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Nanocomposites of metallic copper and spinel ferrite films: Growth and self-assembly of copper particles

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Abstract

Nanocomposites of metallic copper and iron oxides films have been prepared by RF-sputtering of pure CuFeO_2 delafossite target. The films are made of copper and spinel ferrite crystallites of less than 10 nm in diameter. The content of metallic copper and the ferrite composition depend on the sputtering conditions. For the shortest substrate-target distances, films are made of copper and copper substituted magnetite with low copper content. The formation of the metallic and spinel phases is due to the loss of a small quantity of oxygen during sputtering. When annealed under inert atmosphere, nanometric copper particles located in the upper part of the film, move on the surface and grow due to coalescence phenomena. The particle motion can be stopped by small grooves allowing the self-assembly of copper particles.

Keywords: Metal oxide; Self-assembly; Composites; Transmission electron microscopy

1. Introduction

Composites made of micronic or nanometric metallic particles dispersed in an oxide matrix, have received great attention because of their specific or improved mechanical, optical, electrical, thermal or magnetic properties [1–8]. In the form of thin films, these materials could be used for different technological applications, for instance in magnetic recording media or electronic and optical devices. However, some of these applications require well-controlled film microstructures and, sometimes, precise spatial organisation of metal particles in the oxide matrix [9].

For thermodynamical reasons, stable ($M/M'_x\text{O}_y$) composite films have to be made of M and M' elements having different oxido-reduction potentials. Consequently, composite films with M chosen among the metals which appear in the upper part of the Ellingham diagram (i.e. M =noble

metals, Co, Ni, Fe. . .) and M' coming from the lower part (i.e. M' =Al, Cr, Mg. . .) are the easiest $M/M'_x\text{O}_y$ composite films to prepare.

Radio frequency (RF)-sputtering is most appropriate for the preparation of metal/oxide composite films, because it can operate under quite low oxygen partial pressures, over a wide range of temperatures and under various electronic, ionic and atomic bombings. Consequently, the required thermodynamic conditions to prepare $M/M'_x\text{O}_y$ films, can potentially be found by this process, even if M and M' display close oxido-reduction properties.

The purpose of our research is to prepare $M/M'_x\text{O}_y$ composite films, with M and M' metals both located in the upper part of the Ellingham diagram. In this paper, our work has been focused on copper/iron oxide films. Due to the above recalled versatility of RF-sputtering, this technique was chosen to prepare the samples. Moreover, heat treatments were carried out to modify film microstructure and to induce self-assembly phenomena in films deposited on patterned substrates.

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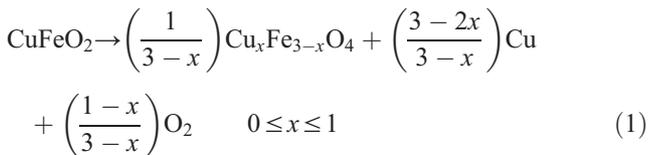
2. Experimental and analytical techniques

Nanocomposite metallic copper–iron oxide films were deposited on glass substrates by RF-sputtering using an Alcatel-SCR650 apparatus. Sintered ceramic of pure CuFeO_2 with a relative density of 70% was used as the target. The RF power was set at 4.5 W/cm^2 and the pressure inside the deposition chamber was lower than 4.10^{-7} Pa before deposition. The target-substrate distance d was chosen between 6 and 8 cm, the argon gas pressure during deposition was fixed at 0.5 Pa and the film thickness would vary from 50 to 100 nm. A summary of the deposition conditions is given in Table 1.

Thickness measurements were performed with a DEK-TAK 3030ST profilometer, the structural properties were determined by grazing angle X-ray diffraction ($\alpha=1^\circ$) with a Siemens D5000 diffractometer ($\text{Cu K}\alpha: \lambda=0.15418 \text{ nm}$). To study the microstructure of the films, Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and Optical Microscopy were performed with Veeco D3000, JEOL 2010, JEOL JSM 6700F and Nikon EPIPHOT apparatus, respectively. AFM, SEM and optical observations were done on films deposited on glass substrates. TEM observations were carried out on films directly deposited on carbon covered copper grids. The electrical properties were characterized using a 2-probe method. In $R=f(1/T)$ plots were obtained under air from room temperature to 280°C . Samples were heated at a heating rate of 150°C/h .

3. Results and discussion

All the as-prepared samples displayed X-ray diffraction patterns of both the spinel structure and the cubic metallic copper (Fig. 1). These phases were also identified in better-crystallised films, annealed under inert atmosphere at 400°C . The delafossite phase (CuFeO_2) was never revealed for either as-deposited or annealed samples. Atomic Cu/Fe ratios in the films are the same as the target ones. Consequently, the overall reaction of the preparation process can be described by the following reaction:



The sputtering of an oxide target by pure argon plasma generally involves films with lower content of oxygen than

Table 1
Experimental RF-sputtering conditions

Substrate	Gas	rf power	d (cm)	Thickness (nm)	Pressure
Glass	Ar	4.5 W/cm^2	6	50	0.5 pa
			7	100	
			8		

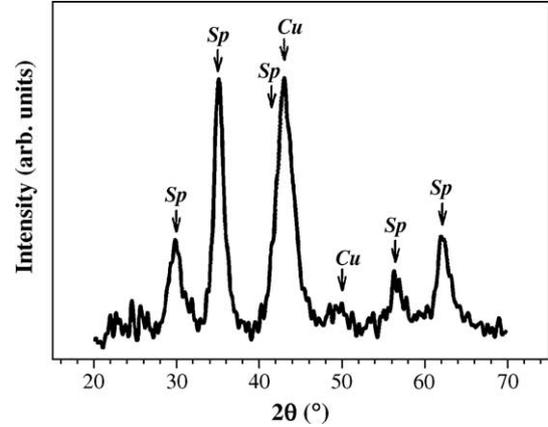


Fig. 1. Typical grazing angle X-ray diffraction pattern of as-deposited film.

that of the target [10]. The formation of copper and ferrite instead of delafossite, could then be favoured by a low oxygen loss during sputtering. In fact, the Cu–Fe–O phase diagram applies to this reaction for low oxygen partial pressures [11].

According to Eq. (1), the mole numbers of ferrite, copper and oxygen evolve versus x , as described by Fig. 2a. Taking into account a linear variation of the unit cell volume (v) for the $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ ferrite phase, from Fe_3O_4 ($x=0$, $v \# 0.593 \text{ nm}^3$) to CuFe_2O_4 ($x=1$, $v \# 0.605 \text{ nm}^3$), the calculated volume fractions of the ferrite and the metallic copper are plotted on Fig. 2b. This plot shows that the volume fraction of the ferrite phase is always more important than that of the metallic copper. Semi-conducting properties have then to be

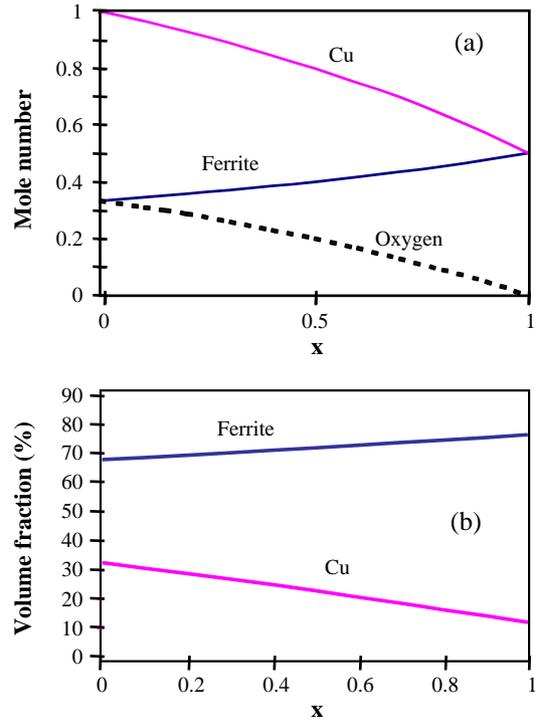


Fig. 2. (a) Calculated mole fraction of Cu, $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ and O_2 as a function of x in the reaction (1), (b) resulting volumetric fraction of Cu, $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ considering a linear variation of the unit cell volume.

observed for as-prepared films. In fact, the spinel oxides display semi-conducting properties due to the electron hopping in a same sublattice, from one cation to another one having the same chemical nature, but a different valency state [12]. For copper ferrites or magnetite, electron hopping can occur through $\text{Fe}^{2+}/\text{Fe}^{3+}$ pairs located on octahedral sublattice [13–15].

Moreover, when x is equal to zero, the metallic copper reaches the maximal rate and the spinel phase becomes Fe_3O_4 . The optimisation of octahedral $\text{Fe}^{2+}/\text{Fe}^{3+}$ pairs in Fe_3O_4 , leads to a very low electrical resistivity (about $5 \cdot 10^{-3} \Omega \text{ cm}$ [16]). Consequently, the lowest resistivity of the films can be expected when x is equal to zero, because of both the low resistivity of the ferrite phase and the high metallic copper content. By contrast, when x is equal to 1, the CuFe_2O_4 phase formed displays a high resistivity. Moreover, the content of the metallic phase is low. The overall resistivity of the film must then be high.

The electrical properties of the as-prepared films are in agreement with the expected properties. In fact, the electrical resistivities decrease from room temperature to about 110°C (Fig. 3a), showing an overall semi-conducting behaviour for all the films. Fig. 3a shows also a sudden change in resistivity from 110 to 200°C . As revealed by X-ray diffraction, this phenomenon is mainly related to the oxidation of copper into copper monoxide, which is an insulator. The films prepared at short distances from the

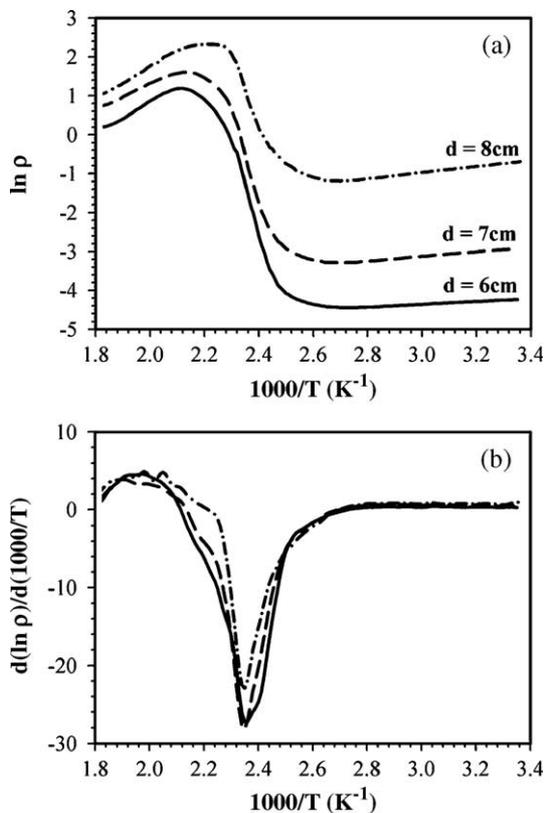


Fig. 3. Electrical resistivity versus oxidation temperature for $\text{Cu}/\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ thin films prepared at 6, 7 and 8 cm from the target: (a) $\ln \rho$ and derivative (b) $d(\ln \rho)/d(1000/T)$ vs $1000/T$ curves.

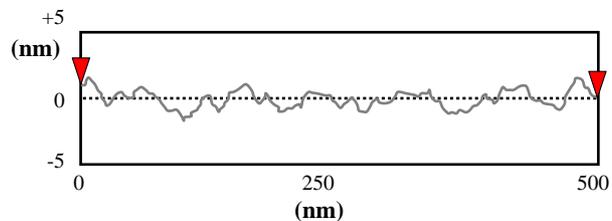


Fig. 4. Typical roughness of as-deposited films measured by Atomic Force Microscopy.

target display the strongest changes in resistivity. It can then be assumed that these films have the highest metallic copper content and are made of copper poor ferrite. This assumption is confirmed by both the low thermal dependence of the resistivity ($-4 \cdot 10^{-5}$ to $-3 \cdot 10^{-3} \Omega \text{ cm K}^{-1}$), in agreement with the high rate of the metallic phase, and the very low resistivity at room temperature ($0.015 \Omega \text{ cm}$), which is consistent with the electrical properties of a ferrite phase closer to Fe_3O_4 than to CuFe_2O_4 .

From reaction (1), the formation of a ferrite “close” to Fe_3O_4 means there is a loss of oxygen when substrates are located near the target ($d < 6 \text{ cm}$). This reduction becomes however, less important when the d distance increases. For the experiments carried out, it is thus possible to get films containing less oxygen than the target. Consequently, the metallic copper content in the samples can vary, according to the preparation conditions. This content is however limited by the balancing coefficients of reaction (1).

Fig. 3b shows shoulders on the $d(\ln \rho)/d(1000/T)$ derivative curves. These shoulders can be ascribed to oxidation of ferrous ions inside the spinel phase, because in ferrite thin films these ions are generally oxidized under air to form mixed-valence defect ferrites [17], in a temperature range lying from about 150 to 200°C . The oxidation phenomenon is more important for samples prepared at low distances, in agreement with the previous results ascribing the lowest copper content (x) to the spinel phase of these films. In fact, copper ferrites can be roughly described by a formula such as $\text{Cu}_x^{2+}\text{Fe}_{(1-x)}^{2+}\text{Fe}_2^{3+}\text{O}_4^{2-}$ which implies high ferrous ion content when x is low.

For the sputtering conditions used, the films deposited on glass substrates are made of small crystallites (mean

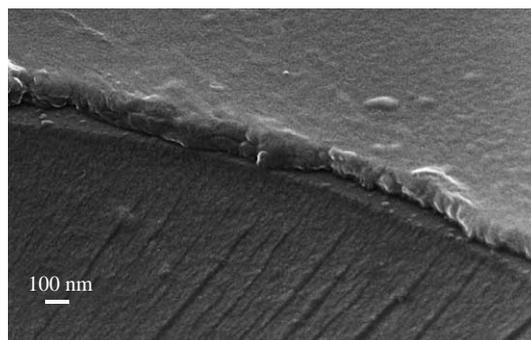


Fig. 5. Scanning electron micrograph of film deposited on glass substrate at $d = 6 \text{ cm}$ (sample surface-electron beam angle $\# 45^\circ$).

diameter close to less than 10 nm) and display very low roughness. AFM measurements show that the roughness (R_a) is close to 0.6 nm for the as-deposited films (Fig. 4). SEM observation brings also to the fore the low roughness and the good homogeneity of the films (Fig. 5). TEM micrographs of films directly deposited on carbon grids mainly reveal very small particles from 2 to 3 nm and some other which display larger sizes (# 5 to 10 nm) (Fig. 6a). Because of the very small size of the crystallites, it was not possible to focus the electron microdiffraction analysis on a single metallic or spinel particle. However, some crystallites, which display a high electronic absorption, could be identified as metallic copper (Fig. 6a). The copper crystallites which were identified by X-ray diffraction are the result of these particle aggregations.

When annealed at 400 °C in inert atmosphere, the surface of the films is strongly modified. Bumps of several hundreds nanometers height and larger than about 1 μm are formed. These bumps, which appear as coppery dots on optical micrographs (Fig. 6b), are unambiguously identified as copper particles by SEM chemical analyses. They result from the coalescence of smaller particles. It is difficult to precisely determine the growing mechanism of metallic islands. Nevertheless, some experiments carried out on patterned substrates with groove thread, width and depth of

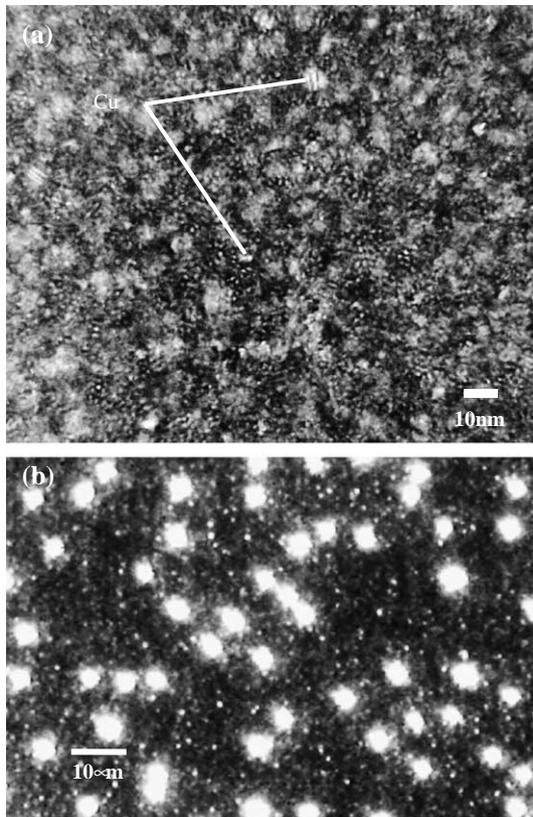


Fig. 6. (a) Transmission electron micrograph of film directly deposited on carbon grids, (b) Optical micrograph for films annealed at 400 °C under nitrogen.

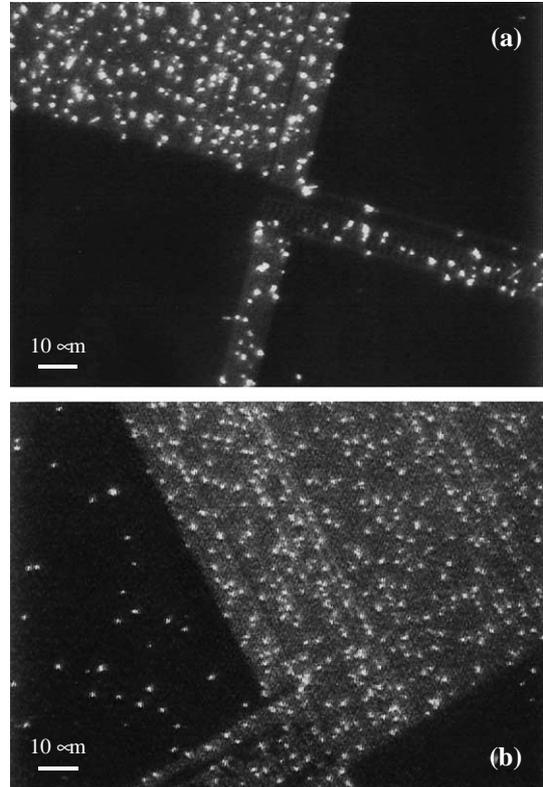


Fig. 7. Optical micrographs of copper particles self-assembly on patterned copper/ferrite film annealed in inert atmosphere at 300 °C (a) and 400 °C (b).

1 μm , 0.5 μm and 100 nm respectively, give interesting information.

When prepared on patterned substrates, as-deposited films display the same microstructure as that previously described. Copper grains of about 1 μm in diameter progressively appear after annealing in inert atmosphere from 150 to 400 °C. At first, these particles are observed in the patterned regions and then on the whole film. Above 250 °C however, a self-assembly phenomenon occurs and the

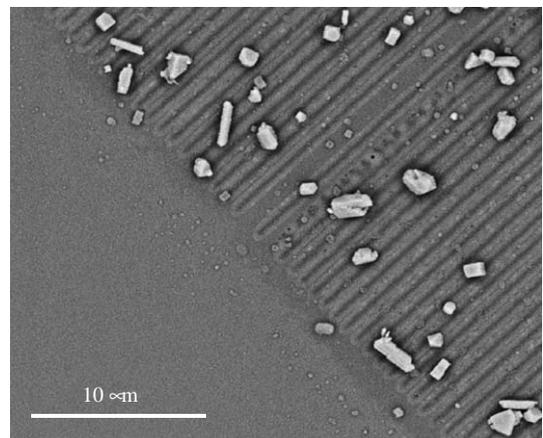


Fig. 8. Scanning electron micrograph of copper particles self-assembly on patterned copper/ferrite film, annealed in inert atmosphere at 400 °C.

particles are gathered in the patterned regions, leaving the other parts of the film surface almost free from metallic particles (Figs. 7 and 8). These observations suggest the starting small copper crystallites collide with each other because they are subjected to an increasing Brownian movement when annealed. The collisions involve the coalescence of the particles and their displacement tends to be stopped by the roughness of the substrate in the patterned regions. This mechanism is probably responsible for the self-assembly phenomenon, at least at the surface of the film. Similar self-assembly mechanism was already observed for colloidal particles deposited on patterned surfaces [18].

It is not easy to know whether the metallic particles located inside the film are subjected to the same in-plane migrations as the copper particles located on or near the surface. One could imagine that this mobility is less important inside the film. But, the copper crystallites can migrate from the core to the surface because of the small thickness of the film. When located at the surface, they could then follow the above described mechanism of growth and self-assembly. However, the resulting samples ought to display a very rich metallic copper surface in the patterned regions. On the other hand, the Cu/Fe ratio in the other regions ought to be lower than 1/2. The 1/2 ratio is fixed by the maximal x value in $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ ferrite.

Energy Dispersive X-ray analyses show that the Cu/Fe ratio is almost the same and close to 1 on the whole film for all deposition conditions. Secondary Ion Mass Spectroscopy also confirms a quite good homogeneity of the chemical composition, except at the extreme surface where copper content is higher in the patterned regions. It can then be assumed that the copper particles observed in these regions only come from the aggregation of small particles located at, or very near, the film surface.

4. Conclusion

Nanocomposite thin films made of metallic copper and spinel ferrite have been prepared by the sputtering of pure delafossite target. The formation of the metallic and spinel

oxide phases is due to low losses of oxygen during the sputtering, making the two-phased system more stable than the delafossite. The metallic copper content of the films depends on the substrate-target distance. The highest content of copper is observed for short distance.

The very small crystallites of copper can grow during annealing treatments carried out under inert atmosphere from room temperature to 400 °C. The growing process is mainly due to the motion of the crystallites at the surface of the films. This motion can be stopped by grooves inside the composite layer, making self-assembly of copper particles possible.

References

- [1] K. Niihara, A. Nakahira, T. Sekino, *Mater. Res. Soc. Symp. Proc.* 286 (1993) 405.
- [2] J. Narayan, Y. Chen, *Philos. Mag.*, A 49 (1984) 475.
- [3] B. Abeles, Ping Sheng, M.D. Coutts, Y. Arie, *Adv. Phys.* 24 (1975) 407.
- [4] D. Chakravorty, *Bull. Mater. Sci.* 15 (1992) 411.
- [5] J.L. Dormann, C. Sella, P. Renaudin, A. Kaba, P. Gibart, *Thin Solid Films* 58 (1979) 265.
- [6] J.L. Dormann, C. Djega-Mariadassou, J. Jove, *J. Magn. Magn. Mater.* 104/107 (1992) 1567.
- [7] A. Marchand, X. Devaux, B. Barbara, P. Mollard, M. Brieu, A. Rousset, *J. Mater. Sci.* 28 (1993) 2217.
- [8] A. Malats I Riera, G. Pourroy, P. Poix, *J. Magn. Magn. Mater.* 125 (1993) 125.
- [9] O. Fruchart, M. Klaua, J. Barthel, J. Kirschner, *Appl. Surf. Sci.* 162/163 (2000) 529.
- [10] S. Ben Amor, B. Rogier, G. Baud, M. Jacquet, M. Nardin, *Mater. Sci. Eng., B, Solid-State Mater. Adv. Technol.* 57 (1998) 28.
- [11] A.E. Katkov, A.A. Lykasov, *Inorg. Mater.* 39 (2003) 171.
- [12] E.J.M. Verwey, P.W. Haayman, F.C. Romeijn, *J. Chem. Phys.* 15 (1947) 174.
- [13] E. Kitzinger, Z. Simsa, *Czech. J. Phys.*, B 18 (1968) 955.
- [14] N. Namba, S. Kobayashi, *Jpn. J. Appl. Phys.* 17 (1978) 1819.
- [15] Ph. Tailhades, C. Villette, A. Rousset, G.U. Kulkarni, K.R. Kannan, C.N.R. Rao, M. Lenglet, *J. Solid State Chem.* 141 (1998) 56.
- [16] R. Parker, in: D.J. Craik (Ed.), *Magnetic Oxides Part 1*, John Wiley and Sons, London, 1975, p. 461.
- [17] S. Capdeville, P. Alphonse, C. Bonningue, L. Presmanes, Ph. Tailhades, *J. Appl. Phys.* 96 (2004) 6142.
- [18] K.H. Lin, J.C. Crocker, V. Prasad, A. Schofield, D.A. Weitz, T.C. Lubensky, A.G. Yodh, *Phys. Rev. Lett.* 85 (2000) 1770.