



Mechanical and electrical properties of micron-thick nitrogen-doped tetrahedral amorphous carbon coatings

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ABSTRACT

The effect of nitrogen doping on the mechanical and electrical performance of single-layer tetrahedral amorphous carbon (ta-C:N) coatings of up to 1 μm in thickness was investigated using a custom-made filtered cathode vacuum arc (FCVA). The results obtained revealed that the hardness and electrical resistance of the coatings decreased from 65 ± 4.8 GPa (3 k Ω /square) to 25 ± 2.4 GPa (10 Ω /square) with increasing nitrogen gas ratio, which indicates that nitrogen doping occurs through substitution in the sp^2 phase. Subsequent AES analysis showed that the N/C ratio in the ta-C:N thick-film coatings ranged from 0.03 to 0.29 and increased with the nitrogen flow rate. Variation in the G-peak positions and $I(\text{D})/I(\text{G})$ ratio exhibit a similar trend. It is concluded from these results that micron-thick ta-C:N films have the potential to be used in a wide range of functional coating applications in electronics.

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1. Introduction

Tetrahedral amorphous carbon (ta-C) is an excellent coating material for mechanical machinery, optical lenses and many components in automobiles as it provides enhanced durability due to its high number of sp^3 bonds. Unfortunately, the high compressive stress in ta-C coatings tends to limit their thickness, in that the high intrinsic stress of thick coatings makes them prone to delamination and reduces their adhesive strength to substrates. As a result, the usefulness of ta-C films has so far been limited to tribological applications. To address this, we recently developed single-layer ta-C coatings with a thickness of up to 9.5 μm using a multi-cycle FCVA coating method [1].

This broadened the potential applicability of ta-C coatings to fuel cell bipolar plates or semiconductor packaging inspection devices, which are applications that require both good electrical conductivity and low wear resistance.

The effect of nitrogen doping on the physical properties of diamond-like carbon (DLC) thin films has been previously researched [2–5]. This was found to be an effective method for adjusting the sp^2/sp^3 ratio in these coatings, and various studies into DLC coatings have reported that this also causes a decrease in electrical resistance due to the formation of C–N clusters on the sp^2/sp^3 bonded phase [7–8]. This has led to, nitrogen-doped ta-C (ta-C:N) thin coatings being fabricated on various substrates [9], but only to a thickness of <0.1 μm . Thus, the relationship between the structure, hardness and electrical resistance of nitrogen-

doped ta-C:N films of up to 0.7 μm in thickness has not yet been studied. This is in part due to the difficulty in producing such thick single layers of ta-C on a substrate, as the high residual stress tends to cause delamination.

In this study, micron-thick ta-C:N coatings with different nitrogen contents were prepared using FCVA, and their nitrogen/carbon ratio (N/C), structures, hardness, and electrical resistance were analyzed to assess their suitability for functional coating applications. The relation between nitrogen content and the mechanical-electrical properties of the thick ta-C:N coatings is also discussed.

2. Experimental

2.1. FCVA deposition of ta-C:N coatings

The ta-C:N coatings investigated in this study were deposited onto tungsten carbide (WC) using the FCVA system, shown in Fig. 1(a), which consisted of a vacuum arc source with a T-shaped filter attached to the left and right side of the coating chamber. Before setting-up this FCVA system, a numerical analysis was performed using finite element method magnetics (FEMM) to calculate the arc plasma direction at the T-shaped filter and the magnetic field position, as shown in Fig. 1(b). A magnetic solenoid was employed in the FCVA system to separate charged carbon ions from neutral atoms and macro/micro-particles. Fig. 1(c) shows the arc plasma beam moving through the filter from the cathodic arc source. A carbon target 55 mm in diameter and of 99.99% purity was mounted on the arc cathode parts of the chamber and the magnetic coil current was fixed to 5 A.

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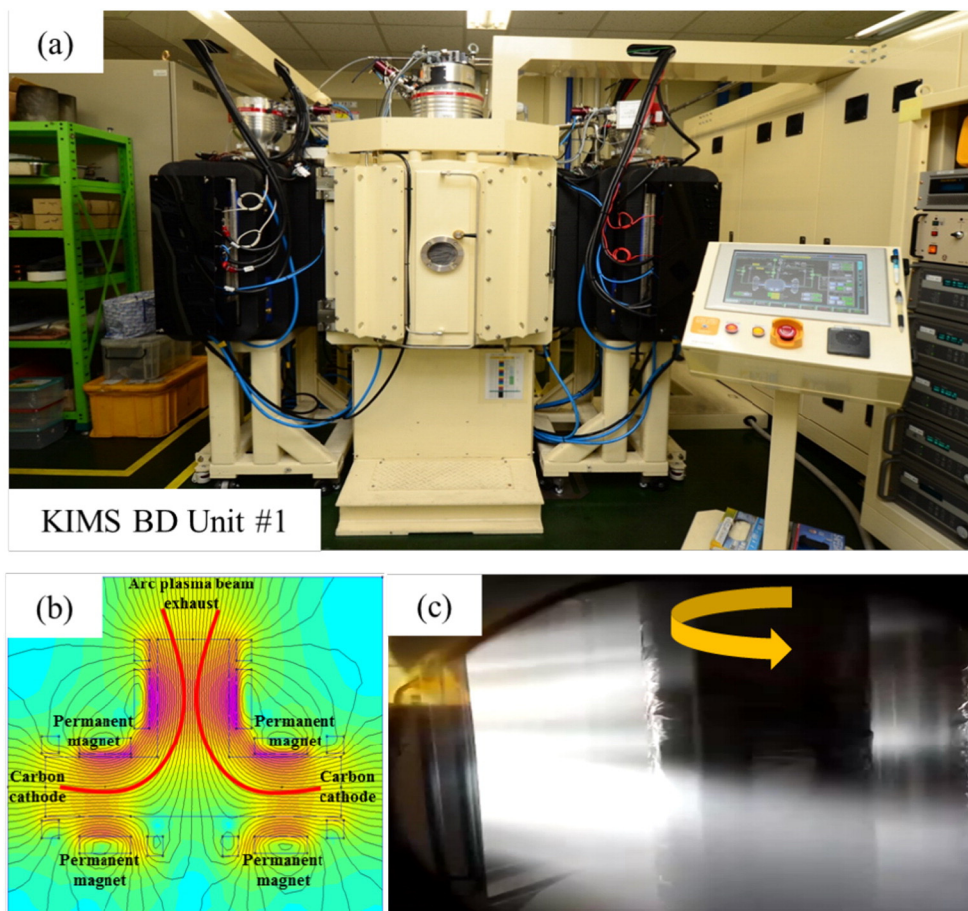


Fig. 1. (a) Multi-cathode FCVA coating system (b) arc plasma beam direction, calculated by numerical analysis (FEMM code), and (c) photograph of the arc plasma beam during deposition.

Prior to deposition, the WC substrate was cleaned with alcohol and de-ionized water, and then placed into a holder positioned perpendicularly on a sample carrier to allow rotation during ta-C:N coating deposition. After pumping the chamber to a pressure below 5×10^{-3} Pa, the WC was etched for 20 min in Ar plasma at 2.0×10^{-1} Pa. Deposition was achieved using a 15 V_d duct bias at the filter and a substrate bias of 75 V_b in the chamber. Nitrogen gas was introduced into a carbon arc source through a mass flow controller (MFC) at flow rates of 0, 5, 10, 20, 25, 30, and 40 sccm to generate carbon and nitrogen arc plasma.

2.2. Coating analysis

The thickness of the ta-C:N coatings was measured by FE-SEM (Tescan, Korea), and their hardness was measured using a micro-indenter (CSM Co., Ltd., Korea) with a Berkovich tip. The final load and indentation depth were 10 mN, and ~200 nm, respectively, from which the Poisson ratio of the ta-C:N coatings was assumed to be 0.3 [10].

The structural composition was measured using an electron beam (Auger electron spectrometer, AES) with incident energy of 3 and 1 KeV, giving resolution of 3 eV. Any oxygen contamination was removed from the samples by Ar sputtering for 1 min. A Raman spectroscopy (Horiba Co. Ltd.) equipped with an Ar laser with an excitation wavelength of 514 nm was used in backscattering geometry mode to examine the physical structure of the coatings at 23 °C and 40% humidity. The incident power on the sample was 2 mW, and the scanning range was 800–1700 cm⁻¹. The electrical conductivity of 1 μm-thick ta-C:N coatings deposited on WC substrates was measured using a four-point probe device.

3. Results and discussion

3.1. Physical properties

The ta-C:N coatings deposited at different working pressures are shown in Fig. 2, which demonstrates that the coating thickness was consistent at a low working pressure of $<5.0 \times 10^{-2}$ Pa. In addition, the average thickness was not significantly dependent on the working pressure used at 1.5 and 3.0×10^{-2} Pa. In contrast, the ta-C:N coatings grown at higher working pressures of 5.0 and 6.5×10^{-2} Pa were found to be more effected by nitrogen, leading to a decrease in thickness to 0.89 μm. This means that using a high concentration of nitrogen gas to increase the scattering effect of carbon species during nitrogen ion energy generation reduces the thickness of the final coating.

This change in coating thickness at different pressures may be related to the difference in ion bombarding energy affecting the sp²/sp³ content. That is the coating thickness decreases at high working pressures due to a decrease in sp³ phase content caused by the lower carbon ion energy and higher nitrogen ion energy, as deduced from the Raman results in Fig. 7.

Fig. 3 shows cross sections of 0.7 μm thick, single-layer ta-C:N coatings (N₂: 20 sccm) on WC substrates. It is evident from this that these coatings were homogeneous and contained an interlayer of Cr of about 0.4 μm in thickness. Thus, thick and well-adhered coatings with reduced stress were successfully formed by FCVA.

As can be seen from the relation between the hardness of the ta-C:N coatings and the nitrogen flow rate used to create them (Fig. 4), there was a significant decrease from 63 ± 4 GPa to 25 ± 2 GPa as the flow rate was increased from 0 to 40 sccm. This decrease was particularly pronounced at 10 sccm (49 ± 6 GPa), and so might be attributed to

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