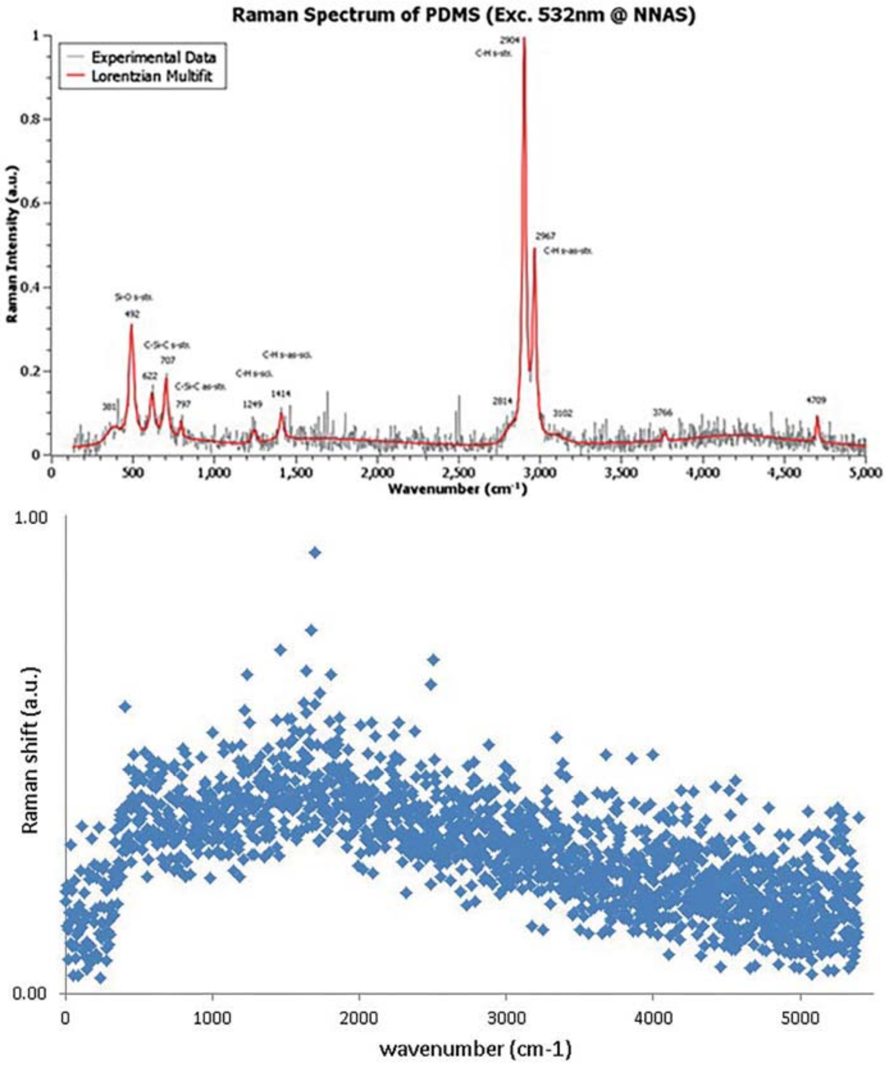

Figure 5. a) PDMS polymer measurement used for calibration, b) Raman Spectra of BN which was coated on cutting tool (First result at Nanoscopy Lab.).

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