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A thermal study of amorphous and textured carbon and carbon nitride thin films via transient grating spectroscopy

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ABSTRACT

In this study, we are considering a novel way of growing carbon nitride (CN) films by using High Power Impulse Magnetron Sputtering (HiPIMS). Carbon and CN thin films were grown on silicon substrate with varying nanocrystalline texturing: some samples were amorphous while others were either nanocrystalline graphite (for the carbon sample) or fullerene-like (for the CN sample), with both samples having a graphitic nanostructure vertically ordered throughout the film. Their thermal diffusivity was computed using transient grating spectroscopy in order to compare the impact of the material's nanostructure on its thermal property as well as benchmarking the performance of CN. It was found that the thermal properties of carbon thin films were decreased when doped with nitrogen, which is attributed to the increased atomic disorder introduced by the nitrogen cross-linking, impacting the phonon propagation. The impact of nitrogen doping on thermal properties opens new avenues in engineering materials with tailored and varying thermal properties at the microscale.

1. Introduction

The discovery of β-C_3N_4 by Liu and Cohen in the 90s triggered a surge in interest in carbon nitride (CN) materials, as its computed hardness makes it harder than diamond [1,2] with high thermal conductivity [3]. Many attempted to obtain the β phase of CN in a controllable way without much success, and attention turned towards the growth of amorphous CN (a-CN) thin films which exhibit improved hardness [4] and elastic recovery [5,6] when nitrogen is implanted into the carbon film. The growth of CN has been studied using various methods, such as DCMS [6], RF sputtering [7], ion plating [8], pulsed laser deposition [9], ion vapor deposition [10], and ion beam assisted deposition [11,12]. Using the extensive amount of growth data on CN, Hellgren et al. established a diagram defining the various microstructural formations of amorphous CN depending on nitrogen concentration and growth temperature [13]. They observed a fully amorphous region for any nitrogen concentration below temperatures of 200 °C, while a two-structure zone was observed at higher temperatures. This included graphitic structures for low nitrogen content (below 5 at. %) to a fullerene-like structure for higher nitrogen content (up to 25 at. %). In this study, we consider a novel way of growing amorphous CN films with various microstructures by using High Power Impulse Magnetron Sputtering (HiPIMS), using a carbon target reactively sputtered in nitrogen gas. HiPIMS is a relatively recent physical vapor deposition (PVD) method introduced by Kouznetsov et al., in 1999 [14]. It can produce high power densities at the sputtered target surface, thus enhancing the deposition rate and the ionization rate of the plasma, facilitating bonding with nitrogen. Amorphous CN thin films have a unique nanostructural variation, in particular the fullerene-like structure which does not exist in pure carbon thin films. As such, it is expected that the microstructure would greatly affect the thermal properties of the material. However, no such work on the thermal properties of CN has been reported, and this study aims to provide some initial insights on the thermal behaviour of HiPIMS-grown CN, as well as to report the first instance of fullerene-like CN structure using HiPIMS. Various thin films were grown on silicon substrates using HiPIMS, such as amorphous carbon and carbon nitride, as well as nanocrystalline

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carbon and CN with vertical ordering. Some control over the film nanostructuring as well as nitrogen doping in thin films could enable new ways to control the thermal properties of a material, which can be used as an advantage for thermoelectric applications for instance, where it has been shown that a reduction in thermal conductivity can increase the thermoelectric efficiency [15–17]. Transient grating spectroscopy (TGS) [18] was used to measure the materials' thermal diffusivity in order to compare the impact of the material's nanostructure on its thermal properties, as well as to benchmark the thermal performance of CN and assess the impact of nitrogen on its thermal properties.

2. Experimental setup

2.1. Sample preparation

The samples were grown using HiPIMS applied to a 3″ diameter carbon target of purity 99.995%, except for the nanocrystalline graphite (NCG) sample which was obtained using the filtered cathodic vacuum arc (FCVA) method as described elsewhere [19]. The use of FCVA for the growth of NCG was necessary as the HiPIMS system available at the moment of making the samples was not capable of ionizing the carbon target sufficiently. This low carbon ionization rate in HiPIMS prevents the growth of denser carbon films and has been discussed extensively elsewhere [20]. In our experiments, the lack of control over film density during growth prevents the generation of a film stress high enough to obtain NCG [21]. This is due to the ionizing energy of argon, which is too low to obtain a plasma with sufficiently ionized carbon atoms, which is critical in obtaining NCG [20,21]. However, it has been shown that one can alleviate this issue and enable HiPIMS to produce high density (hence high sp^3) carbon films by either using neon as the ionizing gas [22], lengthening the discharge pulse sufficiently to transition from a glow discharge to an arc discharge mode [23,24], or shortening the pulse to sub 10 μs and using permanent magnets to facilitate arc discharge [25] which significantly increases the carbon species ionization. Unfortunately, our HiPIMS system was not designed to use either method in a safe manner at the time of this work and thus could not be applied. When it comes to the remaining three samples (amorphous carbon, amorphous carbon nitride and fullerene-like carbon nitride), HiPIMS was used to obtain them as this method has been proven to produce samples with good density [26] and adhesion [27] in a straightforward fashion. In addition, HiPIMS offers great process scalability as well as film uniformity. One of the goals of this work is to report a way to control the microcrystalline structure of carbon nitride via HiPIMS in order to obtain either an amorphous or fullerene-like phase. The objective is to provide a readily available solution to produce amorphous/fullerene-like CN thin films for the industry. The growth methodology was based on the work of Hellgren et al. [13] who produced a phase diagram for amorphous CN growth. Their work focused on three factors impacting the end results microstructure: temperature, ion energy and nitrogen concentration in the film. Each of these three parameters would affect the stress or amount of sp^3/sp^2 ratio which would in turn impact the end result. Following the diagram, the amorphous samples were produced at room temperature to limit graphitization, while the fullerene-like sample was obtained at 400 deg C with high DC bias to increase the ion energy. Previously, reports of HiPIMS grown CN were always limiting the temperature factor (<200 degC) as the main goal was the study of amorphous CN (or CN_x) by using low-cycle high power pulses to increase ionization [25,28,29]. Here, the approach is different as less focus is given to ion energy, hence lower power and more frequent pulses are used to improve the growth rate. Instead, the temperature and nitrogen content were used to induce a crystalline change. The nitrogen gas was initially set to 100% but would produce unstable films that would fully delaminate within 24 h. The nitrogen gas ratio was then gradually reduced to 20% to obtain stable samples. A similar method was attempted for NCG without success, which is most likely due to the low carbon ionization rate of HiPIMS [30], which prevents a sufficient stress build up to force a reordering of the graphitic planes in the normal direction to the substrate. For the amorphous carbon film, the carbon target was sputtered in argon gas, while for the CN samples, the sputtering occurred in a mixture of argon and nitrogen gases. Single crystal silicon (001) samples were loaded into the HiPIMS chamber and pumped down until the base pressure reached at least 10^{-6} mbar. Due to the introduction of argon and nitrogen to initiate the glow plasma discharge during growth, the pressure would increase to between 3×10^{-3} to 7×10^{-3} mbar. A Hipster 1 pulsed power supply from Ionautics was used to generate the pulsed current waveform. Each sample was obtained using a different recipe, and the successful ones used for this study are described in Table 1 below:

The “room temperature growth” temperatures for amorphous C and amorphous CN actually ranged from 25 to 80 degC, which is due to plasma energy being dissipated as heat in the substrate holder and sample. The growth time was changed from one recipe to another in order to obtain approximately the same thickness of 150 nm for each sample, except for NCG which was grown using FCVA and is around 100 nm thick.

2.2. Sample characterization

Film microstructures were first analyzed by a Witec Raman spectroscope, with a laser excitation wavelength of 532 nm. The Raman spectra were acquired from 900 cm^{-1} to 1900 cm^{-1} and the data was analyzed using the software OriginPro 9 to do the necessary curve fitting based on the work by Ferrari et al. [31] regarding the Raman study of CN films. This study is an extension of the work he did on the three-stage model in carbon thin films [32]. Using this model, one can resolve the microcrystalline structure of

Table 1
Summary of the successful recipes used for the growth of carbon and carbon nitride thin films. All films were grown using HiPIMS, except the NCG sample which was grown using FCVA based on a technique reported elsewhere [19].

	Sample name	Gas mixture (sccm)	Growth pressure (mbar)	T (degC)	Bias voltage (V)	Pulse current (A)	Pulse freq (Hz)	Pulse voltage (V)	Peak power density (W/cm^2)
Amorphous Carbon	**aC**	Ar:32	3.7×10^{-3}	25 −80	0	22	4000	750	180
Nanocrystalline graphite with vertical ordering	**NCG**	N/A	Below 1×10^{-5}	600	200	N/A	N/A	N/A	N/A
Amorphous carbon nitride	**aCN**	N:40	6.8×10^{-3}	25 −45	0	28	4000	650	122
Nanocrystalline graphitic carbon nitride with vertical ordering	**flCN**	Ar:32 N:8	4.5×10^{-3}	350	500	1	4000	535	29