

Plasma engineering of multilayered carbon coatings.

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Introduction

Thin films with alternating layers (multilayers) of different materials have exhibited enhanced mechanical properties compared to single phase coatings[1-3]. Nature provides a dramatic example in the nacre of the abalone shell which consists of alternating layers of brittle and soft materials. This naturally occurring material is extremely tough, and the prospect of fabricating such nanostructured materials for practical applications has recently attracted much interest. By investigating the structure and properties of such multilayer systems, new composite materials with enhanced properties can be developed. Amorphous carbon (a-C) materials with a wide range of structure and properties can readily be produced by energetic condensation methods. Therefore, a-C is potentially a useful material to use as a “building block” for synthetic multilayer coatings, which mimic naturally occurring materials such as the abalone shell.

The structure and properties of a-C films have been studied extensively [4]. When produced by physical vapour deposition techniques, a wide range of structures can be produced depending on the deposition conditions. At high substrate biases, low density films are produced which are relatively soft and have a structure containing a high proportion of graphite like (sp^2) bonding. On the other hand, films deposited using moderate substrate biases in the vicinity of 80-100 V have high density and hardness because they contain a high proportion of diamond like (sp^3) bonding.

In this work we investigate the synthesis of carbon multilayers produced using cathodic arc physical vapour deposition in combination with ion implantation. By applying various DC and pulsed substrate biases, carbon layers with different structure and properties can be formed. Cross sectional transmission electron microscopy (X-TEM) is used to provide a detailed analysis of the samples. X-TEM combines detailed structure and bonding information using electron diffraction and electron energy loss spectroscopy (EELS).

Experimental Methods

Two approaches to producing a-C multilayers have been investigated. In the first, a pulsed filtered cathodic arc was used to initially deposit a single high density carbon film. Plasma immersion ion implantation (PIII) was then used to modify the surface of the film to produce a second layer. This sample was deposited onto a silicon oxide coated silicon wafer using a pure graphite cathode which was ablated with 1 kA, 50 V, 0.5 ms pulses at a frequency of 10 Hz to produce the depositing plasma beam. PIII allows ion implantation to occur by

applying periodic pulses to the substrate holder. In this case, argon ion implantation was performed by providing a 3.8 mTorr argon background gas and applying -10 kV pulses at a frequency of 1 kHz for a duration of 50 μ s to the substrate holder after the film had been deposited. The high voltage pulses accelerated the argon ions across the plasma sheath which developed around the substrate resulting in ion implantation into the deposited carbon film. The second type of a-C multilayer was prepared by periodically varying the level of DC bias between -150 V and -720 V in a cathodic arc with a continuous source. A Si substrate was used, and by alternating the bias between these two values, 10 layers were deposited as shown in Part 2 of the section below. This sample was also annealed to 600°C after the deposition process.

For X-TEM analysis, the cross sectional specimens were prepared using a mechanical polishing method, and then thinned to electron transparency using an ion beam thinner. The microstructures of the carbon coatings were analysed using the JEOL 2010 TEM operating at 200 kV in conjunction with a Gatan Imaging Filter. Using STEM mode, EELS linescans were performed to determine the fraction of sp^2 bonded carbon present and its distribution.

Results and Discussion

Part 1: Carbon bilayer produced by PIII

In this section we investigate the use of PIII to modify the surface structure of a high density a-C film. Figure 1a shows the cross-sectional TEM image for the a-C bilayer and visually it is possible to detect a slight variation in the films contrast at a thickness of approximately 15 nm from the surface. EELS linescans allow detailed structural and bonding information to be determined from the carbon bilayer. Figure 1b shows the relative concentration of Ar, O and C determined from the characteristic absorption edges in the EELS spectra [5, 6]. Ar is present within the first 10 nm of the C film as a result of the ion implantation. The carbon concentration remains reasonably constant throughout the film thickness until the substrate begins. At the substrate we observe a rapid decrease in C and an increase in O due to the SiO₂ layer. The glue used during sample preparation, which can be seen in Figure 1a to the left of the film, contains high levels of carbon. This explains the presence of C before the film begins. Figure 1c shows the fraction of sp^2 bonded carbon (black solid line) and the density (grey dashed line) throughout the film thickness. The sp^2 fraction is calculated from the C K edge as described elsewhere [7]. The density can be estimated from the plasmon peak positions [8]. The sp^2 fraction is expected to be the reciprocal of the density as high density carbon will have a low sp^2 fraction. Figure 1c shows that at approximately 20 nm, the film changes from predominantly high sp^2 bonded carbon (~75% sp^2) to high sp^3 bonded carbon (~25% sp^2) suggesting that a change in the carbon structure has occurred as a result of PIII treatment. It has been shown that ion implantation promotes sp^2 bonding in high density a-C [9]. Therefore, it is expected in this case that the Ar implantation will modify the surface of the carbon film to a depth corresponding to the depth of the ion implantation. This result shows how a combination of film deposition and implantation can be used to form multilayers of different types of a-C.

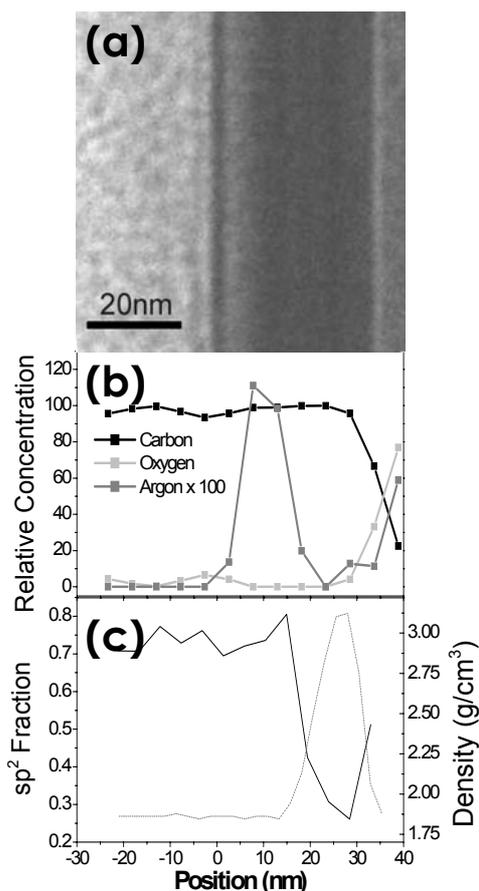


Figure 1(a-c): (a) X-TEM image of the carbon bilayer, with the glue being to the left of the film and the substrate to the right, (b) The relative concentration of Ar, C and O as a function of the position, (c) The fraction of sp² bonded carbon atoms (black solid line) and the density of the carbon (grey dashed line) determined from the plasmon peak positions. The 0 nm position represents the surface of the film.

Part 2: Multilayer a-C produced by varying the DC bias

Table 1 displays the varying level of DC bias between the layers from -150 V and -720 V in a cathodic arc with a continuous source. By alternating the bias between these two values, 10 layers were deposited. Figure 2(a-b) shows bright field and dark field X-TEM images and a diffraction pattern for the multilayer sample prepared by varying the DC bias. The diffraction pattern shows strong preferred orientation arcs associated with graphite-like regions aligned with their basal planes perpendicular to the plane of the layers. Dark field images taken with an aperture over these arcs showed that many of these graphite-like regions extend continuously across the low sp³ fraction layers (720 V) (see figure 2(b)). Figure 2(c) is an EELS linescan taken across the arrow shown in Figure 2(b), showing the fraction of sp² bonded carbon (black solid line) and the variation in density determined from the plasmon peak position (grey dotted line). The sp² fraction as a function of depth is measured by integrating the 1s to π* feature for a series of carbon K edge spectra taken through the coating. The layers deposited using 150 V were found to have a density in the vicinity of 3.20 g/cm³ as expected for a-C, while the 720 V layers had a lower energy plasmon peak corresponding to a density of approximately 2.5 g/cm³. From this plot it can be seen that the uppermost 20 nm of layer B (deposited using 720 V) has a higher density compared to the remainder of this layer. These results indicate that depositing a film at 720 V on top of a pre-existing film causes some modification to a depth consistent with the penetration distance of ions of that energy. This post deposition modification effect appears to increase the density (and sp³ fraction) of the low density carbon.

Layer	A	B	C	D	E	F	G	H	I	J
Bias (V)	-720	-720	-150	-720	-150	-720	-720	-150	-720	-150
Time (s)	120	120	120	120	60	60	60	60	60	60
Thickness (nm)	55	55	60	40	20	20	25	25	20	35

Table 1: Details of the a-C multilayer samples prepared by varying the DC bias. The film surface is the A layer, and the J layer is at the interface between the film and the substrate.

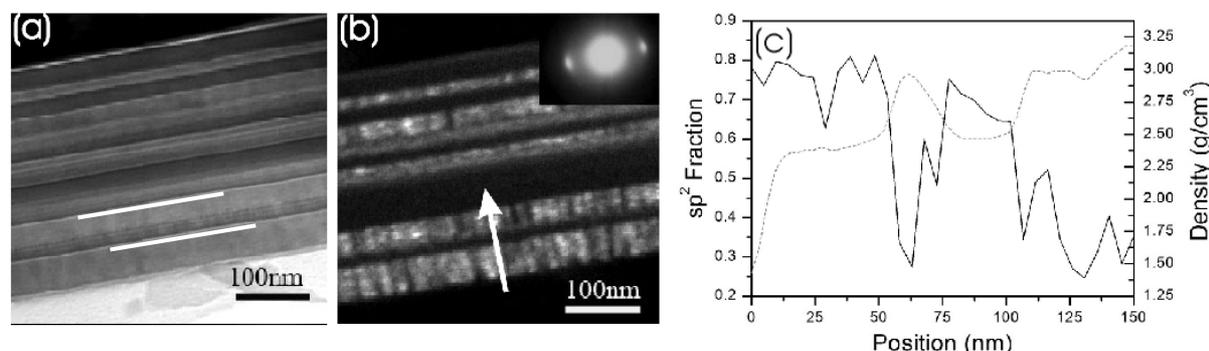


Figure 2(a-c): (a) X-TEM image of the multilayer carbon film prepared by varying the DC bias between -720 V (low density - light layer) and -150 V (high density - dark layer) as shown in table 1., with the surface of the film being at the bottom of the image and layer B being between the two white lines, (b) Dark field image taken from the {002} reflection from the graphitic arcs, (c) The fraction of sp^2 bonded carbon atoms (solid black line) and the density of the carbon (grey dotted line) determined from the plasmon peak positions.

Conclusion

We investigated the potential of synthesizing carbon films with modified surface structures using a combination of plasma deposition and processing. Using both a pulsed filtered cathodic arc in combination with PIII, the surface coating was modified from high sp^3 bonded carbon to high sp^2 bonded carbon to the depth of the ion implantation. Densification was observed using an energy modulated DC cathodic arc. High sp^2 bonded carbon was modified increasing the density of the layer. This effect is only observed after a pause in the deposition thus implying that cooling of the subsequently implanted film, surface relaxation and or a build up of contamination may be contributing factors.

References

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