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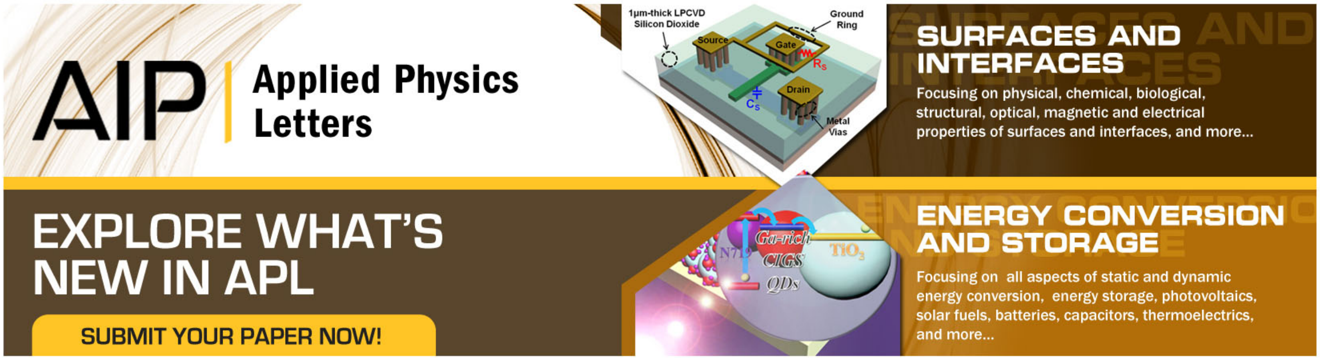

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Pulsed laser deposition of liquid crystals

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Thin films of 4-cyano-4'-pentylbiphenyl (5CB) liquid crystal have been fabricated by pulsed laser deposition. The suitability of different lasers (ArF, KrF and CO_2) has been investigated over a range of fluence using visible-UV and infrared absorption and optical microscopy to characterise the films. High performance liquid chromatography (HPLC) and matrix assisted laser desorption ionization mass spectroscopy (MALDI-MS) were used to assess the extent of decomposition of the films. The results suggest that the CO_2 laser acts as a quasi-steady heat source, while for ArF laser irradiation severe photodecomposition is observed. However, use of the KrF laser allows the production of excellent quality submicron films, showing properties similar to the 5CB target with only slight photodecomposition. © *1997 American Institute of Physics.* [S0003-6951(97)00845-0]

The production of liquid crystal (LC) thin films is expected to become important in the development of optoelectronic devices such as optical modulators, frequency convertors, tunable optical filters and flat screen displays among others.[1] A variety of processing methods for film formation are available based on, for example, capillary action, vacuum evaporation or dispersion of the LC in a polymeric matrix. Nevertheless, these methods are not always suitable for certain materials or applications, e.g. ultra-thin, uniform films of ferroelectric or discotic LCs; thus, the development of alternative methods for producing these films for advanced technological applications is of considerable interest.

During the past decade pulsed laser deposition (PLD) has developed rapidly and is now one of the most general techniques for the production of thin films of inorganic compounds.[2] In contrast, except for some polymers,[3–5] the application of PLD to organic compounds has been less widely investigated. This stems, in part, from the existence of photodisociative processes during the laser target/plume interaction[5,6] that may alter the chemical properties of the deposited films, although PLD has recently been applied successfully to complex organic compounds such as Pentacene,[7] Copper-phthalocyanine and 4-dialkylamine-4'-nitrostilbene.[8]

The aim of work reported here was to evaluate the suitability of PLD for the deposition of LC thin films and to investigate the influence of laser fluence and wavelength on the properties of the deposited material. We demonstrate that by suitable choice of the laser parameters, high quality uniform films with thicknesses <1 μm can be formed, albeit with some degree of decomposition accompanying the deposition step.

The LC investigated was 4-cyano-4'-pentylbiphenyl (5CB, BDH, Poole Ltd.) whose molecular structure is shown in the inset of Fig. 1. It has a nematic range of 24.0-35.3 °C[9] and a normal boiling point $\geqslant 400$ °C. PLD from a 5CB liquid target held in a 7 mm diameter horizontally mounted stationary dish, was used to grow films on various substrates (glass, fused silica, NaCl) held at room temperature in a vacuum chamber at 1×10^{-5} mbar. The laser was focused onto the liquid surface to form a 1-2 mm^2 spot and the ejected material was collected on substrates placed 30 mm above the target surface. ArF (193 nm, $\tau=25$ ns pulse width, $\nu=10$ Hz pulse rate), KrF (248 nm, $\tau=25$ ns, $\nu=10$ Hz) and CO_2 (10.6 μm, $\tau=100$ ns, $\nu=8$ Hz) lasers were used as the deposition sources. The effect of fluence was investigated in the range 20–100 mJ/cm^2 for the ArF and KrF lasers, and 0.6–3.0 J/cm^2 for the CO_2 laser, the lower value in each case corresponding to the threshold below which film formation could not be detected. In no case was a visible plume seen to accompany the interaction. During the deposition, a thermocouple was used to measure the average temperature of the 5CB liquid pool which was found to reach up to 70 °C in the case of the CO_2 (mean power=160 mW at 1.4 J/cm^2), but remained near room temperature ($\sim$20 °C) for the ArF and the KrF lasers (mean power=20 mW at 100 mJ/cm^2).

The optical properties of the deposited films were characterised by visible-UV and infrared (IR) absorption and optical microscopy. High Performance Liquid Chromatography (HPLC) and Matrix Assisted Laser Desorption Ionisation Mass Spectrometry (MALDI-MS, 3 ns, N_2 laser desorption source) were used to assess the extent of 5CB decomposition in the films. The properties of the laser deposited films were compared with those grown by thermal evaporation at 70 °C in vacuum and with reference samples obtained by wiping a small amount of 5CB on the appropriate substrate.

Visible-UV absorption spectra in the range 200-600 nm

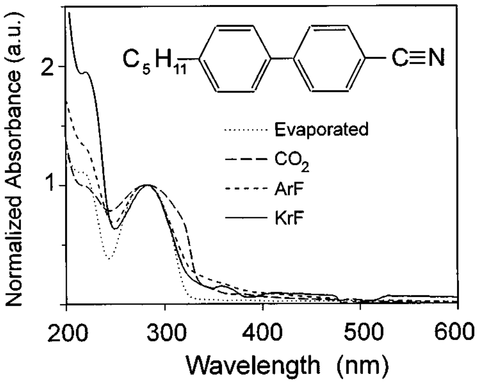

FIG. 1. Normalized absorption spectra of: thermally evaporated film and films deposited with CO_2 laser at 1.4 J/cm^2, ArF laser at 30 mJ/cm^2 and KrF laser at 60 mJ/cm^2. The inset shows chemical structure of 5CB.

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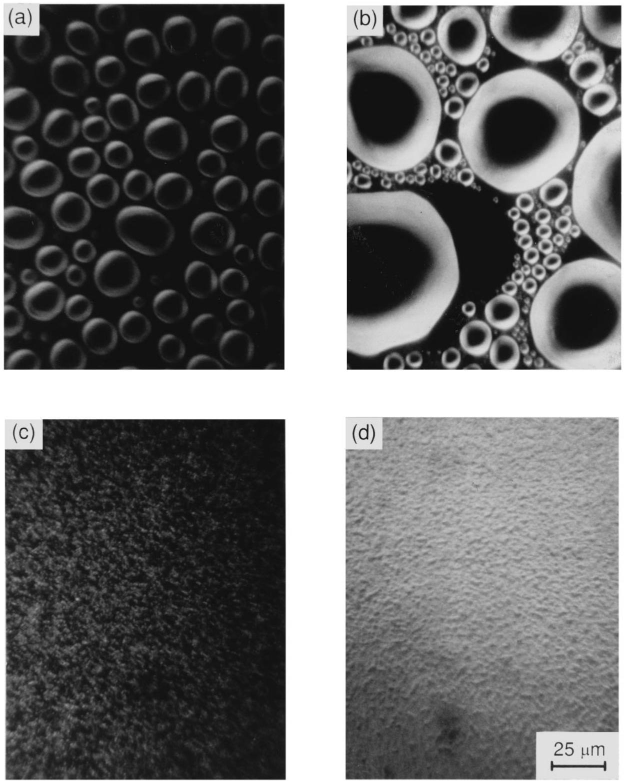

FIG. 2. Optical micrographs (×400 magnification) of films prepared by (a) CO_2 laser at 1.4 J/cm^2, (b) thermal evaporation, (c) ArF laser at 30 mJ/cm^2 and (d) KrF laser at 100 mJ/cm^2.

(1 nm resolution) are shown in Fig. 1 for thermally evaporated and ArF, KrF and CO_2 laser deposited films. As these films have different thicknesses the spectra have been normalised to the absorbance at 280 nm to ease comparison. The spectra shown in Fig. 1 are broadly similar to that of the 5CB reference sample, with two bands centred at 200 and 280 nm related to $\pi \rightarrow \pi^*$ electronic transitions in the phenyl rings.[9] This gives qualitative evidence for the phenyl rings remaining basically unaltered in the molecules of the deposited films. The electronic transitions responsible for these absorption bands have been assigned to be polarised parallel (280 nm) and both parallel and perpendicular (220 nm) to the long axis of the biphenyl group.[10] Therefore, the difference in the intensity ratio (I_{220}/I_{280}) between films grown with UV lasers (>1) and either with the CO_2 laser or by thermal evaporation (~ 1) suggests a different orientation of the molecules in the films. The origin of this difference is unclear, but could be related to the laser-LC interaction process and a possible difference in the ejection mechanisms between UV and IR lasers.

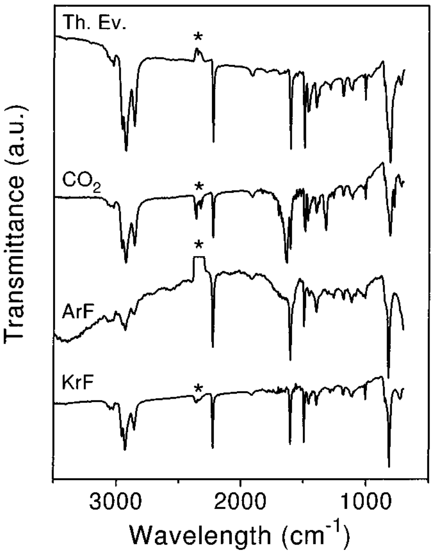

FIG. 3. Infrared spectra of thermally evaporated film and films grown with CO_2 laser at 1.4 J/cm^2, ArF laser at 30 mJ/cm^2 and KrF laser at 100 mJ/cm^2. In order to ease the comparison, the transmittance of the CO_2 and the ArF laser deposited films is scaled by a factor of 4 and 6.5 respectively. The feature designed by (*) corresponds to the water vapour absorption band that is incompletely cancelled in the differential measurements.

Optical microscopy of films grown using the three laser wavelengths revealed significantly different morphologies. For the CO_2 laser (Fig. 2a) the film consisted of an aggregation of droplets homogeneously distributed on the substrate, the typical droplet diameter being ~ 15 μm at 1.4 J/cm^2. The droplet size decreased with increasing fluence. This morphology is qualitatively similar to that for thermally evaporated films (Fig. 2b) although these showed a much broader range of droplet diameters. In contrast, films formed using the ArF and KrF lasers were, in relative terms, extremely smooth (Figs. 2c and 2d) and no significant features could be resolved above 1 μm. Based on their 280 nm absorption,[9] the thickness of the ArF and KrF laser produced films was estimated to be 0.2–0.4 μm, corresponding to an average growth rate of $\sim 5 \times 10^{-3}$ nm per pulse.

HPLC analysis of reference samples, and the thermally evaporated and CO_2 laser grown films, revealed only a single peak corresponding to the 5CB molecule. It can thus be ascertained that up to at least 3 J/cm^2 the CO_2 laser produces no appreciable decomposition. For the ArF laser, HPLC analysis of the films showed extensive fragmentation, four peaks appearing at earlier retention times in the spectrum in addition to a peak for 5CB. These fragment signatures became more pronounced as the fluence was raised, and even at as low as 60 mJ/cm^2 5CB was rendered a minority peak. MALDI-MS spectra of ArF laser deposited films on a Coumarin 120 matrix confirmed the decomposition, many fragment peaks appearing in the mass spectrum (e.g. at 74, 103, 165, 217 Da; 5CB molecular weight =249 Da). For CO_2 laser deposited films, a peak was observed at 231 Da in addition to the 249 Da peak. The fact that such decomposition could not be observed by HPLC suggests a small fractional decomposition, or that these similar mass components could not be resolved. Finally, the HPLC spectra of the KrF laser deposited films showed the 5CB peak and a weaker one appearing at an earlier time, and thus probably corresponding to a smaller molecule.

IR spectra were obtained for the thermally evaporated and the laser deposited films (Fig. 3) as well as for the 5CB reference sample on NaCl. All bands, with the exception of a weak feature at 1287 cm^{-1}, could be assigned from tabulated data.[11] There is a close match between the spectra for thermally evaporated and CO_2 laser deposited films (Fig. 3) although for the latter, two new weak bands at 1640 and 1320.8 cm^{-1} and significant broadening of the 1600 cm^{-1}

band are evident. These changes could be related to the partial decomposition of the 5CB molecules suggested by the MALDI-MS experiments. Considering the bond strengths (C-C and C-H dissociation energies are ~3.5 and 4.2 eV respectively),[12] and the fact the phenyl rings remain unaffected (Fig. 1), the fragmentation of the molecule likely takes place by the loss of C and/or H atoms in the alkyl chain, leading to the formation of C=C bonds. These side chain bonds could account for the appearance of the bands at 1630-1660 cm^{-1} (C=C, vibration mode) and 1305-1335 cm^{-1} (=C- bending mode).[13] For films grown using the ArF laser, the C-H related bands have strongly decreased in intensity (3072-3029, 968, 2956-2858 and 1396-1004 cm^{-1}) while those related to C=C stretching modes in the phenyl rings (1607 and 1495 cm^{-1}) and the cyano group (C≡N, 2226 cm^{-1}) remain (Fig. 3). The retention of the cyano group under 193 nm irradiation contrasts with work on ablation of Polyacrylonitrile[5], and may be a result of the much lower fluence used here (~30 $\mathrm{mJ/cm}^2$ .cf. >170 $\mathrm{mJ/cm}^2$ in Ref. 5) and differences in primary UV chromophores for Polyacrylonitrile and 5CB. The IR results support findings using HPLC and MALDI-MS that the ArF laser produces severe decomposition of 5CB and points to a loss of groups from the alkyl side chain. This can be contrasted with the IR spectrum of the KrF laser deposited film grown at higher fluence (Fig. 3) which shows a close similarity with the thermally evaporated film, suggesting that 5CB is the predominant composition of the material. Although HPLC analysis showed partial decomposition for the entire KrF fluence range investigated, the decomposition product is either at a sufficiently low concentration to go undetected in the IR spectrum or has an insufficiently resolved footprint to identify it.

To understand these results we note that 5CB exhibits a much lower absorption coefficient (α) at 10.6 μm than at the deep UV laser wavelengths of 193 and 248 nm. Taking a mean value of $\alpha=47\ \mathrm{cm}^{-1}$ at 10.6 μm[9], the temperature rise per pulse at the focal spot on the liquid pool is estimated to be in the range: 8.4 K (0.6 $\mathrm{J/cm}^2$) to 42 K (3 $\mathrm{J/cm}^2$). However, under repetitively pulsed conditions, the slow cooling of the heated zone (~0.5 s) leads to a large rise (ΔT_s) in the quasi-steady temperature at the focal spot on the target. For example, at 1.4 $\mathrm{J/cm}^2$ and 8 Hz, a $\Delta T_s \approx 400$ K is estimated for a surface source with a 0.6 mm radius spot assuming that convection is negligible.[14] Under these conditions evaporative flux components arise from the entire surface area of the pool (~38 mm^2) as in thermal evaporation, together with a contribution from the focal spot region where the temperature may be sufficiently high to promote some degree of thermal decomposition evidenced in the IR and MALDI results. At 248 and 193 nm 5CB exhibits very strong absorption by virtue of the $\pi \rightarrow \pi^*$ singlet-singlet transitions, with estimated values of $\alpha = 6.6\times10^4\ \mathrm{cm}^{-1}$ and $\alpha=2\times10^5\ \mathrm{cm}^{-1}$ respectively.[9] At 20 $\mathrm{mJ/cm}^2$ this would correspond to a transient surface temperature rise of 1200 K for the ArF laser. Although this is likely an upper limit on the temperature rise as energy loss to photochemical reaction and heat flow from the shallow absorption zone ($\alpha^{-1}=50$ nm) are neglected, this magnitude would be more than sufficient to promote removal through an explosive boiling mechanism. In contrast with the CO_2 laser, the low fluence required for removal, coupled with rapid cooling of the shallow heated layer (~25 ns), restricts the extent of long-term temperature rise and thermal decomposition in the liquid pool. These differences in the ejection mechanism are tentatively proposed as explanation for the different film morphologies observed (Fig. 2). The present results show that the KrF laser wavelength is suitably strongly absorbed to promote an ablative removal of material without excessive fragmentation. This has allowed ultra-thin and uniform films of this LC to be formed, pointing to the potential suitability of PLD for preparing films of other related materials. Work is currently underway to characterise the electro-optic properties of these films and their applicability as liquid crystals.

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