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The microstructure and properties of energetically deposited carbon nitride films

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ABSTRACT

The intrinsic stress, film density and nitrogen content of carbon nitride (CN_x) films deposited from a filtered cathodic vacuum arc were determined as a function of substrate bias, substrate temperature and nitrogen process pressure. Contour plots of the measurements show the deposition conditions required to produce the main structural forms of CN_x including N-doped tetrahedral amorphous carbon (ta-C:N) and a variety of nitrogen containing graphitic carbons. The film with maximum nitrogen content (~30%) was deposited at room temperature with 1.0 mTorr N_2 pressure and using an intermediate bias of −400 V. Higher nitrogen pressure, higher bias and/or higher temperature promoted layering with substitutional nitrogen bonded into graphite-like sheets. As the deposition temperature exceeded 500 °C, the nitrogen content diminished regardless of nitrogen pressure, showing the meta-stability of the carbon–nitrogen bonding in the films. Hardness and ductility measurements revealed a diverse range of mechanical properties in the films, varying from hard ta-C:N (~50 GPa) to softer and highly ductile CN_x which contained tangled graphite-like sheets. Through-film current–voltage characteristics showed that the conductance of the carbon nitride films increased with nitrogen content and substrate bias, consistent with the transition to more graphite-like films.

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1. Introduction

Carbon nitride (CN_x) materials with a disordered graphite-like microstructure exhibit high hardness, low friction co-efficient and chemical inertness making them useful in a range of mechanical, chemical and electronic applications [1,2]. The low work function of CN_x also makes it a promising material for field emission displays [3]. Since Liu and Cohen [4] predicted the existence of a super hard phase known as β-C_3N_4, considerable efforts have been made to produce CN_x materials with varying structure. However, most researchers report largely disordered CN_x microstructures. Physical vapour deposition (PVD) methods including magnetron sputtering [5,6], pulsed laser deposition [7], filtered cathodic vacuum arc (FCVA) [8–10] and ion beam assisted deposition [11] have been used to prepare disordered CN_x films and have shown that the main parameters influencing the microstructure of the deposited CN_x films are nitrogen processing pressure, substrate temperature and deposition energy. In most preparation methods, the concentration of nitrogen in the film is proportional to the nitrogen pressure but the nitrogen level saturates at between 30 and 40% [8,12–15]. Elevated deposition temperatures appear to reduce the retained nitrogen level [8,16] and increase the degree of graphitic bonding. Investigations on the influence of deposition energy on the microstructure of the films deposited using FCVA and reactive magnetron sputtering show that this parameter can have a significant effect on both the N content and sp^2 fraction [17,18].

By systematically varying the deposition energy and substrate temperature, we recently identified the conditions producing the main structural phases in pure carbon films [19]. In this work, we investigate the structure, bonding and properties of energetically deposited CN_x thin films. All three important deposition parameters (nitrogen process pressure, deposition energy and substrate temperature) were considered. A FCVA deposition system was used since its depositing flux is almost 100% ionised, enabling the energy of the depositing species to be controlled using a substrate bias.

2. Experimental

A double bend FCVA deposition system operating with a 99.9% pure graphite cathode at an arc current of 60 A and a base pressure less than 2×10^{-5} Torr was used to deposit CN_x films onto *n*-type silicon {100} substrates. The substrates were cleaned prior to deposition in an ultrasonic bath with acetone, ethanol and then de-ionised (DI) water. The cathodic arc deposited samples were mounted on a metallic bias compatible substrate heater/holder. Depositions were performed with nitrogen pressures of 0, 0.1, 0.5 and 1.0 mTorr at temperatures between 25 °C and 600 °C, with substrate bias voltages between −75 and −600 V.

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The thickness of the deposited films was measured using a Tencor P-16 profilometer and ranged from 50 to 200 nm, depending on the bias conditions. The film stress was determined from substrate curvature using Stoney's equation [20]. Two curvature measurements were performed in orthogonal directions on each substrate before and after deposition to obtain accurate stress values.

The microstructure of the films was characterised using a JEOL 2100F transmission electron microscope (TEM) operating at 200 kV. Plan view TEM samples were prepared using HF/HNO_3 acid etching of the silicon substrates. Electron energy loss spectroscopy (EELS) was performed using a Gatan Imaging Filter (GIF2000). The film densities were calculated from the plasmon peak positions, assuming a free electron model and assuming plasma oscillations involving four valence electrons each with an effective mass of $0.88m_e$ (where m_e is the electron mass at rest) [21].

The near edge X-ray absorption fine structure (NEXAFS) measurements were performed on the soft *X*-ray beam line of the Australian Synchrotron. The NEXAFS spectra at the C and N *K*-edges were recorded using the total electron yield (TEY), collected from the sample at each photon energy. The *X*-rays were polarised horizontally and the sample was tilted at an angle of 45° to the incoming beam. Variations in *X*-ray intensity with energy were extracted from the measured spectra using the signal generated from a standard gold covered grid. Contributions to the C and N NEXAFS from contamination in the beam line were determined by replacing the sample with a reference photodiode and collecting spectra. Data from the CN_x films was then normalised using these spectra.

A Hysitron nano-indenter (TI-950) was used to measure the hardness and ductility of the films on silicon carbide (6H-SiC) substrates. The electrical conductivity of CN_x films deposited on low resistivity ($<10\ \Omega\cdot cm$) n-type 6H-SiC substrates was measured using an Agilent source-measurement unit and probe station. Voltages between ±20 V were applied between two Au probes and the current flow through the film/substrate was measured. The film conductivity was extracted from the linear (high voltage) regions of mainly nonlinear current–voltage characteristics.

3. Results and discussion

The contour plot in Fig. 1(a) shows the nitrogen content in films deposited at room temperature as a function of nitrogen pressure and substrate bias. The nitrogen content of the films increases with increasing nitrogen pressure. The highest nitrogen content of approximately 30% was achieved with a nitrogen pressure of 1 mTorr and with biasses of approximately −400 V. This indicates that moderate substrate bias leads to increased nitrogen content in CN_x films but an upper limit exists, possibly due to self-sputtering. The maximum nitrogen content is comparable to that previously measured in CN_x films deposited using FCVA and laser ablation methods [7,22]. The effect of substrate temperature on CN_x films prepared with a nitrogen pressure of 1 mTorr is shown in Fig. 2(a). The nitrogen content decreases to approximately 0% at the highest bias and temperature. The significant reduction in nitrogen content in films deposited at 600 °C indicates that nitrogen is unstable in these carbon films. A similarly significant reduction in nitrogen content has previously been observed during post-deposition annealing of CN_x films at 600 °C [16,23,24]. Fig. 2(a) also shows that moderate substrate bias assists in nitrogen incorporation with substrate temperatures up to ~400 °C.

Fig. 1(b) and (c) shows the stress and density of films deposited at room temperature as a function of nitrogen pressure and substrate bias. Previously published stress and density data [19] from carbon films deposited at a range of biasses without nitrogen have also been included at 0 mTorr. At a fixed bias, increased nitrogen pressure reduces the stress. Increasing the background gas pressure tends to broaden the energy distribution of the depositing species [25], resulting in lower stress. High-stress (~13.0 GPa) is observed in the films deposited with low nitrogen pressures and substrate biasses of approximately −75 V. High stress in undoped carbon films prepared at room temperature indicates the presence of the high density (~2.9 g/cm^3) [26] form of carbon known as tetrahedral amorphous carbon (ta-C). The films in the high stress region of Fig. 1(b) were also found to have densities of ~2.9 g/cm^3 (as shown in Fig. 1(c)). Their significant nitrogen content therefore proves that N-doped ta-C (ta-C:N) is formed in this region [16–18]. The effect of elevated temperatures on the stress of the films prepared at 1.0 mTorr nitrogen pressure is shown in Fig. 2(b). At a fixed substrate temperature, the stress is minimised at an intermediate bias (Fig. 2(b)). The stress increases as the negative bias exceeds ~400 V, possibly as a result of reduced nitrogen retention. Fig. 1(c) shows that without substrate bias, increased nitrogen pressure gradually reduces the density which corresponds to the decrease of sp^3 content, consistent with the findings of Rodil et al.[27,28]. Using separate ion sources for C and N species, they were able to achieve the highest sp^3 content so far and showed that with increased nitrogen content carbon bonding changes gradually from sp^3 to sp^2.

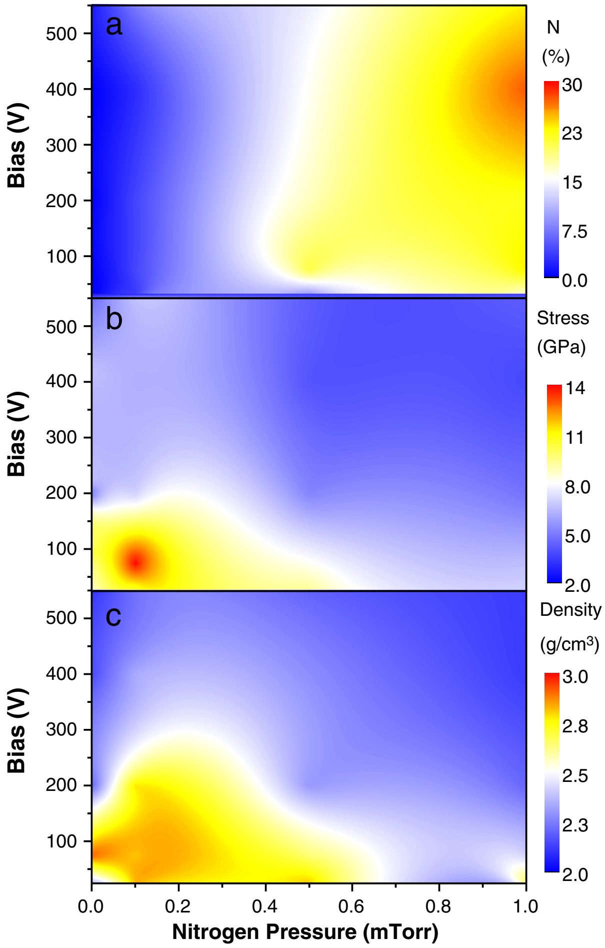

Fig. 1. Contour plots showing the (a) nitrogen content, (b) stress and (c) density of carbon films deposited at room temperature as a function of nitrogen pressure and substrate bias.

Fig. 3 shows plan view TEM images and corresponding diffraction patterns of films prepared with different substrate biasses and nitrogen pressures at room temperature. The film deposited with −75 V bias and 0.1 mTorr nitrogen pressure (Fig. 3(a)) resembles ta-C with high density and amorphous microstructure, confirmed by the diffuse rings in its diffraction pattern. The CN_x film prepared with −75 V bias and a higher nitrogen pressure of 1.0 mTorr (Fig. 3(b)) has a very different microstructure, with fringes indicating the presence of graphite-like layers, despite its ~30% nitrogen content. Increasing graphite-like layering in CN_x films with increasing nitrogen content

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