THERMAL DEPOSITION OF AMORPHOUS CARBON

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ABSTRACT

A method for high rate deposition of amorphous carbon is described. An arc is operated in vacuum between a graphite anode and an auxiliary cathode. Constriction of the arc attachment to the anode is achieved through the graphite material properties, cooling and also magnetic confinement. The present method has been used to deposit films of hard carbon on substrates of glass, silicon and steel at a rate in excess of 1 μm per minute at more then 40 cm from the arc. Raman spectra of the deposited materials show a single wide peak, consistent with amorphous diamond. Numerical simulations of the arc and electrode configuration suggest that the combined effects of the plasma and the high evaporation rate from the anode tip result in the formation of a high pressure zone near the anode tip. The resulting steep pressure gradients induce a plasma jet directed towards the outer region of the arc at velocities more than 30 km/s, corresponding to energies for the plasma species of more than 50 eV and enabling deposition of sp3 rich films.

Keywords: amorphous diamond, plasma, films, deposition, high rate.

INTRODUCTION

Amorphous carbon films (a-C) can be deposited using various processes, including the filtered cathodic vacuum arc process and the pulsed laser arc process. A comprehensive review of the various available technologies for deposition of amorphous carbon films can be found in reference [1]. For most existing technologies, there are important limitations on the deposition rate and also on the deposition area. The pulsed laser arc process seems to provide the highest deposition rate at around 10 μm/hour [1], but on a small deposition area. We have developed a high rate process for deposition of amorphous carbon capable of depositing up to 60 μm/hour over a cylindrical area of more than 1 m² at 40 cm from the source. Details of the experimental method together with numerical simulations are presented in the following sections.
Figure 1: A schematic diagram of the arc and the electrodes

**EXPERIMENTAL SET-UP**

Figure 1 is a schematic representation of the arc and the electrodes arrangement. An arc is struck in a closed vessel at a pressure less than $10^{-4}$ torr between a water-cooled anode rod of graphite and a water-cooled cathode disk, also of graphite. The graphite anode rod is surrounded by a nozzle, preventing the arc from spreading over the cylindrical top section of the rod. A mechanical system moves the anode rod downwards to compensate for losses due to erosion from the tip. Also, a magnetic coil capable of producing a magnetic field of up to 100 Gauss is placed around the anode rod so that its axis coincides with the axis of the rod and the arc. The effect of the magnetic field produced by the coil is to constrict the plasma at the extreme tip of the anode. Under normal operating conditions without an external constricting mechanism, the arc would spread to cover a large area of the anode surface, resulting in a low evaporation rate from the anode and also a low energy for the evaporated species.

For the method presented here, the constriction of the arc at the tip of the anode results in a large increase in the rate of evaporation from the anode and the compounding effects of the plasma produce a large increase in the pressure in the plasma region immediately surrounding the anode tip. The resulting pressure gradients in the arc induce a high velocity jet directed towards the outer regions of the arc. The substrate is placed within the line of sight of the anode tip as shown in Figure 1. For a conducting substrate, a bias voltage may be applied to the substrate so as to influence the energy of charged species from the carbon plasma directed towards the substrate surface. We found that hard carbon films with high $sp^3$ content can be deposited on substrates of silicon, metals and also dielectrics without applying any bias voltage.

The arrangement described here has been used to deposit films of hardness in excess of 30 GPa and with $sp^3$ content of more than 50%. Also, films with a thickness of more than 2 μm have also been deposited.
Figure 2: A magnified view of a film surface; area 80μm x 100μm. The anode is a 6.4 mm diameter rod of graphite and the arc current is 175 A.

Figure 2 shows a micrograph taken using an atomic force microscope (AFM) for a film deposited on a Si substrate. It is seen that irregularities in the film surface are small at less than a few tens of nanometers. However, we find that there are occasional particulate inclusions with dimensions less than one micron. These particulates may be due to sources such as macroparticles from the cathode and/or dust from the internal walls of the arc vessel.

Figure 3 compares Raman spectra for the a-C film in Figure 2 and for the graphite materials of the anode rod. It is seen that for the film, there is a broad peak centered around 1488 cm⁻¹, typical for amorphous diamond [2]. As seen in Figure 3, graphite has two distinct peaks corresponding to the G and D bands. Furthermore, the sp³ content of the film has been determined using Electron Energy Loss measurements (EELS) for a film deposited on a KCl crystal. The measurements indicate an sp³ content of around 50%. As the effects of the plasma sheath at the interface between the non-conducting KCl substrate and the plasma limit transfer of ions to the film, it would be expected that films deposited on conducting substrates would have higher sp³ content.
Figure 3: A comparison of Raman spectra of a deposited a-C film (otherwise referred to as DLC) and the graphite anode material

**THEORETICAL CONSIDERATIONS**

It is generally accepted that deposition of a-C films with high sp³ content requires energetic species with energies around 30 eV. It is commonly considered that conventional anodic evaporation is somewhat similar to conventional evaporation processes and as such the evaporated species would have low energies. As mentioned before, for the process described here, films with 50% sp³ content have been deposited, suggesting that the carbon species emanating from the anode tip may have energies equivalent to those in cathodic vacuum arcs.

The physical characteristics of the process described in this paper have been investigated through numerical simulation of the arc and electrode configuration shown in Figure 1. A detailed description of the model as applied to atmospheric pressure arcs is presented in reference [3]. Here, we only outline the main features of the model and we present brief details about features specific to the vacuum arc configuration used here. The aim of the present calculations is only to predict the main characteristics and behavior of the carbon vapor emitted from the anode. The model is based on the dynamic conservation equations of mass, energy, radial momentum, axial momentum and current, and also the Maxwell equation and Ohm’s law. The calculation domain is divided into an anode region, an arc region and a cathode region. These regions are described relative to a cylindrical coordinate system assuming symmetry around the arc axis. The plasma is assumed to be in local thermodynamic equilibrium and appropriate boundary conditions are used at the edges of the calculation domain, taken to be a zone around the arc and the electrodes inside the arc chamber. For the present calculations, we take the shape of the anode and also the evaporation rate from experimental measurements and we use these measurements as input parameters for the code. Other inputs required by the code include the arc current, the electrode geometrical configuration and materials properties as a function of temperature. The material functions of the carbon plasma at pressures between $10^{-3}$ atm and 1 atm, at temperatures up to 25000 K, are also provided as inputs for the code. The output of the model includes 2 dimensional distributions of temperature, velocity,
pressure and electric potential. For the present calculations, we take the base pressure in the chamber to be $10^{-5}$ atm. As stated before, the aim of the present calculations is only to investigate the behavior of the plasma near the anode tip, and although the pressure used for deposition is less than for the calculation, the results would still be valid at lower base pressure as the calculations are limited to a small region around the arc and the electrodes where the pressure is relatively high, as discussed below.

![Temperature contours for a 175 A arc. The outermost contour is 3000 K and contour intervals are 2000 K.](image)

The assumption of equilibrium used in the plasma may not be valid at pressures less than 0.01 atm in the outer region of the arc chamber, where the mean free path for the plasma species may be comparable to the physical dimensions of the chamber. However, the results are valid near the anode tip where we find that the pressure can increase by several orders of magnitude to near atmospheric, making the plasma in the anode tip region somewhat similar to thermal plasma.

In Figure 4, we present calculated temperature contours in the arc and the electrodes for a current of 175 A. As mentioned before, the base pressure in the vessel is taken to be $10^{-5}$ atm. The maximum plasma temperature predicted here is more than 20000 K in the plasma region near the anode surface, suggesting that the plasma in this region is fully ionized. Also, for this region near the anode surface, the pressure increases to more than 0.5 atm, justifying the use of the equilibrium assumption there. The presence of the high pressure zone near the anode is due to the compounded effects of large evaporation from the anode tip, ohmic heating in the plasma by the arc current and the effects of the magnetic pinch force due to the magnetic field induced by the arc current. Because of the resulting very steep pressure gradients between the region near the anode tip and the outer regions of the arc, the plasma velocities calculated in the region near the anode tip exceeds 50 km/s in the vertical direction and more than 30 km/s in the radial direction. As the outer region of the arc and the chamber are at a very low pressure, it would be expected that the velocities of the plasma species would be conserved as they travel towards the internal walls of the chamber. The velocities
calculated above correspond to translational kinetic energies of more than 25 eV, which may explain the high sp$^3$ content mentioned above.

If the plasma effects are eliminated, we calculate velocities of around 2 km/s, corresponding to energy of around 0.25 eV. For this case without the effects of the plasma, the physical conditions would be equivalent to those for conventional evaporation or for an arc with a wide arc-anode attachment region. The energy of 0.25 eV calculated here is consistent with experimental observations showing that conventional carbon evaporation is inadequate for deposition of amorphous carbon films.

**SUMMARY**

A process for deposition of amorphous carbon films has been described. The process may be used for deposition of films over a very large area with a deposition rate exceeding 50 μm/hour. Raman analysis and EELS measurements suggest that the films are of amorphous diamond with an sp$^3$ content exceeding 40%. Modeling of the process suggests that the species evaporated from the anode tip have energies in excess of 25 eV, enabling successful deposition of high quality amorphous carbon films.

**REFERENCES**