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Growth of anthracene thin films by matrix-assisted pulsed-laser evaporation

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ABSTRACT Thin films of anthracene ($C_{14}H_{10}$) have been grown by matrix-assisted pulsed-laser evaporation. Frozen solutions of 2 wt % anthracene (solute) in ortho-xylene or in chloroform were used as targets and were irradiated by a frequency-quadrupled Nd:YAG laser (266 nm). The deposited films were studied by the complementary use of infrared absorption and photoluminescence emission. The vibrational bands and fluorescence emission of bulk anthracene were clearly identified in the films. This means that the organic molecules were not modified by photochemical reactions during the laser irradiations, despite the strong absorption of anthracene at 266 nm. Among the growth parameters, the laser fluence was found to be critical in order to avoid the fragmentation of the anthracene molecules. The results show that matrix-assisted pulsed-laser evaporation is suitable for growing thin films of organic materials even if they absorb at the irradiating wavelength.

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1 Introduction

Organic materials are increasingly attracting attention as a low-cost and large-area alternative to inorganic materials for a wide variety of applications. Chemical, optical and electronic properties of some organic conjugated materials make the design of devices based on organic thin films, such as field effect transistors [1, 2] and light-emitting diodes [3, 4], conceivable. As a result, various chemical and physical deposition methods have been used to obtain thin films of organic compounds [5, 6]. Pulsed-laser deposition (PLD) has thus been employed for growing thin films of polymer and non-polymer organic materials [7, 8]. Nevertheless, significant changes in chemical nature of PLD-deposited organic compounds are generally observed with respect to the bulk target material.

Recently, matrix-assisted pulsed-laser evaporation (MAPLE) has been developed at the Naval Research Laboratory [9]. MAPLE [10] allows the deposition of homogeneous films of low- and high-molecular-weight organics without physicochemical damage. This method has been used to grow

chemo-selective polymers, carbohydrate molecules, carbon nanotube composites and biocompatible materials [10–12]. Briefly, the MAPLE process involves the laser irradiation of a frozen solution of a molecule (solute) in a volatile solvent. In the ideal case the laser energy is only absorbed by the solvent, which is evaporated (and then is pumped away), and induces the desorption process by driving away the molecule which is non-absorbing at the laser wavelength. The absence of absorption by the organic molecules avoids therefore the bond dissociation and their chemical modification.

In principle, organic molecules are deposited by MAPLE without damage solely when their absorption at the laser wavelength is negligible. It is important to know whether this fact is a severe limitation for this technique or if this obstacle can be overcome by means of the precise control of laser fluence in the case of organic molecules that absorb at the laser wavelength. In this paper, we report on the growth and preliminary characterisations of thin films of anthracene ($C_{14}H_{10}$) deposited by the MAPLE method. Anthracene is a polycyclic aromatic hydrocarbon compound consisting of three benzene rings, and displays luminescence in the visible region (blue light) with a high fluorescence yield. This molecule is a challenging example for studying the possible limitations of the MAPLE technique. Indeed, frozen anthracene solutions have been irradiated by a frequency-quadrupled Nd:YAG laser emitting at a wavelength of 266 nm, where anthracene molecules exhibit a noticeable absorption [13] (molar absorptivity: $\epsilon \approx 10^3 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$). It is worth noticing that because of this absorption in the UV wavelength domain, anthracene has been used as a photosensitiser to induce the growth of thin polystyrene films by PLD, using anthracene-doped polystyrene targets [14]. Therefore, the formation of anthracene thin films by the MAPLE method should demonstrate the potential of this growth method for a broad range of organic materials. The results show that a careful optimisation of the laser fluence allows the formation of anthracene thin films displaying the functional properties of the bulk organic material, despite the strong absorption at the laser wavelength used.

2 Experimental

Solutions of 2 wt % anthracene (99.9% pure) in ortho-xylene ($(CH_3)_2C_6H_4$) or in chloroform ($CHCl_3$) were

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used as targets. Prior to deposition, the chamber was evacuated to a background pressure of 10^{-6} mbar. A frequency-quadrupled Nd:YAG laser (266 nm, 5 ns, 10 Hz) was used to irradiate the solutions, which were frozen at around -70°C . The substrates were placed at a distance of 35–40 mm from the target. Anthracene thin films were grown either on double-side polished crystalline (100) silicon or on quartz substrates kept at -30°C to avoid the incorporation of solvent molecules.

The surface morphology of the films was studied by atomic force microscopy (AFM) using a Nanoscope IIIa from Digital Instruments (Université d'Evry). AFM images were recorded in the tapping mode to avoid mechanical damage to the organic material. The chemical structure of the films (bonding) was evaluated from their infrared absorption at room temperature using a BOMEM Fourier transform spectrometer. The signal was detected with a broadband mercury cadmium telluride detector. The spectra were obtained with a resolution of 4 cm^{-1} and the absorbance was $\ln(I_0/I)$, where I_0 corresponded to the reference bare silicon substrate. The luminescent behaviour of the anthracene films was also studied, using a N_2 pulsed laser (10 Hz, 1 ns, energy $< 25\text{ }\mu\text{J}$) emitting at 337 nm to excite the S_0 – S_1 anthracene transition. The samples were attached to a He circulation cryostat and were cooled to 10 K. The fluorescence light was focused on the entrance slit of the spectrometer (Jobin–Yvon Triax 190) and the dispersed light was detected by a LN_2 -cooled 1024×256 -pixel open collector CCD array. The estimated resolution was 0.5 nm for a slit width of 25 μm .

3 Results and discussion

Figure 1a shows a typical AFM image recorded on a 400-nm-thick film deposited by the irradiation of a frozen anthracene–ortho-xylene solution at a fluence of 0.2 J cm^{-2} . The surface morphology appears as the random stacking of aggregates or clusters. Figure 1b shows the error signal for the AFM image. It corresponds to the derivative of the topographic image and is therefore very sensitive to changes in surface height [15]. This error signal leads to the determination of the in-plane mean size of the aggregates, namely 100 nm. Thus, the MAPLE process permits the growth of reasonably continuous films.

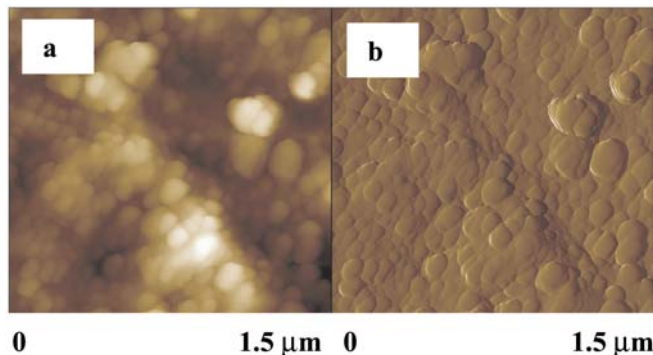


FIGURE 1 **a** AFM image of a 400-nm-thick anthracene film deposited on Si by the irradiation of an anthracene–ortho-xylene solution at a fluence of 0.2 J cm^{-2} under 10^{-4} mbar pressure. **b** The error signal of the tapping-mode image

The chemical characterisation of these films has been carried out by IR spectroscopy. Figure 2 shows the FTIR absorption spectra of anthracene films grown under different experimental conditions. The spectra of the films obtained by the irradiation of anthracene–chloroform solution at 0.04 J cm^{-2} (Fig. 2a) and anthracene–ortho-xylene solution at 0.2 J cm^{-2} (Fig. 2b) present IR bands at the same positions and with the same intensity ratios. Differences in absolute intensity for the two films are due to differences in film thickness. The similarity between both spectra suggests that the solvents used to prepare the targets do not play a dramatic role on the properties of the grown films. The three strongest bands of the spectra are found at 725, 884 and 957 cm^{-1} . They correspond to out-of-plane vibrations of the four free adjacent hydrogen atoms of the anthracene molecule. Other bands of much weaker strength occur at 999, 1148, 1317, 1450, 1540 and 1620 cm^{-1} , which are currently attributed to ring stretching vibrations, and also at 3049 cm^{-1} , which is attributed to $=\text{C}-\text{H}$ stretching vibrations. The comparison with the reference spectrum of pure bulk anthracene [16] shows an excellent agreement with the expected positions of the absorption bands of anthracene molecules. This correlation holds even for the strongest bands, found at 725 (expected value: 726 cm^{-1}) and 884 cm^{-1} (same position as expected), which could change considerably with even small changes in molecular structure [17]. Moreover, no bands corresponding to amorphous carbon or other related materials have been observed. These results lead us to conclude that the anthracene molecules have been collected on the substrate without appreciable physicochemical damage. Thus, non-damaged anthracene films can be deposited by the MAPLE method even if the absorption of the anthracene molecules at the irradiating wavelength is not negligible at all.

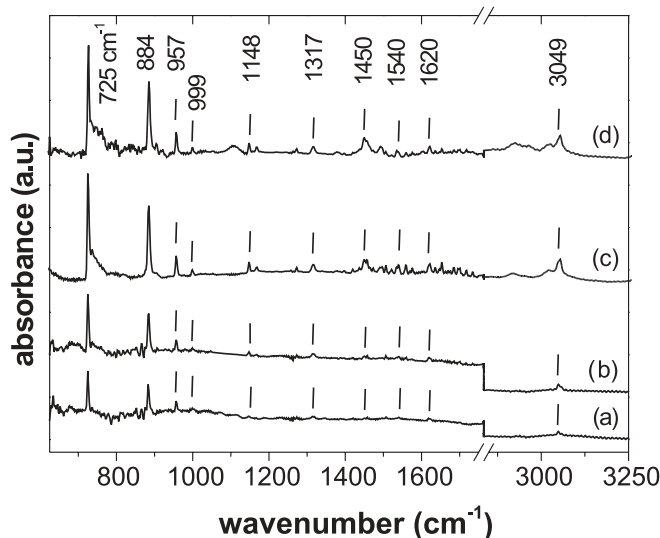


FIGURE 2 FTIR spectra of anthracene films obtained by the irradiation of anthracene–chloroform solution at 0.04 J cm^{-2} (a), anthracene–ortho-xylene solution at 0.2 J cm^{-2} (b), anthracene–ortho-xylene solution at 0.6 J cm^{-2} (c), and anthracene–ortho-xylene solution at 0.7 J cm^{-2} (d). For the purpose of comparison the thickness of the (a) and (c) films are 320 and 700 nm, respectively. The wavelength positions of the main absorption peaks of pure bulk anthracene are shown for reference purposes

The irradiation of the targets at low fluences presents some practical limitations; namely, the deposition rate of the films deposited at 0.2 J cm^{-2} is 0.004-nm per pulse. However, the spectra depicted in Fig. 2c and d show that non-damaged anthracene films can be obtained by the irradiation of anthracene-ortho-xylene solution at 0.6 J cm^{-2} and even at 0.7 J cm^{-2} , which are non-negligible fluences. The latter leads to a deposition rate of 0.007-nm per pulse. A detailed observation of the spectra in Fig. 2c and d also shows that spurious features that cannot be directly attributed to the anthracene fingerprint appear around 2900 cm^{-1} . In fact, an increase of the laser fluence cannot be pursued further without effects on the chemical properties of the deposited films. Figure 3 shows the FTIR spectrum of a film grown by the irradiation of anthracene-ortho-xylene solution at 1.5 J cm^{-2} . This spectrum is completely different from those shown in Fig. 2. The characteristic absorption bands of anthracene have disappeared. The displayed absorptions correspond to infrared vibrational modes of hydrogenated amorphous carbon [18]. The band around 1600 cm^{-1} is assigned to C=C double-bond stretching vibrations, and the absorption at 1695 cm^{-1} , which overlaps the C=C band, can be attributed to a contamination by C=O. The 1378 cm^{-1} and 1446 cm^{-1} bands correspond to the in-phase and out-of-phase deformation vibrations of methyl (CH_3) groups, respectively. The presence of CH_3 groups, which could come from the breaking-up of the molecules of the ortho-xylene solvent, is confirmed by the absorption at 2920 cm^{-1} due to C-H stretching vibrations. Thus, precise control of laser fluence is needed in order to transfer the anthracene molecules from the target to the substrate without any chemical changes. A threshold value of the laser fluence can be evaluated around $0.6\text{--}0.7 \text{ J cm}^{-2}$ for the frozen anthracene-ortho-xylene solutions. The target irradiation must be carried out at lower fluences to preserve the integrity of the organic molecules.

The absence of appreciable physicochemical damage to the anthracene molecules during the deposition process can be also checked by the analysis of the physical properties of the films. The fluorescence emission of thin films grown

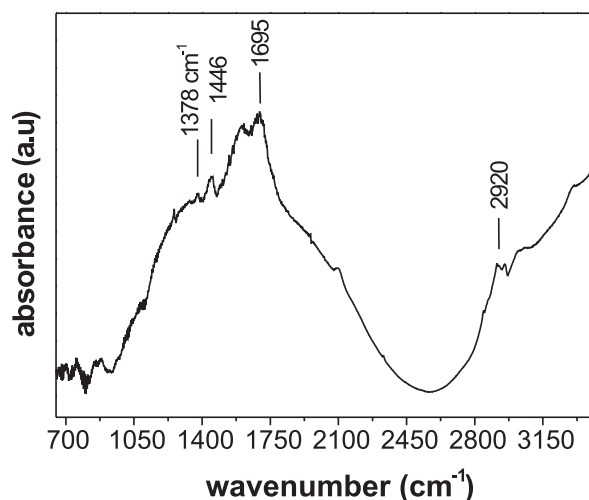


FIGURE 3 FTIR spectrum of a film grown by the irradiation of anthracene-ortho-xylene solution at 1.5 J cm^{-2}

under low laser fluences has therefore been studied. Figure 4a and b respectively shows the fluorescence spectrum of crystalline powder of anthracene and of an anthracene thin film prepared by the irradiation of an anthracene-chloroform solution at a fluence of 0.04 J cm^{-2} . Both spectra show well-resolved successive maxima, which correspond to transitions from the first excited electronic state of the molecule to the vibrational levels of the ground state. The crystalline powder spectrum (Fig. 4a) presents the usual shape [19], with reabsorption in the origin region. The wavenumber positions of the other maxima ($23\,700$, $22\,300$ and $20\,900 \text{ cm}^{-1}$, labelled 1, 2 and 3, respectively) are in excellent agreement with the published values [19]. The spectrum of the anthracene film (Fig. 4b) shows that the emission from the 0-0 band is also reabsorbed and the other maxima keep the same spacing, about 1400 cm^{-1} ($24\,300$, $22\,900$, $21\,500$, $20\,100 \text{ cm}^{-1}$). This observed agreement for the vibrational progression implies that the structure of the anthracene molecules is not modified during the MAPLE process when low laser fluences are used, while the well-resolved vibrational structure indicates that the films contain crystalline material [20]. Thus the aggregates (100-nm in size) observed in the AFM images (Fig. 1) may correspond to anthracene crystallites. The reduced size of the nanocrystallites could be responsible of the blue shift observed in the fluorescence spectrum of the film with respect to the reference spectrum. In fact, theoretical analyses [21] show that the limitation of the long-range dipole-dipole interaction

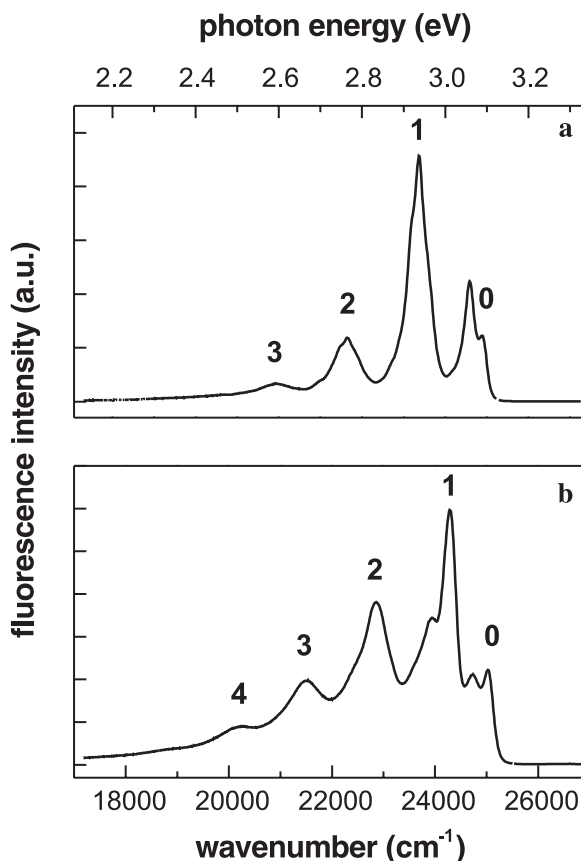


FIGURE 4 Fluorescence spectra of a crystalline powder of anthracene (a), and a film prepared by the irradiation of an anthracene-chloroform solution at a fluence of 0.04 J cm^{-2} (b)

in anthracene crystal leads to a blue shift, this phenomenon occurring for crystallite size lower than the wavelength of the emitted light. Moreover, the crystalline quality of the films has to be taken into account; imperfections of a crystallographic nature or grain boundaries in the nanocrystals can lead to the broadening of the film spectrum. These results have to be compared to those obtained by direct PLD of anthracene-derivative targets [22] when the growth is carried out at a low fluence, which corresponds to a desorption process rather than to an ablation one. Under these conditions the fluorescence emission of the PLD film compared with that of a film deposited by spin coating is largely broadened and does not show the vibronic structure observed in Fig. 4b.

4 Conclusion

The MAPLE technique has been successfully used to grow thin films of anthracene that exhibit the characteristics and physical properties of the bulk organic compound. Despite the strong absorption of anthracene at the laser wavelength used, this molecule is not destroyed during the MAPLE process. IR absorption and photoluminescence experiments show that the chemical integrity of anthracene is preserved during the transfer from the target to the substrate. The most important parameter for achieving this non-damaging transfer appears to be the laser fluence. Pure anthracene films are grown if the deposition is carried out by irradiating the target at fluences lower than a threshold value, while hydrogenated amorphous carbon films are formed at higher fluence values because of the fragmentation of the target molecules. This threshold value is around $0.6\text{--}0.7\text{ J cm}^{-2}$ when frozen solutions of 2 wt % anthracene in ortho-xylene are used as targets. Therefore, the new MAPLE process is suitable for growing thin films of organic materials which absorb at the wavelength of the laser, that it is to say far from the ideal conditions, provided the laser fluence is carefully controlled.

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