Turbostratic-like carbon nitride coatings deposited by industrial-scale direct current magnetron sputtering

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ABSTRACT

Carbon nitride thin films were deposited by direct current magnetron sputtering in an industrial-scale equipment at different deposition temperatures and substrate bias voltages. The films had $N/(N + C)$ atomic fractions between 0.2 and 0.3 as determined by X-ray photoelectron spectroscopy (XPS). Raman spectroscopy provided insight into the ordering and extension of the graphite-like clusters, whereas nanoindentation revealed information on the mechanical properties of the films. The internal compressive film stress was evaluated from the substrate bending method. At low deposition temperatures the films were amorphous, whereas the film deposited at approximately 380 °C had a turbostratic-like structure as confirmed by high-resolution transmission electron microscopy images. The turbostratic-like film had a highly elastic response when subjected to nanoindentation. When a CrN interlayer was deposited between the film and the substrate, XPS and Raman spectroscopy indicated that the turbostratic-like structure was maintained. However, it was inconclusive whether the film still exhibited an extraordinary elastic recovery. An increased substrate bias voltage, without additional heating and without deposition of an interlayer, resulted in a structural ordering, although not to the extent of a turbostratic-like structure.

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1. Introduction

Carbon nitride (CN_x) films have been extensively studied due to their promising mechanical and tribological properties [1–4]. Depending on the growth conditions, CN_x films may be either amorphous or exhibit more ordered structures in the shape of fullerene-like or turbostratic-like morphologies [2,5]. In the literature, the terms fullerene-like and turbostratic-like have sometimes been used interchangeably, which may be due to the fact that the transition between the two structures is not well-defined. However, to the understanding of the authors, the basic difference between the two structures lies in the extension and dimensionality of the graphite-like basal planes. The fullerene-like structures are described as consisting of curved, frequently intersecting and cross-linked graphite-like basal planes, forming onion-like structures at the extreme limit [2]. Turbostratic-like structures are described as graphite-like basal planes, which are rotated randomly with respect to each other [6]. Like in the three-dimensional fullerene-like CN_x, the basal planes in turbostratic-like CN_x exhibit buckling, intersections and cross-links, although restricted to two dimensions. The buckling of the basal planes in both fullerene-like and turbostratic-like CN_x has been suggested to originate from a nitrogen-induced presence of pentagons in the otherwise hexagonal graphite-like basal planes. In addition to stabilising pentagon formation, nitrogen has been suggested to promote the

formation of cross-links between different basal planes through carbon atoms neighbouring the nitrogen atoms [7].

When subjected to nanoindentation, CN_x films having fullerene-like or turbostratic-like structures have been shown to exhibit extreme elastic responses [2,6]. A highly elastic response in combination with a high hardness is desirable in many tribological applications, since the asperity contacts presumably behave elastically, thus reducing the abrasive behaviour [8]. Several reports indicate that the atom mobility at the surface of the growing film plays a significant role in the formation of structured CN_x films [9]. The mobility may be enhanced either by increasing the deposition temperature through applying a heater element, or by increasing the 'surface temperature' by applying a substrate bias voltage. It has been suggested that an increased ion bombardment of the growing film creates defects, resulting in smaller fragment sizes of the ordered structure. On the other hand, the defects provide sites for interplanar cross-links, which may lead to an improvement of the mechanical properties of the films [2,10].

The majority of the literature published on CN_x films is concerned with films produced on laboratory-scale equipment, whereas only a few studies have systematically investigated CN_x films grown on industrial-scale equipment [11,12]. Moreover, no papers on fullerene-like or turbostratic-like CN_x films produced by industrial-scale production units exist. Industrial-scale equipment is often operated at a high base pressure, which diminishes the cleanness as compared to working in laboratories. Furthermore, if the unit is used for production of different types of thin films, the condition of the chamber depends on its history of

production. It may therefore be a challenge to deposit films with a significant degree of ordering on industrial-scale production equipment.

This paper investigates the potential of a commercialisation of the highly elastic CN_x films. First of all, it is investigated whether it is possible to deposit fullerene-like or turbostratic-like CN_x films using an industrial-scale direct current (DC) magnetron sputtering system. Secondly, in attempt to adapt the films to commercial applications as protective coatings for e.g. tools or machine components, the effect of adding a CrN interlayer between the film and the substrate was investigated. The purpose of the interlayer was to improve the adhesion of the film to the substrate and to provide support for the film in tribological applications. The variable deposition parameters included the deposition temperature and the substrate bias voltage, and the deposition parameters were related to the microstructural and mechanical properties of the films.

2. Experimental details

The CN_x films were deposited at different temperatures and substrate bias voltages using a CC 800/9 industrial-scale DC magnetron sputtering system manufactured by CemeCon AG. The deposition chamber ($85 \times 85 \times 100$ cm^3) was equipped with two graphite targets of grade R8710 together with two chromium targets, both of dimensions 85×500 mm^2. The targets were positioned vertically in an alternating configuration, and the substrates were subjected to a two-fold rotation between the targets. The two-fold substrate rotation, which is frequently used in industrial-scale processes, was employed in an attempt to provide uniform deposition conditions. The films were deposited onto 15 mm × 15 mm Si(100) substrates, which were placed at a height approximately at the centre of the target racetrack. Prior to the deposition, the substrates were heated and ion-etched. The CN_x films were deposited from the two graphite targets operated at 3 kW in an atmosphere of 300 sccm argon gas and 100 sccm nitrogen gas of purity 99.999%. The pressure prior to deposition was 1 mPa, whereas the total pressure during deposition was 0.4 Pa. The deposition temperature was adjusted by powering a resistive heater element, and was calibrated using a thermocouple placed at the centre of the deposition chamber (neglecting changes due to ion bombardment for different substrate bias voltages). During the deposition, a substrate bias voltage of -140 V resulted in a temperature of approximately 140 °C, when the heater element was not employed.

A selected film was deposited with a CrN interlayer between the film and the substrate. During the deposition of the interlayer, the two chromium targets were operated at 2 kW in an argon (300 sccm) and nitrogen (80 sccm) atmosphere. The deposition parameters were gradually changed from the CrN interlayer to the CN_x film.

The cross-sections of the films were examined by scanning electron microscopy (SEM) with a Nova 600 nanoSEM instrument manufactured by FEI. From the SEM images the thicknesses of the films deposited without interlayers were evaluated to be between 400 nm and 600 nm. The deposition rates were subsequently determined as the film thickness divided by the deposition time. The CN_x film deposited on a CrN interlayer had a thickness of 1.8 μm, whereas the thickness of the interlayer was 2.5 μm.

Cross-sectional samples for transmission electron microscopy (TEM) imaging were prepared with a Helios Nanolab 600 manufactured by FEI. The samples were milled by a focused ion beam of gallium ions, and the sample current was successively reduced in order to minimise sample damage. The cross-sectional high-resolution TEM (HRTEM) images and corresponding selected area diffraction (SAD) patterns were obtained using a FEI Titan 80-300 instrument with an image corrector. The instrument was operated at 300 kV.

X-ray photoelectron spectroscopy (XPS) analyses were conducted using a Kratos AXIS Ultra[DLD] instrument with a mono-chromated Al K$_\alpha$ (1486.7 eV) X-ray source. Survey spectra, providing information on the chemical compositions of the films, were recorded at 160 eV pass energy. The high-resolution spectra of the C 1s and N 1s peaks were recorded at 20 eV pass energy. The binding energies were referenced to the low binding energy component of the C 1s peak at 284.6 eV, corresponding to carbon atoms bonded to carbon atom neighbours. The spectral background was subtracted using a Shirley background [13]. Due to exposure to the atmosphere, an amount of oxygen (less than 5 at.%) was detected on the surface of the films. In addition, adventitious carbon was presumably present on the surface. These surface contaminants may be eliminated by sputter cleaning the samples prior to recording the spectra. However, sputter cleaning may induce changes in the bonding structure, and preferential sputtering may alter the atomic composition. To avoid such misleadings the samples were not sputter cleaned prior to recording the spectra, and the film compositions were reported as the N/(N + C) atomic ratios. Furthermore, trace amounts of argon from the sputter deposition (up to 0.1 at.%) were detected at high substrate bias voltages of −200 V and −250 V. The high-resolution spectra of the N 1s peak were deconvoluted using the Gaussian–Lorentzian lineshape GL(30). The C 1s high-resolution peak appeared broad and asymmetric, however, due to the excessive amount of possible bonding configurations of carbon to nitrogen and oxygen, a convincing deconvolution was impossible [14].

Raman spectroscopy was performed with a Renishaw inVia Raman microscope with an argon laser of wavelength 514.5 nm. The light exposure of the samples was 0.3 mW for 15 s. By comparing spectra obtained at different laser powers and exposure times and by optical inspection of the probed area, it was ensured that the films were not damaged by the laser exposure. The spectra had the typical shape of amorphous carbon samples and were analysed analogously to spectra from nitrogen-free amorphous carbon films [15,16]. Two broad Gaussian peaks were fitted to the spectrum, corresponding to the G-peak centred around 1550 cm^{-1} to 1580 cm^{-1} and the D-peak centred around 1370 cm^{-1} to 1400 cm^{-1}. The most significant parameters in the fits were the G-peak position, the full-width-half-maximum of the G-peak (FWHM$_G$), and the ratio of the intensity (height) of the D-peak with respect to the G-peak (I_D/I_G).

Nanoindentation was performed with a nanoindenter of the type TI-900 TriboIndenter manufactured by Hysitron Inc. A Berkovich tip was employed, and a series of indents ranging from 1 mN to 2 mN was made for each sample. The area function of the tip was calibrated by indentations in fused quartz. The percentage of elastic recovery was determined as $\%R = (h_{max} - h_f)/h_{max} \cdot 100$, where h_{max} is the indentation depth at maximum load, and h_f is the residual depth after removal of the load [17].

The compressive film stress, σ_f, was determined by the substrate bending method, using the Stoney equation for Si(100) substrates [18]:

$$\sigma_f = \frac{h^2}{6t_f(s_{11} + s_{12})R},$$

where h is the substrate thickness and t_f is the films thickness. The numerical value of the term $1/(s_{11} + s_{12})$, representing the compliance constants, is $1.803(1) \times 10^{11}$ N m^{-2} [18]. $1/R$ is given by the difference in the inverse substrate curvature after and before film deposition ($1/R = 1/R_{after} - 1/R_{before}$). The 5 mm by 20 mm double-side polished Si(100) substrates used for the bending measurements had a thickness of 280 μm.

3. Results and discussion

3.1. Increasing the deposition temperature

The deposition temperature was varied between ~140 °C and ~380 °C by employing a heater element at powers up to 13 kW. The substrate bias voltage was fixed at -140 V, and the films were deposited directly onto Si(100) substrates. When the deposition temperature was