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A model for stress generation and stress relief mechanisms applied to as-deposited filtered cathodic vacuum arc amorphous carbon films

M.M.M. Bilek*, M. Verdon, L. Ryves, T.W.H. Oates, C.T. Ha, D.R. McKenzie

Department of Applied and Plasma Physics Group, School of Physics, University of Sydney, NSW 2006, Australia

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Abstract

The application of plasma immersion ion implantation (PIII) both during and after the deposition of amorphous carbon by filtered cathodic vacuum arc (FCVA) has been shown to significantly lower the intrinsic stress in the coatings. Stress relaxation is found to occur at applied bias as low as 500 V and we observe a trade off between applied bias voltage and pulsing frequency. This paper presents results obtained with pulse bias voltages ranging from 500 V to 20 kV, which show that very thick high strength carbon films suitable for biomedical applications can be grown using this method. In the absence of high voltage pulse biasing during deposition, the intrinsic stress in the films is found to depend on the dc bias applied during growth in the way commonly observed in thin film deposition—an initial increase with bias to a maximum followed by a decrease at higher bias. We propose a model to account for the stress generation energy window commonly observed and to account for the dependence of stress relief, due to the application of PIII during deposition, on both the applied bias voltage and the pulsing frequency.

Keywords: Plasma immersion ion implantation; Filtered cathodic vacuum arc; Stress relaxation

1. Introduction

The energy of species (ions or atoms) impinging on a growing thin film is universally observed to have a dramatic impact on the properties of the resulting material. When all of the impinging species arrive with low energy (say less than a few eV), the films have been found to be porous with a large void fraction and tensile intrinsic stress [1]. As the energy of a fraction of the impinging species reaches a few tens of eV, there is a transition to intrinsic compressive stress and a corresponding densification of the material [1]. As the impinging energy of the energetic fraction reaches a few hundred eV, the intrinsic stress is seen to decrease with increasing energy and the density of the material is found to drop slightly [2] without the formation of voids or pores. These trends with energy seem to be quite general, having been observed in a variety of materials, including micro-crystalline ceramics such as aluminium nitride [3] and titanium nitride [4] as well as amorphous materials such as amorphous carbon. In this paper, we focus on amorphous carbon deposited by the filtered cathodic arc method.

The changes in stress and density have also been found to be correlated to significant microstructural changes in a variety of materials. In crystalline materials, such as TiN and AlN, the preferred orientation of the crystallites may change and appears to be correlated with the intrinsic stress, while in amorphous materials such as carbon the as-deposited phase of the material is found to be correlated with the level of biaxial intrinsic stress [3–8]. Films deposited with low and very high bombardment energies have low levels of stress and are primarily sp^2 bonded [5], while in the energy window which produces high intrinsic stress, the as-deposited coating is found to consist of the sp^3 rich t-aC metastable phase of carbon [5].

Although intrinsic stress is correlated with the deposition of good quality well-densified thin films and interesting phases and microstructures, excessive levels of intrinsic stress are undesirable because they cause films to be prone to delamination [9]. There are a number of methods which

* Corresponding author. Tel.: +61 2 9351 6079; fax: +61 2 9351 7725.
E-mail address: mmmb@physics.usyd.edu.au (M.M.M. Bilek).

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have been shown to relieve stress in cathodic arc deposited carbon materials and they are well summarized in an article by Chhowalla [10]. These methods however all constrain the choice of substrate on which the film can be grown, either because the substrate must be a soft metal which flows to relieve the stress [11] developed in the coating during deposition or because the substrate must be able to tolerate a post-deposition anneal of at least 600 °C [12]. In this paper, we study the physical mechanisms behind a high voltage pulsed biasing process, which can be applied during deposition to reduce the levels of stress in the growing film without placing constraints on the choice of substrate material. We examine the development of stress and its relief as a function of DC bias applied during the deposition of carbon using a filtered cathodic vacuum arc (FCVA) as well as the relief of stress in films growing in the high stress energy window using intermittent high energy (~kV and above) pulsed bias [13] during deposition.

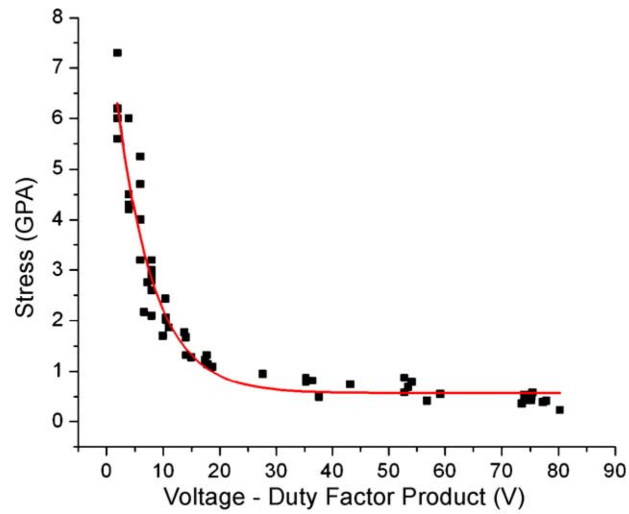

Fig. 2. Intrinsic stress of cathodic arc deposited carbon films subject to PIII as a function of the product of the pulse bias voltage (in volts) and the duty factor. Pulse bias voltages were varied between 0.5 and 20 kV. The pulse length was held constant at 20 μs and the pulsing frequency was varied between 200 and 1200 Hz, resulting in duty factors between 0.004 and 0.024 (experimental data from [8]).

2. Experimental observations in a FCVA deposition system

A cathodic vacuum arc [14] is a discharge between cathode and anode, fuelled with material ejected by explosive processes on the cathode surface. It can be ignited by surface flashover from, or direct contact with, an electrode at potential higher than the anode. Once triggered a low voltage, high-current power supply connected between the cathode and anode keeps the arc burning in a quasi-continuous mode. The plasma is produced by localized high current-density regions termed cathode spots, burning on the cathode surface and is highly ionized (close to 100%). The cathodic arc is therefore a deposition system in which the energy of all of the depositing species can be affected by an applied substrate bias. Cathodic vacuum arc plasma sources are often "filtered" by directing the plasma around a bend using a curved solenoid magnetic filter [15,16] to remove so called "macroparticles"— clusters of neutral atoms up to a few microns in size.

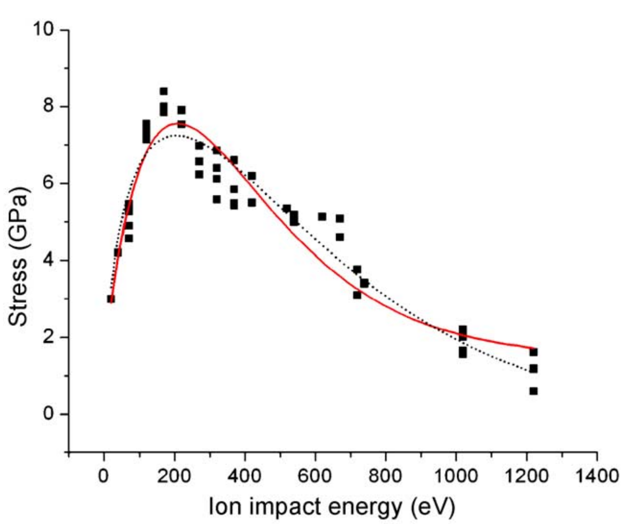

Fig. 1. Intrinsic compressive stress in carbon thin films as a function of ion energy (given by the sum of the energy in eV gained by a singly charged ion falling through the applied substrate bias voltage and the native energy of the carbon arc ion flux [17]).

In the first set of experiments reviewed here, a dc bias ranging from 0 to 1200 V was applied to the substrate to increase the impact energy of the incident ion flux. The carbon ion flux was generated by a dc filtered cathodic vacuum system running at an arc current of 60–80 A. Fig. 1 shows the stress as a function of ion energy (calculated as the sum of the most abundant natural drift energy, which is ~20 eV in carbon cathodic arc plasmas [17], and the energy gained by a singly charged ion falling through the potential of the applied bias). This is a valid approach because the ions in a carbon cathodic arc, running with arc currents such as those used here, are almost exclusively singly charged [17]. The rise of stress with ion energy to a maximum followed by a slower decrease is typical of intrinsic stress versus ion impact energy curves published in the literature.

In another set of experiments [7,13,18], the same cathodic arc deposition system was used with an earthed substrate to deposit carbon films with high voltage (greater than 0.5 keV) pulses applied periodically to the substrate during deposition. The pulse length was maintained at 20 μs, while the frequency of pulsing was changed to vary the duty factor of the high voltage. The intrinsic stress as is plotted as a function of the voltage–duty factor product is shown in Fig. 2. The stress falls monotonically indicating that a bias of 500 V and upward causes stress relief in the films. Note that there seems to be a trade-off between