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Production and characterisation of amorphic diamond films produced by pulsed laser ablation of graphite

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Abstract

Amorphic diamond (a-D) films have been grown by pulsed laser deposition using an ArF excimer laser to ablate material from a dense, ultrapure graphite rod. Deposition rates have been investigated as a function of incident pulse energy and of time. The resulting films have been analysed by scanning electron microscopy (SEM) and by laser Raman spectroscopy, and their electron emission characteristics tested. We confirm the potential of a-D films for use as a cold cathode material. © 1997 Elsevier Science S.A.

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1. Introduction

Pulsed laser deposition (PLD) is finding ever-increasing application as a route to producing thin films of a variety of materials with controlled composition and properties. In early studies of the PLD of high density graphite under vacuum conditions, Davanloo et al. [1] identified two generic forms of hydrogen-free carbon films. These they termed amorphic carbon (a-C) and amorphic diamond (a-D). Their structure and properties appeared to be determined primarily by the kinetic energies with which the ablated carbon particles impacted upon the target substrate. More recent work by this same group, using laser intensities in excess of 10^{11} W cm^{-2} together with an ancillary high current discharge within the small volume defined by the laser focus, has succeeded in depositing hydrogen-free carbon films at ambient temperatures and at growth rates of ca. 0.5 μm h^{-1} (over an area of 100 cm^2) with hardness (>80 GPa) approaching that of natural diamond. Davanloo et al. [2] favour the term nanophase (rather than amorphic) diamond for such material, which they argue to be a unique product of the energetic condensation of multiply charged carbon ions produced in the laser plasma. The combination of hardness, adherence, infrared transparency and comparatively low residual compressive stress exhibited by these films has led to the suggestion that they should find considerable application as abrasion- and corrosion-resistant coatings for infrared optical materials.

The electron emission properties of carbon films are another topic of great contemporary interest, particularly the so-called negative electron affinity (NEA) exhibited by hydrogen-terminated diamond surfaces such as are grown in typical chemical vapour deposition (CVD) processes [3–7]. For such materials the conduction band minimum lies close to, or even below, the vacuum level, so even small bias voltages can lead to efficient electron emission. Okano et al. [8] have recently reported electron emission from a nitrogen-doped CVD polycrystalline diamond film for bias field strengths, E, as low as 0.5 V μm^{-1}. Field-induced electron emission has also been observed from individual Si or Mo tips coated with synthetic high pressure diamond particles [9]. All of these types of diamond-based films are attracting considerable interest as potential cold cathode materials in diodes and field emission display devices [10].

Here we present a preliminary report of the use a high powered excimer laser operating at 193 nm (ArF) to prepare a-D films by PLD from a high density graphite target. Both continuous and patterned films were prepared in this way; the latter using TEM grids to mask selected portions of the substrate. The resulting films are characterised by optical and scanning electron microscopy, and by Fourier transform infrared (FTIR),

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laser Raman and Auger spectroscopy, and their electron emission properties investigated under vacuum by repeated cycling of an applied bias voltage over the range of (typically) 0–2 kV. Using sample–probe separations in the range 10–50 μm, we establish that these a-D films show a turn-on voltage of ca. 20 V μm^{-1} and emission current densities of the order of a few A cm^{-2} at bias voltages ca. 1 kV. For completeness, we draw attention to one other, very recent, related study of field emission from amorphous tetrahedrally bonded diamond-like carbon films (both with and without added nitrogen) grown by PLD methods [11].

2. Experimental

a-D films were produced on single crystal (100) silicon, on quartz and on NaCl substrates by ablation of a high density (2.09–2.23 g cm^{-3}), Ultra F (99.9995%) graphite rod (Johnson Matthey) in vacuum, using the 193 nm output of a Compex 205 excimer laser (Lambda-Physik) operating on ArF at a repetition rate of 10 Hz. The laser output was steered using two mirrors, irised to a spot 15 mm in diameter, then focused using a 20 cm f.l. plano-convex fused lens through an entrance window onto the target graphite rod. The rod, which is first polished with fine emery cloth and cleaned in a jet of compressed air, is mounted vertically and rotated and translated during an ablation run using a screw-thread mechanism and a 1.8°, four-phase stepper motor operating at half step mode, giving an angular frequency of 1.0 revs min^{-1}. The energy incident on the rod was typically 300 mJ $pulse^{-1}$ in a focal spot size of 0.5 mm^2 which, given the laser pulse duration (ca. 20 ns), equates to a power density at the target approaching 10^{10} W cm^{-2}. The focal volume and the ablated material (which appears as a divergent conical plume concentrated around the normal to the surface at this spot) are both clearly visible as a result of the accompanying optical emission. The former appears as an intense blue–white spot but the emission becomes progressively redder as the plume expands towards the target. The ablated material deposits on one of six suitably positioned substrates (each typically of area 1 cm^2) mounted behind a mask on a rotatable carousel. The substrates are cleaned successively with 2% ammonium bifluoride solution, deionised water and *iso*-propanol prior to use. The target–substrate distance is adjustable in the range 2–5 cm. Plan and side views of the vacuum chamber are shown schematically in Fig. 1. It is equipped with Pirani and Penning gauges, a port for viewing the ablation process and three additional (spare) flanges, and is maintained at ca. 10^{-6} Torr using an Edwards 100 mm Cryo-Diffstak diffusion pump in series with a two-stage rotary pump.

Field emission tests were carried out in an evacuated glass bell jar. The sample under test is mounted on an insulated and translatable glass support and biased relative to a (fixed) cylindrical anode probe 3 mm in diameter. The surface–probe separation is user-adjustable via a micrometer and I–V curves are measured by ramping the bias voltage up and down between 0 and ca. 1.5 kV (typically in 20 V steps) whilst measuring any emission current with a multimeter. The emission measurements were fully automated, with a PC controlling both the power supply and data logging (both I and V).

3. Results and discussion

Fig. 2 shows an SEM image of a 95 ± 5 nm-thick a-D film on Si(100) obtained by PLD of a high density graphite rod for 20 min using an ArF laser delivering 250 mJ pulses at a repetition rate of 10 Hz. This shows the film to be generally nanophase, uniform and smooth, but also reveals the presence of occasional larger, randomly distributed sputtered particles that seemingly are endemic in such films [2,12]. Analysis of cross-sectional images such as that displayed in Fig. 2 enables construction of plots of film thickness, d, as a function of laser pulse energy and time duration of the PLD process. Representative sets of results are shown in Fig. 3(a) and 3(b). Such measurements are somewhat complicated by the fact that some unwanted deposition occurs on the inside of the entrance window, with the result that its transmission gradually declines with time. Nonetheless the trends are clear: Fig. 3(a) shows that there is a threshold fluence (energy per unit area) below which no ablation occurs; thereafter the deposition rate increases with incident fluence but ultimately starts to plateau at the highest pulse energies used in the present work, whilst Fig. 3(b) demonstrates that, at constant incident fluence (corresponding to 360 mJ $pulse^{-1}$ in the present case), the deposition rate is essentially constant with time. It is worth mentioning, however, that attempts to deposit yet thicker films using still longer deposition times were unsuccessful; the a-D films were found to delaminate, presumably because of the accumulated compressive stress within the film. As Fig. 4 shows, the typical as-grown a-D film shows a characteristic broad, asymmetric Raman profile when excited using a 632.8 nm He–Ne laser, peaking around 1495 cm^{-1}. Fig. 5 shows an SEM image of a patterned a-D film on silicon; note the good (< 1 μm) edge resolution. Such selective area deposition of a-D is readily achievable simply by affixing a suitably pre-patterned mask (here a Cu TEM grid) to the substrate prior to PLD.

The main thrust of this work concerns the electron emission properties of such a-D films. I–V curves were measured for several different samples at a number of sample–probe separations in the range 10–50 μm. For any given sample, the voltage was first ramped from

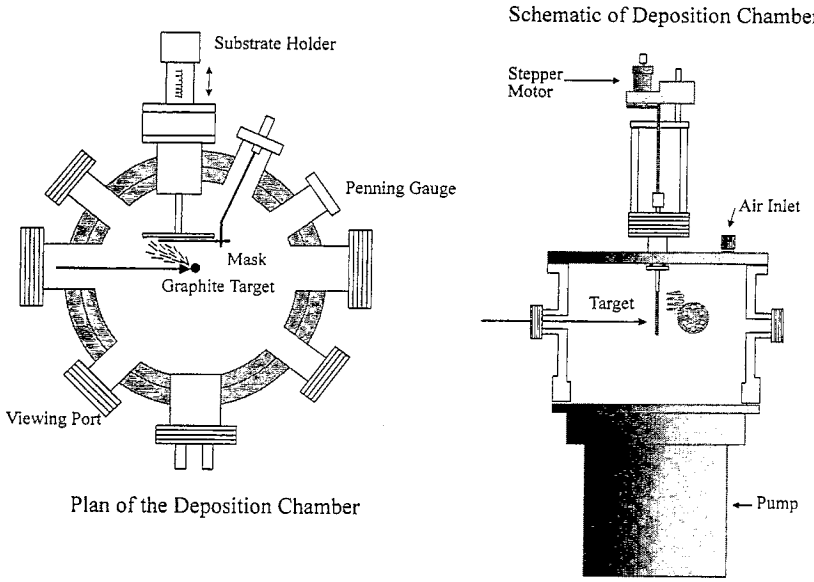

Fig. 1. Plan and side views of the ablation chamber.

Fig. 2. SEM image of an a-D film on Si(100) obtained by PLD of a high density graphite rod for 20 min using an ArF laser delivering 250 mJ pulses at a repetition rate of 10 Hz.

zero up to ~1.5 kV in 20 V steps and then stepped back to zero; this up–down cycle was then repeated several times. For all films investigated, the emission current measured on the "down" leg was found to be consistently larger (for a given bias voltage) by some 25%, presumably as a result of some surface conditioning. Fig. 6(a) shows a representative set of results for a 150 nm-thick a-D film on silicon. These curves were each measured whilst the bias voltage was being ramped down, using 10, 20 and 30 μm sample–probe separations, respectively. Surface conditioning also affects the emission current observed on subsequent cycles. For any given sample–probe separation the emission current (for a given applied voltage) was found to vary by as much as 25% from one run to the next; this variation can

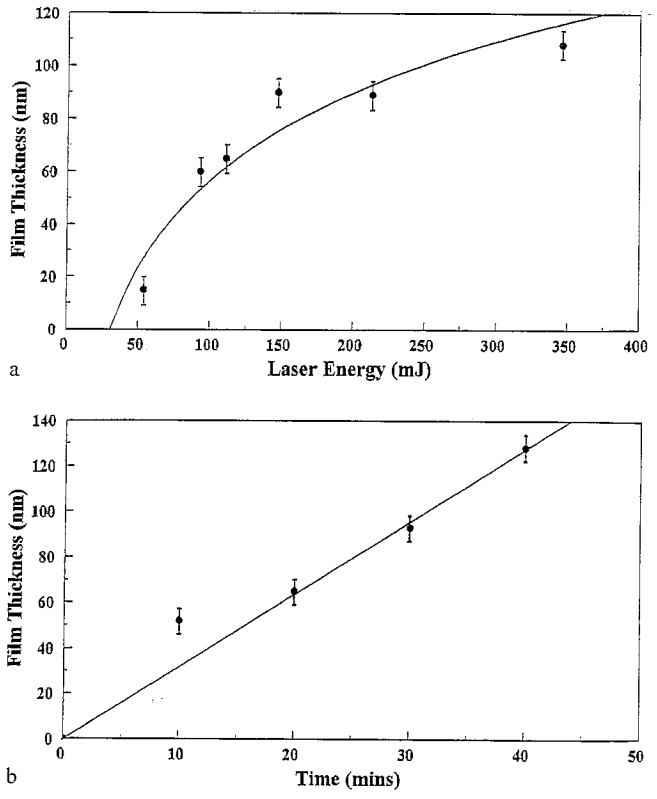

Fig. 3. Representative plots showing the variation of film thickness with (a) laser pulse energy and (b) duration of the PLD process. Each of the data points shown in (a) was obtained by irradiating the graphite rod for 15 min at the specified energy and a repetition rate of 10 Hz, whilst all data shown in (b) were obtained using 360 mJ pulses, again at a 10 Hz repetition rate.

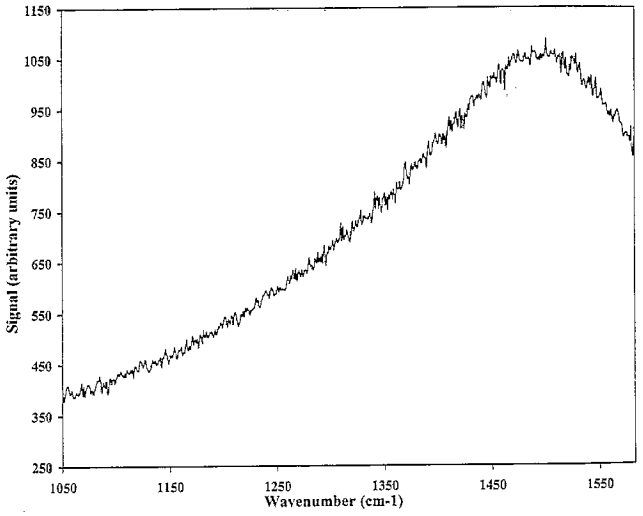

Fig. 4. Laser Raman spectrum of an a-D film on Si(100) obtained using a 632.8 nm He–Ne laser.

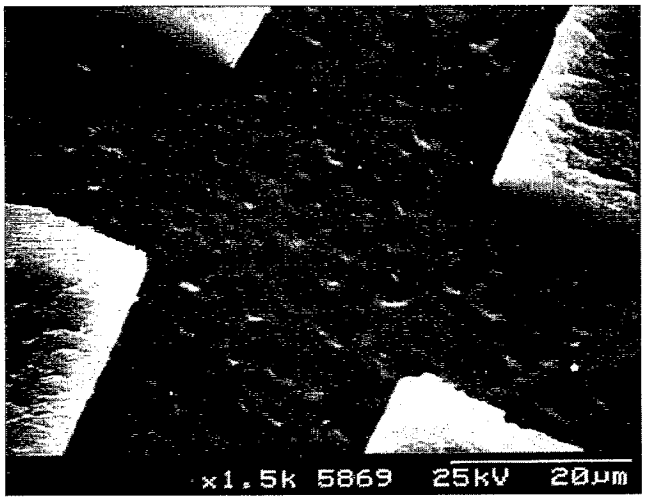

Fig. 5. SEM image showing a small portion of a patterned a-D film on Si(100) produced by PLD through a TEM mask affixed to the substrate.

manifest itself as an increase or decrease in emission efficiency, depending on the particular sample under investigation. The emission stability was investigated briefly. In all cases the emission current was found to drop, typically by a factor of two, within ca. 2 min but thereafter to decline much less steeply. The turn-on voltage is observed to scale with the sample–probe separation, having a value ca. 20 V µm^{-1}. Such field emission data are traditionally analysed in terms of the Fowler–Nordheim theory describing emission via barrier tunnelling. The Fowler–Nordheim equation can be written in the form [7]

$$I = k\left(\frac{\beta V}{d}\right)^2 \exp\left(\frac{-6530 d\phi^{3/2}}{\beta V}\right) \quad (1)$$

where k is a constant related to the emission area, V

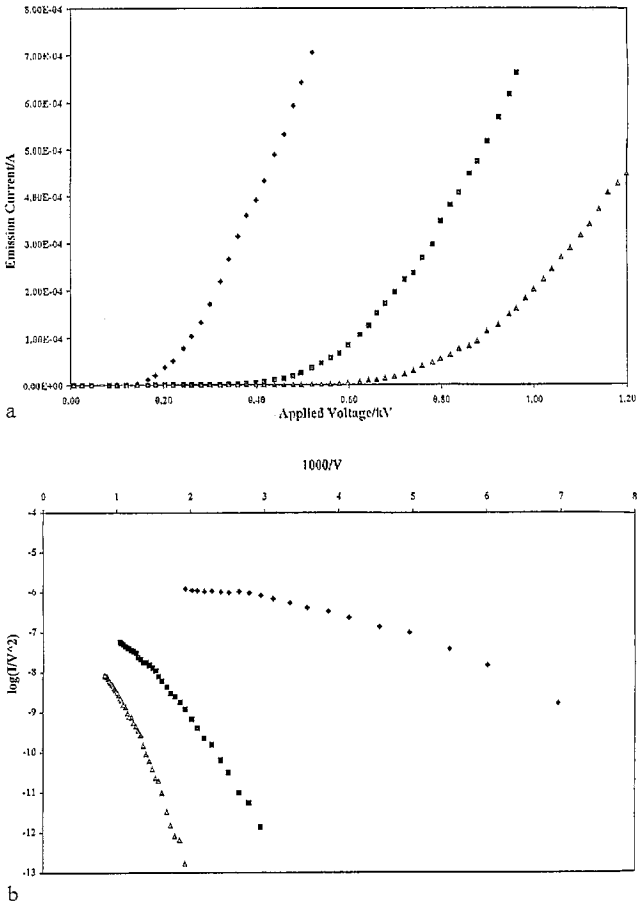

Fig. 6. (a) I–V curves for a 150 nm-thick a-D film on Si(100) obtained using 10 (◆), 20 (■) and 30 µm (▲) sample–probe separations. (b) Fowler–Nordheim plots [$\log_e(I/V^2)$ versus V^{-1}] of the data shown in (a).

is the applied bias voltage (in V), d (µm) is the sample–probe separation, ϕ (eV) is the barrier height, and β is the geometric field enhancement factor. Fig. 6(b) shows plots of $\log_e(I/V^2)$ versus V^{-1} for the three I–V data sets displayed in Fig. 6(a). None is strictly linear but the best-fit straight line through each provides some indication of the size of $\phi/\beta^{2/3}$ and thus an effective barrier height. The values so derived are ~0.05, ~0.10 and ~0.12 eV when using nominal 10, 20 and 30 µm sample–probe separations, respectively. Quantifying ϕ, the work function of the as-grown a-D films, requires a value for the geometric enhancement factor β. In the absence of other information, β is often assumed to be unity [7]—the value appropriate for a uniformly flat film. Such an approximation is likely to be least valid for small d (e.g. 10 µm) given the occasional lumps embedded in the surface (recall Fig. 2). This may explain the low value of $\phi/\beta^{2/3}$ deduced using the smallest sample–probe separation and suggests that ϕ is $\geq$0.1 eV. SEM images, such as that shown in Fig. 7, also allow an estimate of the emission current density since the conditioned surface shows a markedly different

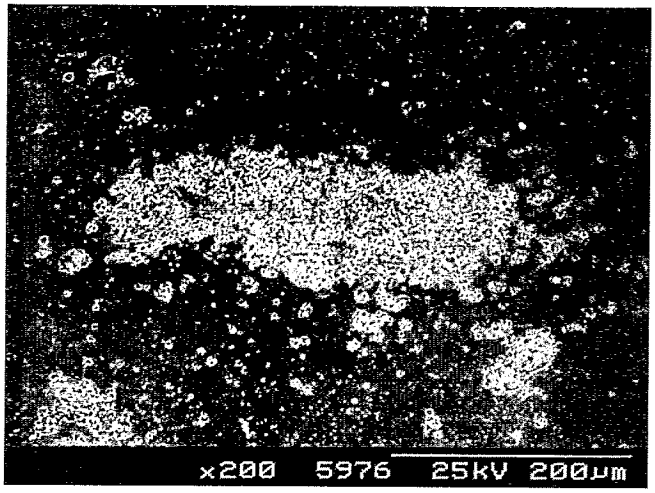

Fig. 7. SEM image of the surface of a 120 nm-thick a-D film (prepared under very similar conditions to that shown in Fig. 2) after electron emission testing. Note the very different morphology of the conditioned surface.

morphology and response to electron irradiation. Thus we establish that the measured emission current emanates from an area of $\sim 3 \times 10^4$ µm^2 and that the emission current density can be ca. 2–5 A cm^{-2} at bias voltages ca. 1 kV.

In conclusion, we have demonstrated that hydrogen-free amorphic diamond films produced by 193 nm PLD of a hard ultrapure graphite target represent another class of carbon film meriting serious consideration as a cold cathode material. We are presently conducting analogous experiments on carbon films ablated from other carbon-rich target materials, whilst planned studies will address the possibility of doping the growing a-D films in situ and thereby altering their electrical properties.

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