Spatial control of organic nanocrystal nucleation in sol–gel thin films for 3-D optical data storage devices or chemical multi-sensors

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Abstract

We have controlled the spatial distribution of organic nanocrystals grown in sol–gel thin films prepared by spin-coating. This spatial control of nucleation is carried out through the difference in confinement between the surface and the depth of the sol–gel thin films at the first stage of the coating process. Thus, we can direct the nucleation sites in grooves or wells of textured substrates. We have achieved, respectively 1- and 2-D ordering of nanocrystals while 3-D patterns have been obtained through a multi-layer process. This nucleation control gives an opportunity to design new 3-D optical data storage or 2-D arrays of luminescent crystals for chemical or biological multi-sensors.
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1. Introduction

Extensive researches on organic crystals have evidenced their promising optical properties in luminescence, photochromism, nonlinear optical (NLO) processes and electro-optics for example. Moreover, they are associated to unlimited

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molecular engineering through the great flexibility of their chemical synthesis. In order to combine these optical properties with the higher stability of the inorganic compounds, we have developed a new type of hybrid organic–inorganic materials constituted of organic nanocrystals embedded in silicate matrices. They are prepared by a generic process based on the confined nucleation of molecular crystals in the pores of sol–gel matrices, bulk or thin films [1–3]. These materials can associate the optical properties of organics with the stability and transparency of inorganics but they also possess the advantages of nanocrystals (size effects, noncentrosymmetry) as well as those of the amorphous matrix: convenient processing and shaping. We have first obtained dispersed nanocrystals grown in gel glasses leading to isotropic macroscopic properties such as nonlinear absorption for optical limiting devices [4] or luminescence for sensors [5]. In this study, we have undertaken to control the spatial distribution of organic nanocrystals in sol–gel thin films prepared by spin-coating. This spatial control of nucleation is carried out by assisting the nano-crystallisation process through nanostructured substrates. The substrates exhibit arrays of grooves or wells where the dye nucleates when the initial solution is deposited. That way, we have obtained 1- and 2-D ordering of nanocrystals and the 3-D spatial control is achieved through a multi-layer process. This nucleation control gives an opportunity to design new 3-D optical data storage or 2-D arrays of luminescent crystals for chemical or biological multi-sensors [6].

2. Nanocrystallisation method

The nanocrystallisation of organic phases in sol–gel thin films is based on the control of the nucleation and growth kinetics of the dye confined in the pores of the silicate coating. We start from solutions containing a solvent, the dye, silicon alkoxides as gel precursors and a small amount of water to hydrolyse the alkoxides. These solutions are prepared according to literature procedures [7] with equimolar mixtures of tetramethoxysilane and methyltrimethoxysilane alkoxides as gel pre-

cursors. The solvents are ethanol in the case of DEANST molecule with $s = 6$ (s is the molar ratio: solvent/alkoxide) and tetrahydrofuran for rubrene with $s = 5$. The sols are synthesised under acid (HCl) catalysed conditions by one step hydrolysis and condensation of the alkoxide precursors with one H_2O molecule per -OR function ($h = [H_2O]/[-OR] = 1$). The organic powders are introduced at room temperature in these solutions and dissolved at $80\,^\circ C$ using airtight cells in order to obtain homogeneous sols that are then kept at $80\,^\circ C$ during 3 aging days. It allows to rapidly dissolve the organic powder and to enhance the hydrolysis and condensation kinetics leading to the formation of silicate chains dispersed in the solution. This sol aging is necessary to obtain high-quality films, to ensure the control of particle growth and to avoid crystal coalescence. The nature and the amount of solvent are adjusted for each organic compound in order to control the sol viscosity, around 10–20 cps, and to favour the coating process. The resulting sols, which are stable for several weeks, can be deposited at room temperature by spin coating onto various substrates such as glass strips, silicon wafers or polymers. Thus, using a rotation speed of 4000 rpm applied during 10 s, thin films of about 0.5 μm thick have been prepared.

At the first stage of the coating process, when the drops of solution are spread out on the substrate, the solvent evaporation increase the sol viscosity due to the cross linking of the silicate network. This polycondensation of the silicate matrix forms pores which confine the solution and act as nanometer-scaled reactors for crystal nucleation and growth in solution. Under these confined conditions, the nucleation probability decreases, and even tends to zero, with decreasing volume of the growth solution. Indeed, the probability to form a stable nucleus, P, in a volume of solution, V, during a period of time, dt, is $P = JV\,dt$, where J is the stationary nucleation rate [8]. Thus, the nucleation probability after a period of time $t-t_0$ is

$$P_{t0}(t) = 1 - e^{-JV(t-t_0)}. \tag{1}$$

For this reason, high supersaturations (i.e. high nucleation rates J) are required to initiate the

nucleation process in the pores of wet gels [9]. In this nanocrystallisation process, a very high supersaturation is applied by the fast evaporation of the solvent when the initial sol is spread out onto the substrate. This leads to an instantaneous "burst" of nucleation inducing the germination of a high number of organic nuclei in the interconnected pore network. This burst of nucleation suddenly drop the dye concentration dissolved in solution. This important decrease of supersaturation ends the nucleation step and limits the subsequent growth stage. On the other hand, the silicate framework getting denser avoids the coalescence of nanocrystals. Thus, as the dye nucleation is strongly confined in space (pores of gels) and in time (around 1 s for the coating process), well-dispersed nanocrystals can be prepared with narrow size distributions [10–12].

In order to demonstrate the validity and the flexibility of this nanocrystallisation process, we have grown several types of organic nanocrystals involving different solvent and gel precursors [3]. In all cases, by using typical substrates, the particles are randomly dispersed and well embedded in the depth of the sol–gel thin films. This latter point is due to the formation of a "skin" in the early stage of the coating. Indeed, the solvent evaporation begins at the surface promoting there the polymerisation of the silicate framework. This skinning effect in coatings, previously observed in other works [13,14], leads in this study to a nucleation of the organic crystals in the depth of the coating, where the growth solution is less confined than at the coating surface. Indeed, the nucleation rate, depending on the pores volume [9], drops and tends to zero at the surface where the silicate framework exhibit smaller pores. This buried nucleation explains why these nanocomposite thin films exhibit such a good surface quality with a very low roughness, around 1 nm [2]. In this study, we have made use of this buried nucleation of organic crystals in sol–gel films to control their arrangement. We have first searched to obtain one-dimensional ordering of nanocrystals before exploring higher organisation levels.

3. One-dimensional control of nucleation sites

We have selected 4-(diethylamino)-β-nitrostyrene (DEANST) as dye whose nanocrystallisation on typical substrates is well defined [1]. The substrates are silicon plates exhibiting regular patterns of grooves, Fig 1a. These patterns are carried out through an electro-chemical etching of silicon under a laser beam ($\lambda = 0.515\,\mu m$) by anodic attack of porous silicon in concentrated solution of fluorydric acid (15 wt%). Indeed the laser beam favours the chemical etching of porous silicon by creating p-type defects. Thus, by exposing a silicon plate to laser interference fringes one can obtain regular pattern of grooves [15]. Fig. 1a shows the $0.6 \times 0.6\,\mu m$ grooves, periodi-
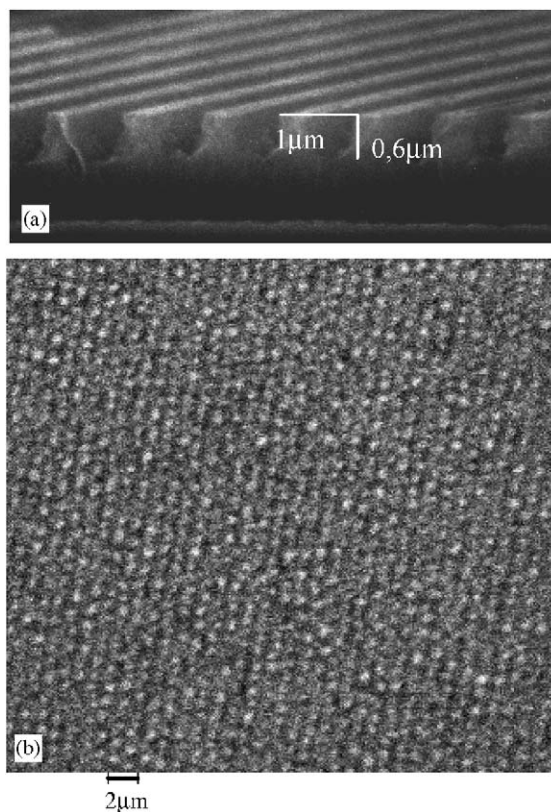

Fig. 1. (a) SEM image of regular patterns of grooves on silicon substrate (b) DEANST nanocrystals grown in the grooves of the silicon substrate shown by fluorescent confocal microscopy: fluorescence excitation by the 633 nm ray of a 5 mW He–Ne laser and fluorescence selection by a 660 nm long-pass filter.

cally spaced (1 μm period), which were used in this study. We have involved initial solutions constituted of silicon alkoxides, ethyl alcohol DEANST and water with amounts previously defined to obtain by spin-coating nanocrystals with diameters ranging between 300 and 400 nm (see
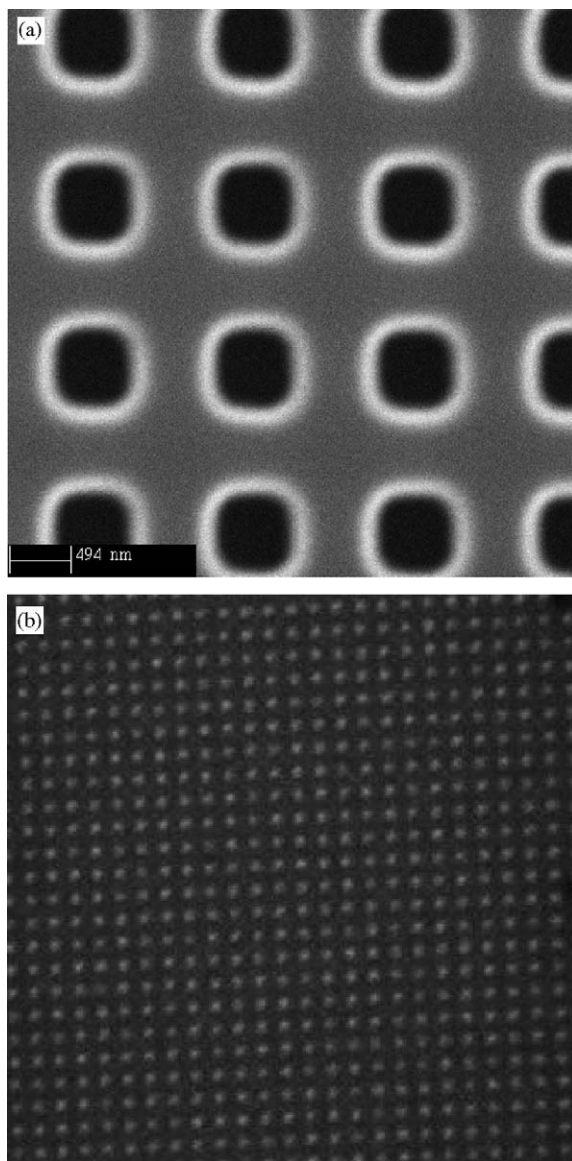

Fig. 2. (a) SEM image of 2-D pattern of $0.5 \times 0.5 \times 0.5 \, \mu m^3$ wells on silicon substrate. (b) Confocal fluorescence microscopy image of 2-D array of DEANST nanocrystals grown in the holes of the silicon substrate.

above). From the first experiments, we observed directly by optical confocal microscopy well aligned luminescent nanocrystals of DEANST nucleated and grown in grooves of the silicon substrates Fig. 1b. The confocal laser scanning microscope is a LSM410 from Zeiss (Iena, FRG). Fluorescence images can be recorded as 2-D confocal XY sections (Figs. 1b, 2b and 3b), or as a Z section (Fig. 3c). As these first promising experiments confirmed the possibility to control the nucleation sites of organic nanocrystals we followed this work towards 2-D ordering.

4. Two-dimensional arrays of nanocrystals

In this case, we used silicon substrates exhibiting 2-D patterns of $0.5 \times 0.5 \times 0.5 \, \mu m^3$ holes regularly spaced, Fig. 2a. These substrates are prepared through typical photolithography and plasma etching techniques [16]. In order to demonstrate the generality of this process we have carried out nanocrystallisations for two different dyes: DEANST and rubrene. The former exhibits a crystal structure based on a 3-D network of hydrogen bonds [17] while the latter is a pure molecular crystal involving only Van der Waals bonds between the polyaromatic molecules [18]. For these two dyes, by decreasing the thickness of the sol–gel film to avoid the nucleation of crystals between wells, we have obtained 2-D ordering of nanocrystals. By confocal microscopy imaging, we have observed at wide range 2-D arrays of fluorescent nanocrystals grown in the holes of the silicon substrates, Fig. 2b.

5. Multiple layer process

To prepare multiple layers we turned to polymers substrates and particularly to poly(methyl methacrylate (PMMA) which exhibits high optical qualities and low glassy transition temperature (114 °C). The spin-coating conditions (rotation speed of 4000 rpm applied during 10 s) were first adjusted to obtain 15 μm-thick films of PMMA on silicon wafers through a single coating. In this case, chloroform/chlorobenzene equimolar solu-
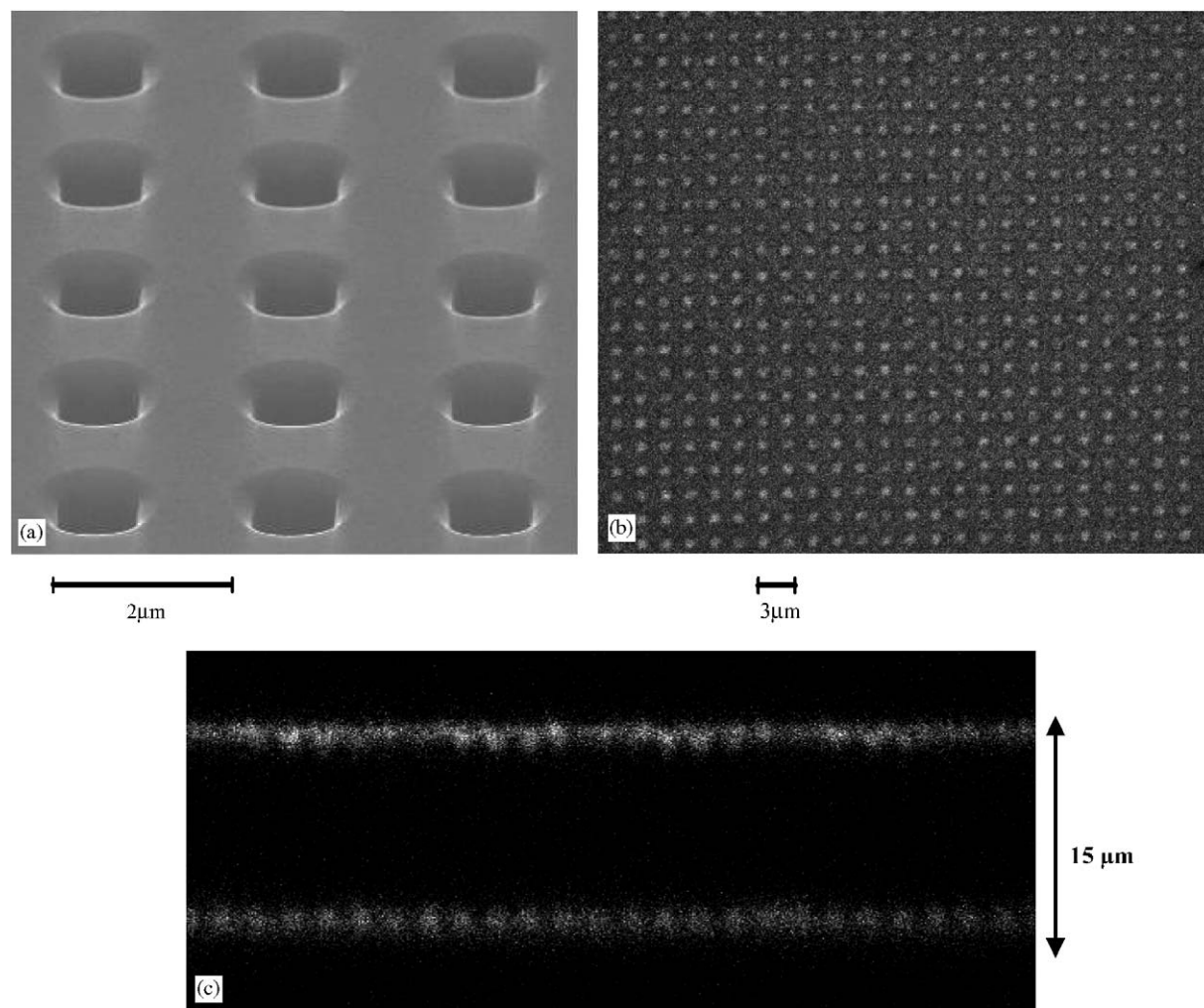
Fig. 3. (a) SEM image of regular 2-D patterns prepared by embossing of PMMA substrates. (b) Scan in the depth (Z section) of two layers of 2-D array of rubrene nanocrystals. (c) Confocal optical microscopy visualisation of 2-D array of fluorescent rubrene nanocrystals grown in the wells of PMMA substrate: fluorescence excitation by the 488 nm ray of a 15 mW Argon laser, and fluorescence selection by a 520–560 nm band pass filter.

tions containing 40 wt% of PMMA were used. Glasses, polycarbonate or other basic substrates can be also used to support this PMMA layer. Then, regular 2-D patterns of $0.9 \times 0.9 \times 0.7 \, \mu m^3$ wells (Fig. 3a) can be made on PMMA by nanoimprint lithography [19]. The patterns are first defined into silicon which is used as a mold. The PMMA layer is heated at a temperature higher than the polymer glass transition temperature (150 °C), and the Si mold is pressed into the polymer with a pressure of 15 bars. After cooling and demolding, the holes are patterned in the PMMA layer. On these as-prepared substrates, 2-D arrays of rubrene nanocrystals have been made under the experimental conditions given above. On these nanocomposite layers, 15 µm-thick PMMA coatings were deposited and embossed again at 150 °C to obtain a similar textured substrate as shown in Fig. 3a. This process preserves the first layer of the buried 2-D patterns of rubrene

nanocrystals which are stable over 200 °C, (Fig. 3c). Finally, second 2-D arrays of rubrene nanocrystals were made to obtain two layers of 2-D arrays of fluorescents nanocrystals. These double layers were observed by scanning in the depth the samples by optical confocal microscopy, Fig. 3b. The resolution in this case is lowered by the high thickness analysed, over 20 μm. This process can be repeated several times to obtain multi-layered samples.

Finally, we have recently specified the mono-crystalline nature and the 3-D orientation of these organic nanocrystals embedded in a sol–gel layer, using a polarized nonlinear microscopy technique that combines two-photon fluorescence and second harmonic generation [20].

6. Conclusion

In conclusion, through the difference in confinement between the surface and the depth of the sol–gel thin films at the first stage of the coating process, we can direct the nucleation sites of organic nanocrystals in grooves or wells of textured substrates. Thus, we have obtained perfect 1-D and 2-D arrays over wide ranges. Involving a multiple layer process we have also achieved a 3-D ordering. In addition, this process seems to be generic as we successfully used two different types of dyes. The 2-D arrays of fluorescent nanocrystals could be used for the fabrication of integrated chemical or biological multi-sensors as indicated by our first promising results [5]. The multi-layers of 2-D nanocrystal arrays seem to open a new possibility for the fabrication of high-density optical data storage. Indeed, it has long been recognized that 2-D storage carriers are insufficient for future generations of memory devices. The data capacity can be increased by stacking several layers in one disk. Fluorescent nanocrystals can be excited by a laser focused on the read layer while their incoherent light can significantly avoid problems of inter-ference, scattering and intra-layer cross talk. Moreover, fluorescent nanocrystals form well-defined bits with a better contrast and a higher photostability than dispersed dye molecules in a matrix.

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