Investigation of hydrogenated amorphous carbon (a-C:H) films produced by ArF (193 nm) laser ablation of poly(methyl methacrylate)

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Abstract

Hydrogenated amorphous carbon (a-C:H) films have been deposited on Si, quartz and NaCl by pulsed 193-nm laser ablation of poly (methyl-methacrylate) under vacuum. Wavelength dispersed studies of the visible emission accompanying the ablation plume show it to be dominated by the Balmer series of atomic hydrogen. The extent of the emission plume suggests that electronically excited H atoms are created in flight, probably via collisions between much larger particles produced in the primary ablation process. Such a picture accords with the results of microcombustion analysis and infra-red transmission spectroscopy, both of which indicate that, compared to the original target material, the deposited a-C:H film is deficient in H (and O). © 1998 Elsevier Science S.A.

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1. Introduction

Pulsed laser ablation (PLA) of a suitable target material in vacuo is now an established route for forming carbon containing films, the detailed composition and properties of which depend sensitively upon the precise parameters employed in their preparation. Of the various possible target materials, graphite has received most attention, at ablation wavelengths ranging from the deep ultraviolet (193 nm) to the near infra-red (1064 nm) [1–3]. The mass distribution and the kinetic energies of the ablated material, and its dependence on ablation wavelength, fluence and intensity, have been probed by time-of-flight (TOF) mass spectrometry [4,5], whereas electronically excited species in the ablation plume have been investigated via optical emission spectroscopy (OES) [6–10]. Condensation of these high energy carbon ions, atoms and clusters on to a substrate results in the formation of a diamond-like-carbon (DLC) film with a high sp^3:sp^2 ratio. Such hydrogen-free DLC films with a high proportion of tetrahedral bonding are often termed amorphous carbon (a-C) films [2]. These films are of interest because they can be deposited on a very wide range of substrate materials, at room temperature,

and because of the combination of properties that they exhibit, e.g. high hardness (~ 30 GPa) and density (2.5–3.0 g cm^{-3}), chemical inertness, good electrical resistivity and broad IR transparency [2]. The first reports of the electron emission properties of such a-C films are now starting to appear [11–13], but much remains to be done before we have a clear understanding of the way in which the various film characteristics correlate with the composition and properties of the ablation plume, or how they are influenced by factors such as substrate temperature, the application of a DC bias, or the introduction of foreign gases.

PLA of graphite in the presence of hydrogen offers one means of depositing hydrogenated amorphous carbon (a-C:H) films. PLA of polymeric targets like poly(methyl methacrylate), $[C_5O_2H_8]_n$, or polycarbonate, $[C_{13}O_3H_{14}]_n$, under vacuum [14,15], or in a low pressure of H_2 [16], provides another. a-C:H films offer many of the same attractive properties as hydrogen-free a-C films and, in addition, allow variation of the optical band-gap simply by varying the H content [16,17]. The relative importance of thermal versus photochemical driven material removal mechanisms in the PLA of organic polymers has been a matter of longstanding debate [18,19]; recent TOF measurements of the neutral fragments resulting from pulsed irradiation of a poly (methyl methacrylate) [PMMA] target at 248 nm support

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a so-called incubation model in which single photon absorption by the carbonyl group (the chromophore) is the precursor to side-chain scission [20]. The applicability of this model over a wide range of ablation wavelengths remains to be tested.

Here, we present results relating to various aspects of the PLA of poly(methyl methacrylate) at the ArF excimer laser wavelength, 193 nm, in vacuo, as a precursor to similar studies involving graphite targets. Specifically, we use OES to probe the spatial and velocity distributions of the excited H atoms produced in the ablation process, and investigate the as-grown a-C:H films by scanning electron microscopy (SEM), by microcombustion analysis and by IR spectroscopy.

2. Experimental

Much of the experimental apparatus and procedure has been described previously [13]. An excimer laser (Lambda-Physik, Compex 201) charged with ArF (193 nm) and operating at, typically, 10 Hz is focused using a fused silica lens (f.l. = 27 cm) on to a target mounted in a stainless steel vacuum chamber maintained at $\sim 10^{-6}$ Torr by a 100-mm diffusion pump plumbed in series with a two-stage rotary pump. In the earlier experiments, the target took the form of a cylindrical rod, suspended vertically from the lid of the chamber and rotated and translated via a stepper motor so as to ensure that each ablating laser pulse strikes a fresh surface, close to tangentially. The shot-to-shot reproducibility of such an arrangement is extremely sensitive to any eccentricity in the rod rotation. Thus, the more recent experiments have employed the more traditional side mounted, rotating disc target arrangement [14], with the laser incident at 45° and the substrate aligned parallel to the front face of the target at a user selectable distance in the range of 30–50 mm. The energy incident on the target was typically ~ 300 mJ pulse^{-1}, in a focal spot $\sim 2 \times 0.5$ mm^2.

Both the focal volume itself and the ablation plume (which appears as a divergent conical plume normal to the target surface) are clearly visible as a result of the accompanying optical emission. The emission was sampled using a quartz-fibre optic bundle (Oriel) positioned so as to view (through a lens/iris combination and appropriately positioned quartz observation ports) both along, and perpendicular to, the surface normal. The other end of the fibre bundle butts up against the entrance slit of a 0.5 m monochromator (Spex 1870) equipped with a 2400 lines mm^{-1} holographic grating. Light emerging from the exit slit is detected with a red-sensitive photomultiplier, the output signal from which is sent via a boxcar and a V/F converter to a PC where spectra are recorded and stored for subsequent analysis. Spectra were calibrated by directing the output from a

neon hollow cathode lamp through a separate quartz fibre on to the monochromator entrance slit and thereby recording simultaneously an appropriate part of the well documented emission spectrum of Ne.

a-C:H films were deposited on various substrates, including single crystal silicon, quartz and NaCl each ~ 1 cm^2 in area. The former substrates were cleaned successively with deionised water and iso-propyl alcohol and dried prior to use, whereas the NaCl substrates were simply wiped with CHCl$_3$ prior to use. Microcombustion analysis (~ 0.5-mg samples) was used to determine the C:H ratio (and, by mass conservation, the O content) both in the starting PMMA target and in the deposited films. Film morphology and growth rates were investigated by SEM analysis, whereas Fourier transform IR transmission spectroscopy was used to provide insight into the nature of the residual C–H bonding in the deposited material.

3. Results and discussion

OES studies of the plume accompanying PLA of graphite at UV wavelengths reveal contributions from electronically excited neutral C atoms and C$_2$ species, and a range of singly, doubly and even triply charged carbon ions, many of which are born with very high (10–100 eV) kinetic energies [6–10]. In contrast, UV PLA of PMMA exhibits an intense blue–white plasma in the immediate vicinity of the irradiated surface area and a divergent red plume expanding around the surface normal. This emission is dominated by the Balmer series of atomic hydrogen and, in particular, by the $n = 3 \rightarrow n = 2$ Balmer-α emission at 656.3 nm. Fig. 1 shows two representative H Balmer-α emission lineshapes recorded using the rotating disc PMMA target viewing (a) along and (b) perpendicular to the expanding plume (and thus to the surface normal). The former signal is actually stronger because of the greater depth of plume sampled, but the signal to noise is degraded by shot to shot fluctuations in the intensity of the focal spot, which falls within the viewing region. The lineshape in Fig. 1(a) is biased towards the blue, consistent with the recoiling H atoms having an anisotropic velocity distribution, skewed towards the observer. The wavenumber calibration and dispersion are obtained by arranging for the complete scan to span the known Ne transitions at 15 149.74, 15 302.95 and 15 364.94 cm^{-1}; these lines also provide a ready measure of the instrumental lineshape function (see inset). The second horizontal scale in Fig. 1 indicates the H atom velocities (v_z) in the direction of the observer implied by a given frequency shift from the transition line centre, in the limit that we neglect any instrumental contribution to the measured linewidth. Obviously, such an approximate analysis overestimates the spread of recoil velocities, but already, it is clear
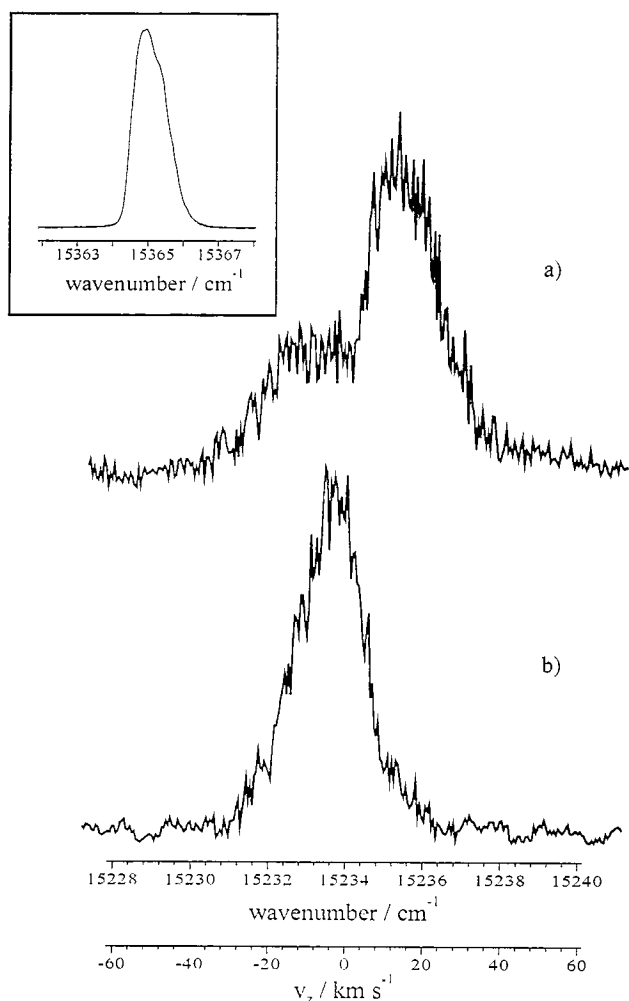
Fig. 1. H Balmer-α emission lineshapes recorded (a) looking towards the laser focal volume along the surface normal and (b) perpendicular to the suface normal, with the optical fibre centred at $d=6$ mm. The inset, which shows the 15 364.94 cm^{-1} Ne line recorded using the same (30 μm) monochromator slitwidths and plotted on the same wavenumber dispersion, provides a measure of the instrumental lineshape function.
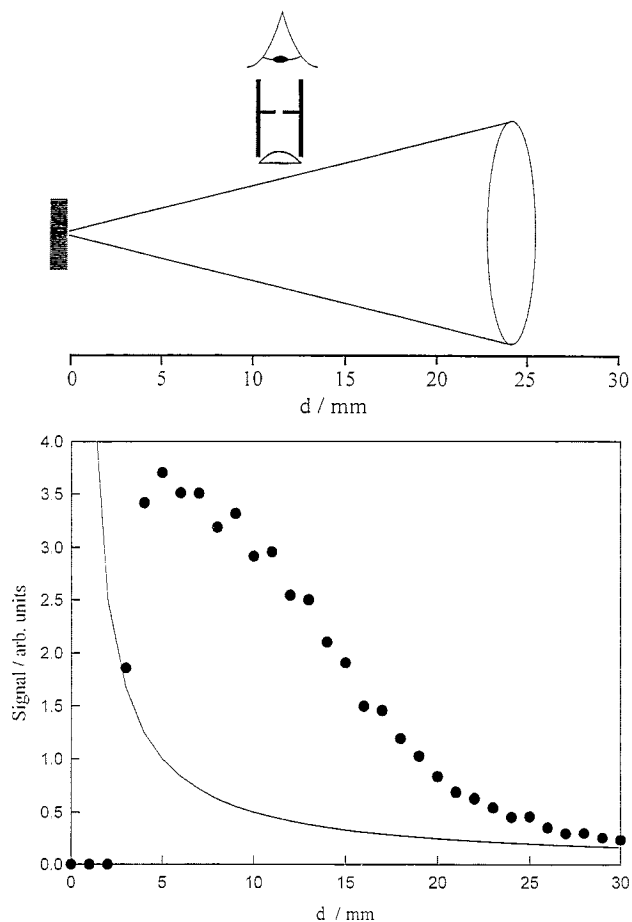

Fig. 2. H Balmer-α ($n=3 \rightarrow n=2$) emission intensity viewed from above (see schematic), measured as a function of d, the distance from the target surface along the surface normal. The solid line illustrates the d^{-1} dependence expected for the total density of ablated material in the viewing column.

from the size of the Doppler shifts that these H($n=3$) atoms arising in the UV PLA of PMMA have rather modest recoil velocities.

Fig. 2, which shows a plot of the H Balmer-α emission intensity measured for ablation of the rotating PMMA disc, viewed from above, as a function of distance (d) along the surface normal, represents a first attempt at obtaining spatially resolved H* concentrations. Spatial resolution was achieved by positioning the quartz fibre at the end of the lens/iris combination in a translatable tube mounted externally to the observation windows, thereby restricting the viewing zone in the vicinity of the plume to a column ∼2 mm in diameter. The ablation plume has a greater horizontal than vertical divergence, but for now, it is sufficient to assume that the total number density in the viewing column will fall off as ∼d^{-1}. However, and notwithstanding our limited spat-

ial resolution (which is reflected by the observation of some emission when the fibre optic is centred at $d<0$), the measured H* emission intensities show a very different dependence, peaking at $d>0$ and extending to the edge of the viewing zone ($d>30$ mm). The mean lifetime of H atoms in their $n=3$ state is ∼10 ns [21]. Such an H atom would require a velocity of ∼10^6 m s^{-1} in order to travel even 10 mm within one radiative lifetime. This velocity would correspond to a ∼50 cm^{-1} Doppler shift, in marked contrast to experimental observation (Fig. 1). One possible explanation for such persistent H Balmer-α emission might be radiative (or collisional cascade) of population from H atoms formed in higher n,ℓ quantum states. This seems unlikely given our observation of a similar d dependence for the H Balmer-δ ($n=6 \rightarrow n=2$) emission intensity. Rather, we propose that the H* species must be created 'in flight', probably as a result of collisions between ablated particles (electrons, ions and/or neutrals) within the expanding plume, but also perhaps from unimolecular decay of internally hot ablated particles. Future time-

resolved studies of the plume emission should help clarify this process further.

We now turn attention to the deposited a-C:H films themselves. Fig. 3 shows SEM images (plan and cross-section) of an a-C:H film deposited on Si, which bears a close resemblance to the heterogeneous morphology reported in previous studies of a-C:H films formed by PLA of polycarbonate targets [14,15]. The cross-section analyses provide a measure of the deposition rate, ~ 0.1-nm pulse^{-1} (285 mJ incident pulse energy), i.e. about 10 times faster than that observed for a-C film growth from PLA of a dense graphite target under otherwise similar experimental conditions [13]. Microcombustion analysis revealed a marked reduction in the relative H and O content in the deposited film (C:O:H = 77:19:4 by weight, cf. 60:32:8 expected, and measured, for the PMMA target material). A similar H atom deficiency was deduced via elastic recoil spectroscopy measurements of the a-C:H films growth by PLA of polycarbonate targets [15] and would be consistent

with the collisional ejection of light H atoms as the ablation plume evolves from target to substrate as indicated by the present OES results. Even if they strike the substrate, such light H atoms are unlikely to be accommodated and incorporated within the film; more probably, they will recombine with other slow-moving atomic or molecular fragments, form stable gas phase species and be evacuated from the chamber. Such a view is further reinforced by Fig. 4, which compares the transmission IR spectra of a ~ 500-nm-thick a-C:H film deposited on NaCl following PLA of a PMMA disc target and of a thin wafer of the PMMA target material itself. Both show the expected characteristic absorption features at $\sim 2950 \, cm^{-1}$, $\sim 1730 \, cm^{-1}$ and (not shown) $\sim 1200 \, cm^{-1}$, traditionally associated with, respectively, sp^3 C–H, C=O and O–CH$_3$ stretching vibrations [15]. However, a more careful inspection of these two spectra and, in particular, of the relative intensities of the two higher wavenumber features indicates relatively less C–H absorption in the deposited film (consistent with preferential H atom loss during the PLA process). The FTIR spectrum of the a-C:H film also shows a weak 'new'
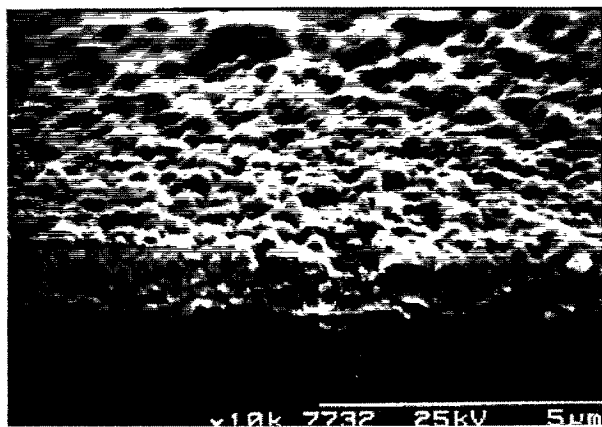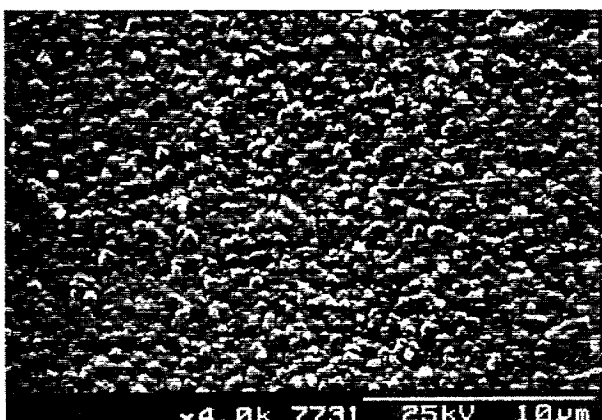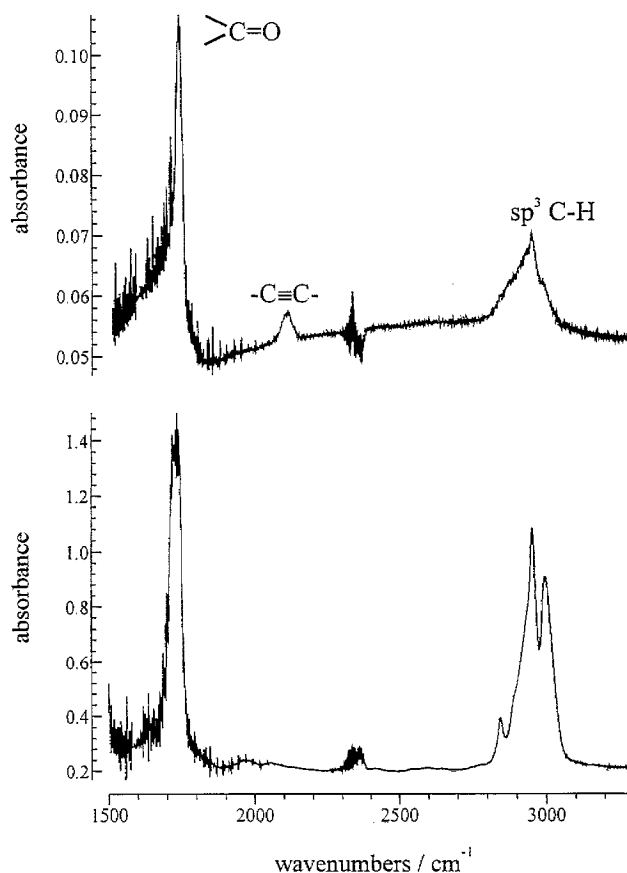

Fig. 3. Top view and cross-sectional SEM images of an a-C:H film on Si(100) obtained by PLA of a PMMA disc target for 15 min using 285-mJ pulses of 193-nm radiation (10-Hz repetition rate).

Fig. 4. Comparison of the FTIR spectra of a ~ 500-nm-thick a-C:H film on NaCl produced by PLA of PMMA in vacuo (top) and that of the original target material (below). Key spectral features are indicated.

peak at ∼2100 cm^{-1} that may indicate the presence of some C≡C triple bonding in the deposited material.

In conclusion, a-C:H films have been deposited on Si, quartz and NaCl by pulsed 193-nm laser ablation of PMMA under vacuum. Analysis of the visible emission accompanying the ablation plume reveals a dominant contribution from the Balmer series of atomic hydrogen. Investigations of the Doppler lineshape of the Balmer-α emission—which shows the H* atoms to have rather modest velocities—when combined with observations of the spatial extent of this emission plume, suggest that most of the excited H atoms must be created in flight, probably via collisions between larger particles produced in the primary ablation process. Such a picture accords with the results of microcombustion analyses and FTIR spectroscopic studies of the deposited a-C:H material, both of which indicate that the deposited film is relatively deficient in both H and O. Future studies will address the time evolution of the ablation plume and explore the field emission characteristics of such a-C:H films grown by PLA of organic polymers.

Acknowledgement

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