# *Chapitre 9 :*

# *Conclusions de la Partie II*

# 9 Conclusions de la Partie II

Dans la Partie II, nous avons étudié des transitions reliées aux phénomènes de séparation de phase, d'ordre de charge et orbital.

La migration électronique dans les plans (chapitre 6), la ségrégation de phase électronique (chapitre 7) et la coexistence de phases macroscopiques (chapitre 8) sont des sujets controversés. Nous les avons étudiés afin d'améliorer leur compréhension avec l'aide de techniques de diffraction à haute résolution (neutrons et synchrotron) et des techniques complémentaires comme la relaxation de muons et des mesures d'aimantation sous champs magnétiques intenses.

Dans le chapitre 6, nous avons interprété la transition de l'état ferromagnétique à l'état antiferromagnétique (type A). Elle a pour origine la migration des électrons vers les plans ferromagnétiques de la structure antiferromagnétique (type A). Ce réarrangement électronique donne lieu à une distorsion structurale qui est fortement liée à l'ordre magnétique.

Les propriétés inhabituelles et la nature hétérogène de $Pr_{2/3}Ca_{1/3}MnO_3$ ont aussi été étudiées. Notre travail a révélé la distribution spatiale des phases FM-métalique et AFM-CO dans ce composé. Des données de NPD et de μSR ont permis d'écarter l'image d'un état AFM homogène incliné à basse température. Nous avons trouvé l'existence de larges domaines ferromagnétiques densément distribués. L'origine de la coexistence de deux types d'ordre magnétique différent est la ségrégation de phase électronique.

Des études magnétiques, de transport et structurales ont été réalisées dans la zone riche en trous de la famille $Bi_{1-x}Ca_xMnO_3$ (chapitre 8). Cette étude est centrée sur : a) la détermination des phénomènes de séparation de phase, b) l'identification des différents types d'ordres orbitaux et de charge en fonction du dopage, c) la détermination de la transformation structurale induite par la température, d) la résolution des structures magnétiques à basse température.

Les structures cristallographiques et magnétiques dans la famille de composés $Bi_{1-x}Ca_xMnO_3$ ont été déterminées grâce à l'analyse Rietveld des données de NPD et SXRPD, et leur ordre orbital et magnétique a été identifié et interprété. Cette étude suggère une révision du diagramme de phase due à l'hétérogénéité chimique trouvée dans les phases ségrégées de composés fortement dopés.

Nous avons également étudié l'effet du dopant $Bi^{+3}$ dans la région riche en trous du diagramme de phase. L'ordre orbital quasi-dégénéré dans le composé avec x = 2/3 a été déterminé sans ambiguïté grâce à des mesures de diffraction à haute résolution (NPD et SXRPD).

L'origine du faible ferromagnétisme dans la zone fortement dopée a été associée à l'existence de larges domaines ferromagnétiques dans la phase magnétique de type G. L'existence de ces

domaines semble être une séparation de phase électronique dans la phase orthorhombique de type G qui contient moins d'électrons $e_g$ que la phase monoclinique de type C.

Des études plus approfondies pourraient être dirigées vers la compréhension de la ségrégation de phase électronique dans la phase orthorhombique de type G. Des études de µSR sur des composés monophasés aideront à la compréhension de la distribution spatiale de ces domaines comme dans le cas du composé $Pr_{2/3}Ca_{1/3}MnO_3$.

Les composés dopés au Sr présentent aussi des transitions de phase très intéressantes et des phénomènes de séparation de phase qui demandent des études plus approfondies. De même, la région riche en électrons de la famille de composés $Bi_{1-x}Ca_xMnO_3$ reste encore non explorée, et est une région très attrayante pour étudier l'effet du "lone pair" du $Bi^{+3}$ dans un système à électrons fortement corrélés.

# 9 Conclusions to Part II

In conclusion, in this Part II we have studied a variety of transitions related to the phase separation phenomena, the charge, and orbital ordering.

Electronic migration into planes (chapter 6), electronic phase segregation (chapter 7) and macroscopic phase coexistence (chapter 8) are hot topics, and we have undertaken their study with the aim of getting more insight into their understanding using high resolution diffraction techniques (Neutron powder diffraction and synchrotron X-Rays powder diffraction) and complementary techniques as Muon spin relaxation measurements and magnetisation under very high magnetic fields.

In chapter 6, we have interpreted the FM to A-type AFM transition to be originated from the electron migration to the FM planes of the A-type magnetic structure. Such electronic reallocation gives rise to a structural distortion that is intimately related to the magnetic order.

The unusual properties and mixed nature of $Pr_{2/3}Ca_{1/3}MnO_3$ have been investigated in chapter 7. Our study revealed the spatial distribution of the coexisting FM-metallic and AFM-CO phases in $Pr_{2/3}Ca_{1/3}MnO_3$. NPD data jointly with μSR lead us to rule out the homogeneous canted-AFM state developing at low temperatures. We have found the existence of large FM domains densely scattered in the sample. Hence, the origin of the coexistence of two type of magnetic order is due to electronic phase segregation.

Electrical, magnetic and structural studies have been performed on the hole rich region of the $Bi_{1-x}Ca_xMnO_3$ family of compounds (chapter 8). The present study is focussed onto: a) the determination of phase separation phenomena, b) the identification of the different types of orbital ordering and charge ordered striped structures as a function of the doping ,c) determination of the temperature driven structural transformations, d) resolution of the low temperature magnetic structures.

The crystal and magnetic structures in the $Bi_{1-x}Ca_xMnO_3$ family of compounds have been determined by Rietveld analysis of NPD and SXRPD data, and their orbital and magnetic ordering has been identified and interpreted. A revision of the phase diagram has been suggested in the light of the chemical inhomogeneity in the phase separated highly hole doped compounds.

We have also studied the effect of $Bi^{+3}$ doping on manganites in the hole rich region of the phase diagram. The unambiguous quasi-degenerate state in the orbital ordered state in x=2/3 Ca doping has been studied on the basis of high-resolution NPD and SXRPD.

The origin of the weak FM in heavily doped compounds has been found to be associated to large FM domains in the G-type magnetic phase. The origin of the existence of this FM domains is

likely to be electronic phase separation in the G-type orthorhombic phase which contains fewer $e_g$ electrons than the C-type monoclinic phase.

Further studies can be directed towards the understanding of the electronic phase segregation in the G-type orthorhombic phase. μSR studies on single-phase similar compounds would help the understanding of the spatial distribution of the domains as in the case of $Pr_{2/3}Ca_{1/3}MnO_3$ compound.

The Sr doped compound, which also shows interesting phase transitions and phase coexistence phenomena, requires also further studies. As well as the electron rich region in the $Bi_{1-x}Ca_xMnO_3$ family of compounds is still unexplored and is an interesting region to study the effects of the $Bi^{+3}$ lone pair on the highly correlated electron system.

# *Chapitre 10 :*

# ***Conclusion Générale***

# 10 Conclusion Générale

L'objectif premier de ce travail de thèse a été d'approfondir la compréhension de nouveaux thèmes qui sont associés aux perovskites de manganèse à valence mixte.

Dans cette thèse, nous avons mis en avant la variété de transitions magnétiques, électroniques et structurales des manganites à valence mixte qui ont une grande importance du point de vue de la Physique appliquée et fondamentale. Les propriétés de ces oxydes fortement corrélés proviennent de la compétition d'une série d'interactions complexes et leur compréhension reste un défi primordial pour les physiciens de l'état solide

Dans ce travail, deux sujets importants ont été traités. Tout d'abord, nous avons analysé l'effet de l'existence de joints de grain dans le transport dépendant du spin dans les manganites ferromagnétiques et métalliques. Ensuite, nous avons étudié la tendance vers les inhomogénéités des charges et la séparation de phases dans les manganites fortement dopées en trous.

Les contributions les plus importantes de cette thèse relatives au premier thème ont été la démonstration empirique du caractère inhomogène et percolatif de la conduction électrique dans des couches polycristallines ainsi que l'identification du tunneling inélastique dépendant du spin comme le mécanisme qui contrôle le transport électrique entre les grains. Ce mécanisme dépend de l'orientation relative des moments dans les grains voisins et des moments dans la barrière électrique. La nature de la barrière électrique a été aussi élucidée dans cette thèse grâce à une série d'expériences et mesures sans précédent. Toutes nos expériences s'accordent avec l'hypothèse selon laquelle on considère la barrière électrique existant entre les grains métalliques comme étant la surface des grains. Par ailleurs, il a été démontré que des déformations structurales et le désordre sont à l'origine d'importants changements dans les propriétés de ces composés: par exemple 1% de contrainte epitaxiale donne lieu à l'apparition d'une forte anisotropie magnétique et à une forte modification de la température de la transition méta-isolant. Les évidences plus remarquables permettant d'arriver jusqu'à la nature de la barrière électrique ont été obtenues à partir des résultats des mesures topographiques sur des couches polycristallines bien caractérisées, les mesures sur des couches où des joints de grain ont été créés à température ambiante par la méthode de la scie atomique, et les mesures de magnetoresistance sur des champs magnétiques forts (30T). Grâce à ces techniques, la nature de la barrière électrique dans les joints de grain a été déterminée comme ayant une origine cristallographique et l'idée d'une nouvelle phase chimique a été rejetée.

Beaucoup de progrès ont été faits aussi dans la compréhension de la forte tendance des manganites valence mixte vers la ségrégation / séparation des phases grâce à l'étude combinée des mesures de diffraction des poudres avec des neutrons et rayons X au synchrotron, par des mesures de relaxation des muons et des mesures d'aimantation avec des champs magnétiques intenses sur des

composés bien caractérisés où la stabilisation de l'ordre orbital se réalise par le dopage en électrons ou trous ou par des effets stériques (via substitutions cationiques d'égal valence $Ca^{2+}$-$Sr^{2+}$). Profitant au maximum de la haute résolution des nombreux grands instruments européens, nous avons démontré que la déstabilisation de l'ordre orbital et de charges par effets stériques dans un composé bien connu ($Pr_{1/2}Ca_{1/2}MnO_3$) se fait par l'apparition d'un nouveau ordre orbital et magnétique ($Pr_{1/2}Sr_{1/2}Mn_3$) que permet un nombre majeur de liaisons ferromagnétiques. Nous avons aussi démontré que la déstabilisation d'un ordre orbital et de charge stable par le dopage en porteurs donne lieu à une forte tendance vers des états fondamentaux inhomogènes qui présentent ségrégation électronique et/ ou séparation macroscopique des phases. Une autre contribution forte de cette thèse à ce sujet a été de démontrer que la séparation macroscopique des phases est stabilisée par des inhomogénéités chimiques créés par la tendance intrinsèque à la stabilisation de vacants dans les phases. La ségrégation électronique, par contre, a lieu quand la concentration d'électrons ne permet pas la stabilisation d'un état fondamental plus bas en énergie avec un ordre orbital déterminé. Nos résultats contrastent avec ceux de certains auteurs qui affirment que la séparation des phases est le résultat du développement de contraintes entre grains, mais la haute résolution de nos données rend notre interprétation la plus vraisemblable.

La haute résolution de nos données nous a aussi permis l'observation d'un état fondamental quasi-dégénéré dans le composé $Bi_{1/3}Ca_{2/3}MnO_3$ .

Nous avons interprété la magnetoresistance et le faible ferromagnétisme qui apparaît dans les composés à faible concentration d'électrons et nous avons trouvé une forte relation entre ces propriétés et la séparation électronique et macroscopique présent à ces compositions.

Cette thèse propose une révision des diagrammes des phases des manganites basé dans le fait de la forte tendance intrinsèque vers la ségrégation / séparation électronique ou macroscopique des phases dans les manganites.

Les études réalisées dans cette thèse pouvaient être complétées par une étude systématique de la région riche en électrons du diagramme des phases dans des familles de composés bien choisis. Dans ce cas, la corrélation électronique serait renforcée et pourrait changer complètement la nature des états fondamentaux.

Cette thèse offre aussi un nouveau point de départ pour le développement de systèmes à application technologique à base de manganites grâce à la démonstration du fort effet des contraintes et la possibilité de considérer la surface des grains comme une partie à considérer dans les futurs dispositifs.

# 10 General Conclusion

The main objective of this thesis has been to get further understanding on several hot topics related to mixed valence manganites.

In this thesis, we have shown that mixed valence manganites display a variety of magnetic, electronic and structural transitions of great importance for fundamental and applied physics. The properties of these strongly correlated oxides are the result of the competition of a series of complex interactions and their comprehension remains one of the most important challenge in condensed-matter physics.

In this thesis two main topics have been investigated. Firstly, we have investigated the effect on the spin transport of the existence of grain boundaries in a ferromagnetic and metallic manganite. Secondly, we have investigated the tendency towards the charge inhomogeneity and phase separation in highly hole doped manganites.

The main contribution of this thesis to the first topic has been the empirical demonstration of the inhomogeneous and percolative electrical conduction in polycrystalline films. Experimental proofs have been given evidencing that the spin dependent inelastic tunneling is the most probable mechanism controlling the electrical transport between grains. This mechanism depends on the relative orientation of the moments in neighbouring grains and on the intrinsic orientation of the moments in electrical barrier. The nature of the electrical barrier has also been elucidated in this thesis thanks to different unprecedented measurements and experiments. All of our experiences agree with the hypothesis of considering the electrical barrier between the grains to be the grain surface itself. In this work, it has been demonstrated that structural distortions and disorder are at the origin of important changes in the properties of these compounds, as for example the fact that 1% of epitaxial strain is at the origin of the apparition of a strong magnetic anisotropy and an important change of the metal-insulator transition. Nevertheless the most relevant evidences elucidating the nature of the electrical barriers ha have been the topographic measurements on well characterised polycrystalline films, as well as the measurements on films where artificial grain boundaries have been created at RT by the atomic saw method, or the unprecedented measurements of magnetoresistance under magnetic fields of 30T. Thanks to these techniques, the nature of the grain boundaries has been found to have a crystallographic and not a chemical origin.

Some progress has been also attained on the understanding of the tendency of mixed valence manganites towards phase segregation/separation thanks to the combined study by neutron and synchrotron X rays powder diffraction and by muon spin relaxation and magnetisation measurements under high magnetic field on a series of well characterised compounds where the destabilisation of the

orbital order is performed through hole doping or steric effects ($Ca^{2+}$-$Sr^{2+}$). Taking the maximum profit of the high resolution of the instruments of some important european facilities we have demonstrated that the destabilisation via steric effects of the charge and orbital ordered state in a "well known" commensurate compound ($Pr_{1/2}Ca_{1/2}MnO_3$).is carried out by the apparition of an unexpected orbital and magnetic order ($Pr_{1/2}Sr_{1/2}Mn_3$) which favours more FM than AFM bonding. However, the destabilisation of a strong and extended orbital and charge order via carrier doping seems to give rise to inhomogeneous ground states found to exhibit electronic segregation and/or macroscopic phase separation tendency. Another important contribution of this thesis to this topic is to demonstrate that macroscopic phase separation is stabilised by chemical inhomogeneity originated by the intrinsic tendency of vacancy stabilisation in the phases while electronic ségrégation is stabilised when carrier concentration do not allow the phase to have a orbitally ordered ground state which would lower the energy of the system. Our results contrast with those of certain authors who recently affirmed that phase separation is the result of intergranular strain but the high resolution of our data make our interpretation very likely. In this sense, the observation of quasi-degenerate ground state in the compound $Bi_{1/3}Ca_{2/3}MnO_3$ has been also an interesting result of this work .

In addition to that, a interpretation of the magnetoresistance and weak ferromagnetism appearing in samples with low electron concentration has been given with is strongly related to the electronic and macroscopic phase segregation present at these compositions

This thesis proposes a generalisation of the ideas pointing towards an intrinsic tendency towards electronic or macroscopic phase segregation/separation for a revision of the phase diagrams of mixed valence manganites.

The studies undertaken in this thesis could be completed by a systematic study of the electron rich region of the phase diagram in well chosen family of compounds. In this case, the electron correlation contributions will be enhanced and can change completely the nature of the ground state.

This thesis also offers a new starting point for designing systems for technological application based on mixed valence manganites because of the relevant ideas related to the strong effect of epitaxial strain on the properties of these compounds as well as on the new idea of considering the manganites grain boundary itself as an active part of future technological devices.

# *Appendice A:*

# *Dépôt laser pulsé et conception d'une chambre pour le dépôt des oxydes*

# Appendix A: Pulsed laser deposition and Design of a Chamber for Oxides Deposition

## A.1 Introduction

Deposition techniques are in constant development in order to answer to the requirements of industrials looking for high reproducibility, fast and cost efficient production of large (5-10 inches) films and of researchers who look for high quality deposition techniques, even for small surfaces, for elaborating model systems. The choice of a deposition technique for the growth of a certain material is intimately related to its peculiarities.

Manganite film growth has been carried out using different deposition techniques as:

a) Screen printing (ex. [239]).

b) Sputtering (ex. [83, 240])

c) Physical Vapour deposition techniques as chemical vapour deposition or pulsed laser deposition [51, 66, 91, 92, 241-244].

## A.2 Pulsed Laser Deposition

Pulsed laser deposition has been extensively used for the deposition of complex multielement materials like HTc superconductors that are perovskite cuprates, as well as complex superlattice structures. PLD is well adapted to grow manganite films.

### A.2.1PLD deposition process

Pulsed laser deposition is based on the action of a focalised high intensity pulsed laser beam onto the target of the material to be deposited, inside a vacuum chamber. In a first step, the focalised laser beam locally heats a small volume of material at the target surface to a temperature well above the melting temperature. A plasma is formed, consisting mostly in atoms and ions, but also molecules and free electrons. Micronic particulates (droplets) can be ejected from the liquid surface.

The target is constituted by a dense stoichiometric sample (sintered powder or single crystal) of the studied material. There is no need to have the good crystallographic structure in the target, only the stoichiometry and density are important parameters.

The substrate is located in front of the target and generally parallel to the target surface or some times at 90° in the "in axis" geometry to avoid particulates. However, if several elements are to be deposited the 90° substrate geometry generates composition gradients and non constant thickness which can be improved by substrate rotation [245]. In order to avoid particulate deposition the substrate can be also located completely "off axis". Nevertheless, in this case the stoichiometry of the target is usually not conserved.

Laser characteristics as wavelength, focalisation and power are determined by the material to depose and the background gas.

PLD is a vacuum technique, however low pressures of reactive gases are permitted. For the deposition of manganites we used a few hundreds mTorr of oxygen which allowed a good crystal growth as well as the correct oxidation during the deposition process.

There exist three stages in the PLD evaporation process (Fig. A-1). In the first step, a), the energy provided by the focalised pulsed laser is absorbed by the target. The energy density provided should be larger than the energy density threshold for plasma creation (≈100MW/cm$^2$). To obtain it, the local target surface temperature should be well above the melting temperature of the material so that the target surface becomes a condensed plasma which will then expand. The second step, b), consist in the interaction between the end of the laser pulse and the evaporated species. In this step, the species in the plume will absorb the energy provided by the laser beam proceeding to their ionisation. This process will contribute to the expansion of the plasma. In the third step, c), the plasma expands interacting with the background gas or in the vacuum and the evaporated species reach the substrate with certain energy and with an element distribution.

The generated plume tends to be perpendicular to the target surface because the plasma expands along its smallest direction. The distribution of the species has a non thermal behaviour.

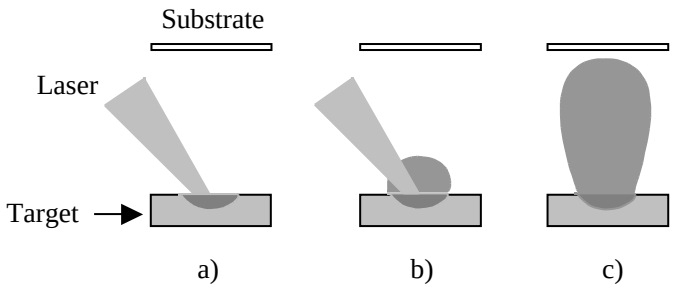



**Fig. A-1** *Schematic description of the PLD process*

## A.2.2PLD characteristics

PLD permits the stoichiometric deposition of the material constituting the target into the film thanks to instantaneous energy exchanged between the laser beam and the target surface during a laser pulse. During the plasma expansion, there could exist a change of the plume stoichiometry as well as a spatial distribution of the species of the plume because of the different diffusion of the species. Nevertheless, the effect of these processes generating a non stoichiometry of the plume can be solved by an averaging action performed on the substrate or target. It consists in generating scanning with the laser beam on the target and/or rotation of the target. Moving the laser also prevents to drill the target.

We have been using a vibrating mirror located outside the deposition chamber to generate the laser movement on the fixed target (Fig. A-12).

PLD allows using small targets due to the reduced laser spot size in contrast to sputtering techniques where several inches of diameter targets are required. In addition, several targets can be introduced in the deposition chamber taking few place because of their reduced diameter. No special electrical connection is needed for the target which allows fast and easy replacement. In our case, a four targets holder, allowed the deposition of heterostructures (Fig. A-12).

Control of the deposition rate can be archived and high as well as very low deposition rates (<Å/min) can be used in order to improve the film growth or to grow very thin films with a good thickness control. Deposition rate can be controlled in different ways as for example changing the focalisation degree of the laser beam on the target or the laser power.

In PLD, the possibility of deposition under a low pressure of a reactive gas has an important role in the plume expansion process as well as in the reactive process. In the case of oxides growth, the introduction of oxygen gas is necessary. In our set-up, a flow of gas is controlled in the 300mTor pressure range. This fact made impossible the use of techniques as RHEED (reflection high-energy electron diffraction) or LEED (low energy electron diffraction) to control the film growth. However, a modification of the standard RHEED system has lately been developed in the University of Twente [246] which, thanks to a double stage differentially pumped electron gun (at very short distances), permits to grow oxides films in an oxygen background pressure of 0.5mbar. Another way of introducing the reactive gas, injecting it very close to the substrate, permits to keep a high vacuum in the deposition chamber and the gas do not contribute to the plume expansion process.

The latter set-up permits to grow oxide films. Some authors have studied the growth of manganites $La_{1-x}Sr_xMnO_3$ films on $SrTiO_3$ substrates using a low background pressure (1mT) [247]. However, at this background pressure the films do not seem to have the correct oxygen stoichiometry.

There are several disadvantages of PLD technique as for example the existence of micronic particulates in the plume, which reach the film as droplets. A reduction of the particulates creation can be obtained using an adequate laser wavelength as will be discussed later, or by tuning the laser fluence, imposing a movement of the laser with respect the target as well as increasing the target density, controlling the target surface or, if possible, increasing the target substrate distance. Other more sophisticated methods have been used to reduce the particulates deposition as the plasma deviation by magnetic fields or by synchronised mechanical choppers [248].

PLD can be considered as a “research technique” because the maximum film size is about $\approx 4cm^2$ ($1inch^2$), hence not suitable for the deposition of large surfaces due to the plume directionality and low deposition rate. Even if a movement can be conferred to the laser spot in order to sweep large

target surfaces giving rise to large films, this is far from being as easy as sputtering techniques, for example, which are extensively used in the industry.

## A.3 Optimisation of PLD parameters for manganite oxides deposition

### A.3.1 Laser wavelength

Laser wavelength has a big effect on the laser ablation process because the absorption length in the target material depends on it and determines the ablation energy threshold.

In the present work we present the difference in particulate content between a Nd-YAG laser tripled (λ=355nm, blue-UV) and another doubled (λ=532nm, green). SEM observations, (Fig. A-2, Fig.A-3), of $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) films deposited with each wavelength agree with the results obtained in HTc superconductors [249] in the sense that a reduction of the wavelength produces a clear decrease of the particulate content on the film.

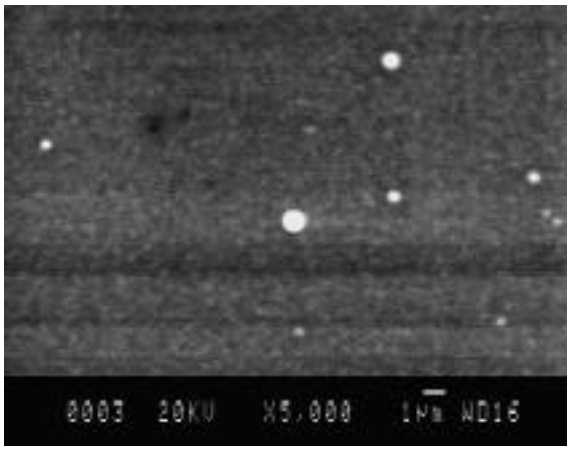



**Fig. A-2** *SEM photograph of a 60nm manganite film deposited on MgO(001) substrate with tripled Nd-YAG*

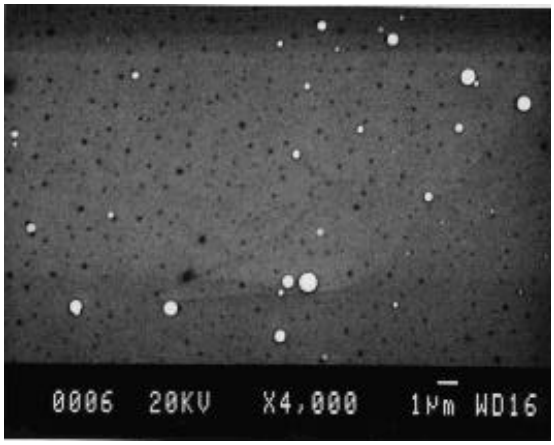



**Fig. A-3** *SEM photograph of a 60nm manganite film deposited on MgO(001) substrate with a doubled Nd-YAG*

The existence of particulates can be related to the absorption coefficient, which depends on the laser wavelength. The larger the absorption coefficient, the thinner the molten zone. In Fig A-4 is displayed the optical conductivity of single crystals of the parent compound $La_{1-x}Sr_xMnO_3$ [250]. In the evolution of the optical conductivity for the compound with x=0.3, it can be observed that the highest optical conductivity is for the UV light. The absorption coefficient η defined as the fraction of the energy of the incident light absorbed by the material when going through a unity of the thickness of the material corresponds to:

$$\eta = \frac{2\kappa\omega}{c} \qquad \textbf{Eq. A-1}$$

where κ is the imaginary part of the refraction index that can be expressed as:

$$\kappa = \mathrm{Im}(N) = \mathrm{Im}\left[\varepsilon(\omega) + \frac{4\pi\sigma}{\omega} i\right]^{1/2} \qquad \textbf{Eq. A-2}$$

ε is the dielectric constant and σ the optical conductivity. From Fig.A-4 we extract that the optical conductivity of the x=0.3 compound is about four times larger for λ=355nm than for λ=532nm. Considering manganites to behave as a good metal and approaching ε ≈0 we estimate the absorption coefficient to $\eta = \frac{2\kappa\omega}{c} \approx \frac{2\omega}{c}\left(\frac{2\pi\sigma}{\omega}\right)^{1/2}$. So, for λ=532nm, the absorption coefficient is half the one for λ= 355nm and thus the absorption depth is twice the value obtained for UV light. If we consider that for 670nm light the refractive index is about $n=N+i\kappa\approx 2.4+0.45i$, using the exact value of κ we obtain a absorption depth of about 0.12μm for λ=670nm, so for UV light the absorption depth is about 0.06μm.

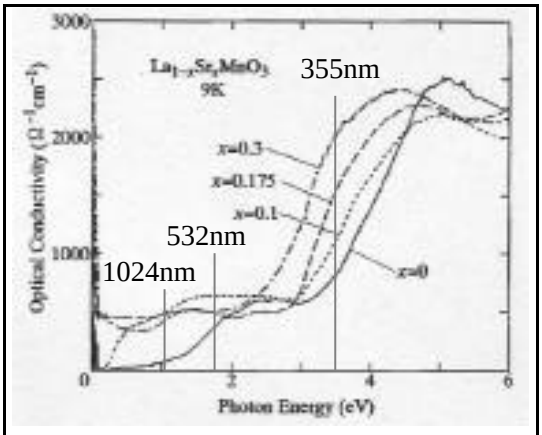



**Fig. A-4** *Optical conductivity of single crystal compounds of the family $La_{1-x}Sr_xMnO_3$*

The extracting effect of the laser beam depends on the laser parameters like pulse energy, duration, shape and wavelength, as well as the temperature dependent optical properties like reflectivity or absorption coefficient, as we have already shown. Finally, it depends also on the thermal properties of the material like heat capacity, density or thermal conductivity. When the volume etched per pulse is large compared to the volume that can be volatilised by the absorbed energy, there exist instabilities in the target surface that result in the emission of micrometric sized particulates [251]. The estimated thermal diffusion length , $L_{th} = (2D_{th}\tau)^{1/2}$, in the insulating state of manganites like LCMO is about 0.05 μm considering the thermal diffusivity to be $D_{th}$= 0.15mm$^2$/s from [252] and τ=10ns. $L_{th}$ is thus of same order than the optical absorption depth for UV light. So most of the etched material can be volatilised when considering that the heat generated at the surface of the target is confined at a depth of the dimensions of the thermal diffusion length.

Another reason that can explain the diminution of droplets for shorter wavelength laser beams consist in the fact that in the ablation process there exist a strong interaction between the plume and the incident laser beam. The absorption of photons from the incident beam has the evident effect of heating up the plasma (typical temperature of $10^4$K) and produces the fragmentation of the particulates existing in the plasma [249].

## A.3.2Laser power and laser fluence

### A.2.3.1 Varying fluence through spot size

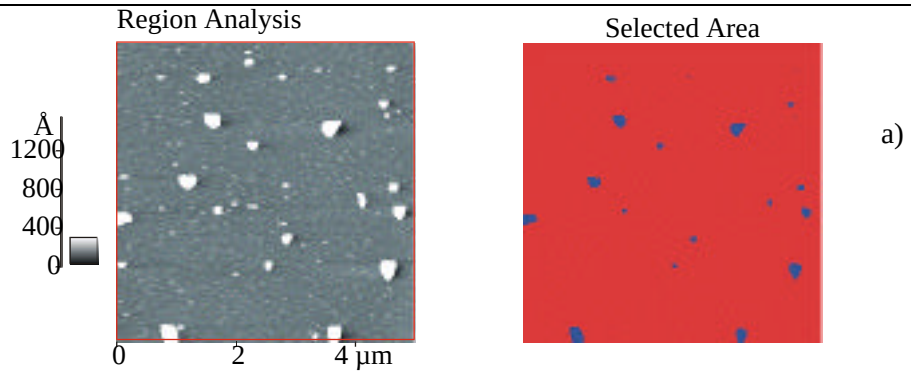
The focalisation of the laser beam has two effects on the PLD process: on the one hand it allows to reach the energy threshold for ablation and on the other hand it determines the size of the beam spot on the target. In our experimental set-up a 50cm focal distance lens is used to focalise the laser beam. In Fig. A-7 it is shown two AFM pictures for films deposited at 39.5cm and 35.5cm of target to lens for a laser beam power of 1W. From the purely optical point of view, for equal laser beam initial diameter, the change in the lens-target distance will give rise to a beam diameter on the target of 0.21 times the initial diameter for a distance of 39.5cm, and 0.29 for a distance of 35.5cm. In terms of fluence, F:

$$\frac{F_C(35.5cm)}{F_f(39.5cm)} = \frac{E/S_c}{E/S_f} = \frac{\left(\frac{1}{d_c}\right)^2}{\left(\frac{1}{d_f}\right)^2} = \frac{(0.21*D)^2}{(0.29*D)^2} = 0.524 \qquad \textbf{Eq.A-3}$$

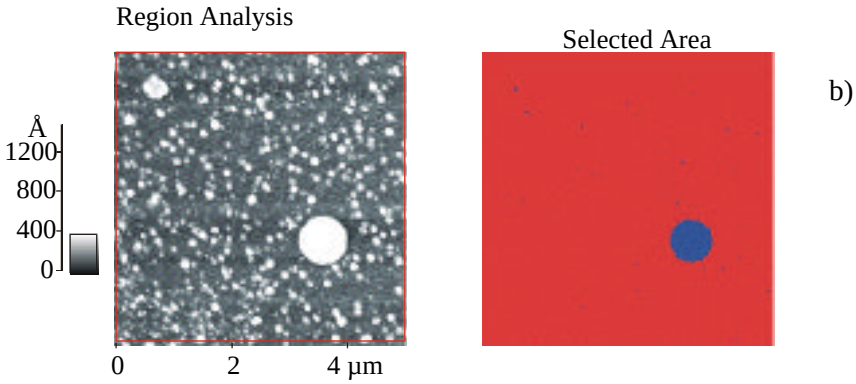
where E is the energy of the laser beam, S is the surface of the laser spot on the target and D is the diameter of the initial laser beam. From Eq.A-3, we conclude that the fluence is doubled for the film deposited with the lens at 39.5cm due to a reduction of the beam area on the surface of the target. The value of the fluence for the film at 35.5 is 3.1J/cm$^2$ pulse. Films shown in Fig. A-7 have the same thickness (60nm), and from the deposition time we can determine the deposition rate: $Drate_C$=60nm/167s= 3.6Å /s while for the 39.5cm film deposition $Drate_f$=60nm/360s=1.6Å /s. That means, about half the deposition rate for the double of the fluence.

The morphology of the manganite films deposited at different fluence is shown in Fig. A-7. For the lowest fluence, a), the film displays few submicronic particulates with no regular shape on a nearly flat background. While for higher fluence, b) displays clear rounded and micronic droplets on a rough background. Consequently, we conclude that higher fluences give rise to bigger droplets and rougher films on manganite films.

Comparing the rms roughness for a 1μm$^2$ area, we obtain values of average rough of 49 Å for the low fluence film and 73Å for the highest fluence film. In order to check the background roughness of the film we excluded the droplets zone by image treatment. The results obtained using such procedure (Fig.A-8) are shown.




| Region | Rp-v | Rms rough | Ave rough | Median Ht | Mean Ht | Surface area | Volume |
|---|---|---|---|---|---|---|---|
| [ A ] | 540 Å | 33.5 Å | 15.6 Å | 150 Å | 157 Å | 25.01 µ? | 0.3858 µ? |




| Region | Rp-v | Rms rough | Ave rough | Median Ht | Mean Ht | Surface area | Volume |
|---|---|---|---|---|---|---|---|
| [ A ] | 697 Å | 107 Å | 74.7 Å | 119 Å | 156 Å | 27.73 µ? | 0.3837 µ? |

**Fig. A-8** *Roughness analysis of the AFM pictures for 60nm LCMO films deposited at a)5 and b)3 J/cm$^2$ of laser fluence.*

The particulates present in the low fluence film are irregular and not disk-shaped. Submicronic particulates shape make us suppose that they come from the ejection of small fraction of target material from cracks in the surface of the target. One of the possible origins of particulate ejection are instabilities on the target surface due to craterisation or splashing [253]. The density of submicronic particulates in this case is larger than in the high fluence case. The high fluence film show disk-shaped particulates which are consistent with the idea of liquid droplets which arrive at the substrate surface and cool down.

For depositing high quality films, a low density of droplets and a small droplet size is required. For that reason we have decided to work in a 35.5cm lens-target distance. The density of the fracto-ejected particulates can also be tuned by the target density, as well as by a proper preparation of the

target surface before deposition. For example, target surface polishing process is able to eliminate all the craters in the target surface. Films with very low particulate content as well as very low roughness have been achieved under optimum deposition conditions.

## A.2.3.2 Varying fluence for fixed spot size

A study of the manganite films roughness as a function of the laser fluence and so keeping the spot size constant, has been performed. The films consist in 85nm thick LCMO on a STO (001) substrate. In this case, deposition conditions were fixed to: $T_{substrate}$=760°C, $P_{O2}$= 300mTorr.

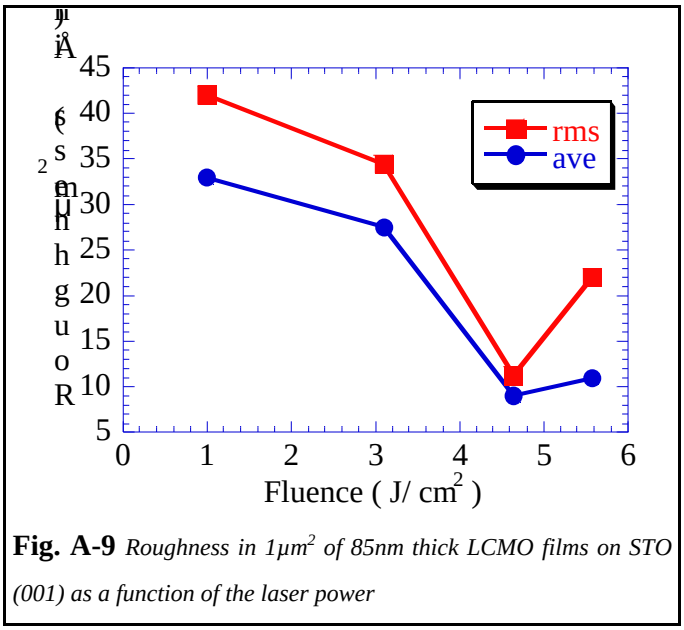



**Fig. A-9** *Roughness in 1μm² of 85nm thick LCMO films on STO (001) as a function of the laser power*

The fluence varied from 0.99 J/cm$^2$ per pulse (99MW/cm$^2$) to 5.56 J/cm$^2$ per pulse (556MW/cm$^2$). The analysis of the films roughness from AFM measurements (Fig. A-9, Fig A-11) confirm that for a fixed spot size low fluence values give rise to films that are rougher than for higher values of the fluence.

The plume under the presence of a background gas is characterised by two different zones: i) the inner zone is the closest to the target surface and it contains high density of species at very high temperature. ii) The outer zone is the zone where the density of species is reduced and it has a different appearance. Some authors suggested that the optimum substrate position for the deposition of oxides like the HTcs is at the border of this outer zone. We have approximately measured the length of both zones as a function of the laser power and we obtained that there exist a parabolic relation between the length of the plasma and the laser power as shown in Fig. A-10. From the plasma photographs we observe that above 1W of laser power, some parts of the visible plume are in contact with the substrate.

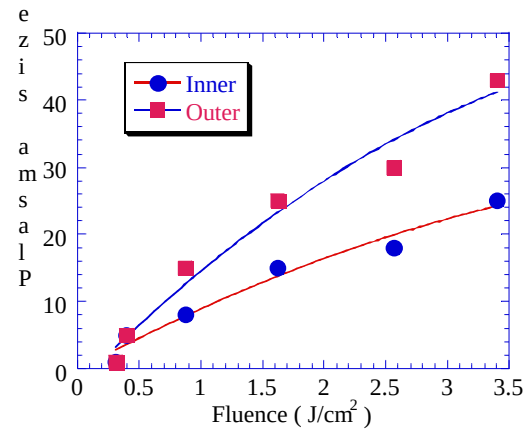



**Fig. A-10** *Inner and outer plasma size as a function of the laser power for λ=352nm*

The energy threshold for laser ablation of manganites using the UV laser is around 100mW of laser power which in terms of fluence is around 0.3 J/cm$^2$ (30MW/cm$^2$) for the existence of a visible spot on the target surface (Fig. A-10).

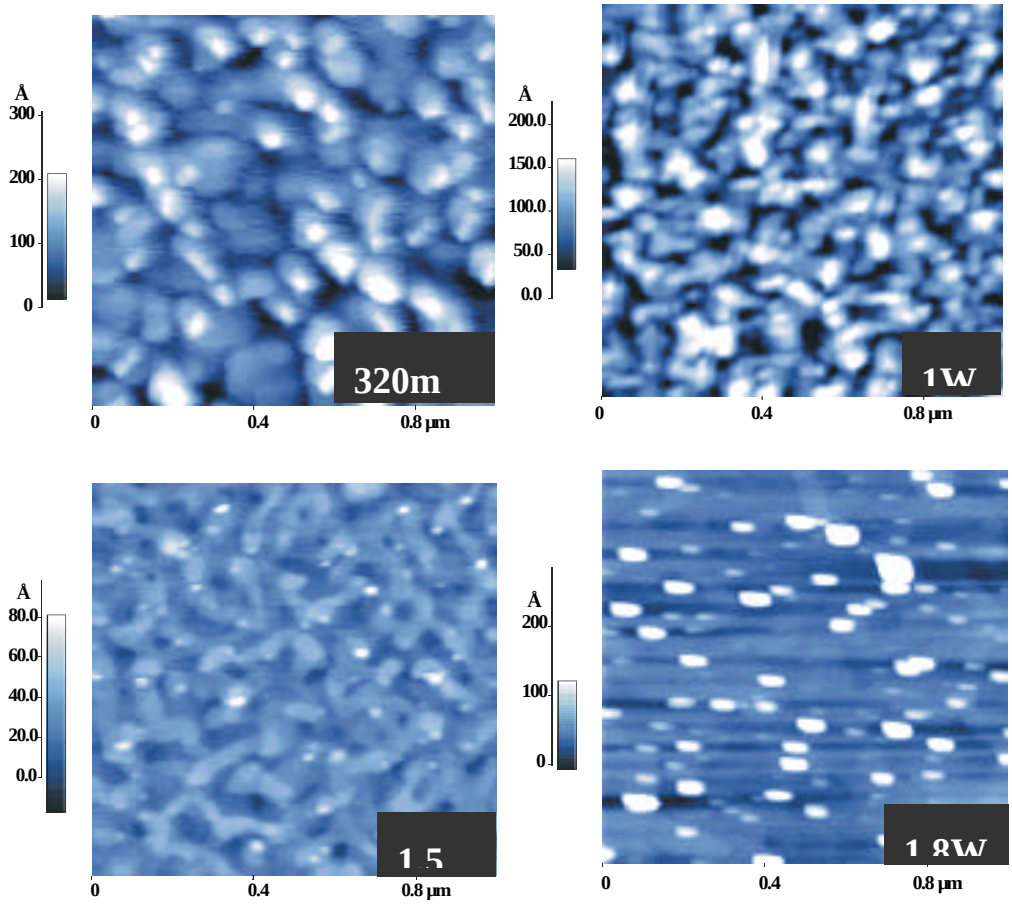



**Fig. A-11** *AFM images of 84nm thick films of LCMO on STO (001) substrate as a function of the laser power*

The plume created under 300 mTorr of background oxygen pressure is quite directional and could give an inhomogeneous film thickness. We have estimated the difference on film thickness taking into account that the deposition profile, in the case were the species in the plume interact with the background gas and with other species as electrons in the plasma, is given by Eq. A-4:

$$D(\theta) \quad \frac{\cos^{p}(\theta)}{h^{2}} \qquad \textbf{Eq. A-4}$$

where h is the distance between the substrate and the target, θ is the angle taken from the centre of the plume in the target position and p is a experimental parameter. Considering the values of our experimental set-up, where h=40mm and the maximum substrate dimension has been 10mm, we obtain that the maximum angle sustained is arctan(5/40)= 7.1 ° or 0.12 rad. Taking the values of *p* from HTCS deposition studies, which varies from 8-14 [251], we obtain that the thickness difference between the centre of the film and the end at 5mm ranges from:

$$1.064\,(p=5) > \frac{D_{center}(\theta)}{D_{5mm}(\theta)} > 1.114\,(p=14) \qquad \textbf{Eq. A-5}$$

That means a 10% variation in thickness between the edges and the centre of a film on a $1cm^2$ substrate. However, due to the fact that, in our case, the laser spot is small (for a lens-target distance of 35.5, the laser spot has a surface of 3.2 $mm^2$) the plume tends to be broad and the thickness distribution tends to low values of *p* and hence to smaller thickness differences. Finally, it should be noted that in our experimental set-up the laser spot scans the target surface. In conclusion, we expect a thickness uniformity better than 1% on 0.5x0.5 $cm^2$ surface films.

## A.4 Design and build up of a chamber for Oxides Deposition

Oxide deposition has been a new research subject in the Laboratory. PLD oxide deposition introduced several problems to the traditional UHV deposition chambers used in the Laboratory for intermetallic (3d-4f) magnetic films, as for example the fact that manganese perovskites oxide deposition requires the introduction of oxygen in the chamber as well as a high substrate temperature (up to 900°C). On the other hand, the possibility of producing multilayers by PLD using oxides was one of our objectives. This required an "in situ" film thickness control compatible with a background atmosphere. These reasons brought us to design and build up a new deposition chamber specially dedicated to oxide film deposition.

The first study of design of the deposition chamber was made using AUTOCAD-Light software. Once this first study was finished, a joint work with the head of the technology department of the Laboratory, J.C. Genna, was carried out using AUTOCAD software.

The chamber has 19 flanges, so in order to reduce the costs we bought the flanges already with sleeves, ready to be welded. All the flanges were provided by MECA-2000[3] .

The top curved cover was made by BONITEMPO[4]. The central part of the chamber is a cylinder of about 40 cm of diameter and 45 cm height. The material is stainless steel of 2mm thickness made by CELLINOX[5].

[3] MECA-2000 (Vide et Ultravide). Rue de Saint Leger, 78540 Vernouillet

[4] BONITEMPO. 94 av Général Leclerc .69 300-Caluire

[5] CELLINOX .BP 17. 73 100 Gresy sur Aix

The welding of the tubes with the flanges was performed by SDMS[6] using Argon welding. After the welding the chamber was ungreased, pickled and passived. An helium leak test of the whole system was performed after 24h pumping and guaranteed a limiting vacuum of $10^{-7}$ mbar.

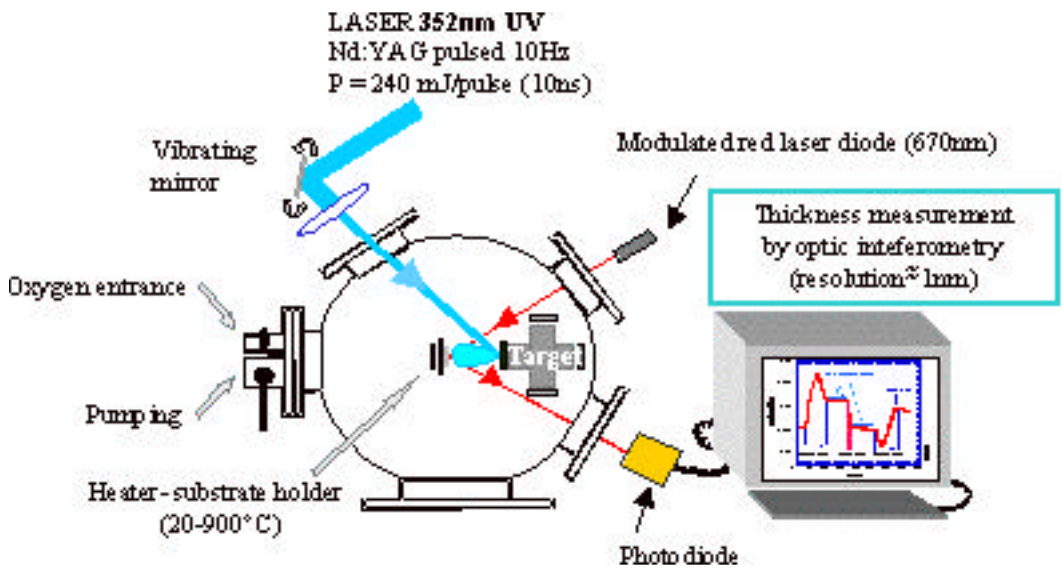



**Fig. A-12** *Schematic top view of the chamber designed and developed for oxides deposition.*

The full development of the deposition chamber took about one year time and its costs has been about 100000Fr (non equipped).

The oxide PLD set-up is shown schematically in Fig. A-12. A Nd:YAG pulsed laser working at 10Hz with wavelength of 352nm reflects into a UV vibrating mirror which has an oscillating movement centred in a adjustable position. After the mirror, a 50 cm focal length UV lens focalises the laser beam. The laser beam crosses a fused Silica window ( =50mm) and focalises onto the target. An additional low power (5mW) 670nm laser is used for the alignment of the pulsed laser.

Four targets are mounted on the sides of stainless steel holder, the centre of which is connected to a rotating axis. There exist a connection for the primary pumping and another for background gas entrance as well as vacuum breaking valve.

The substrate holder is at the centre of the chamber to make the chamber more versatile. Two symmetrical windows, at 45° from the laser entrance window, in front of the substrate position are used for the optical "in situ" monitoring of the film thickness by optical interferometry. In front of one of these windows a frequency modulated 670nm laser diode is disposed, while in front of the

[6] SDMS Chaudronnerie blanche. BP. 4.38160-Saint Romans

symmetrically disposed window there is a photodiode connected to a lock-in amplifier. The thickness measurement has been programmed in Lab-View using a 16bit PCI-MOI-16-E card. The PCI card delivers the reference signal and allows to acquire the analysed signal. The lock-in software was programmed in lab-view was used to analyse output signal.

Both, the photodiode and the red laser diode are mounted on a X-Y table which allow 3 movements in order to be able to align the incoming red laser to the substrate position and the reflected beam to the photodiode entrance. A red filter is in front of the photodiode in order to reduce the detection of light coming from the laser and plasma.

A 16cm viewport allows the observation of the deposition process as well as the verification of the plume direction. This observation window allows performing the alignment of the UV laser into the target and of the red diode used for the thickness measurement before the film deposition.

## A.4.1 Design

The deposition chamber is cylindrical with a diameter of 40cm and 45cm height (without considering the top cover) and has been constructed in stainless steel. The flanges use VITON O-rings which permit high vacuum levels ($10^{-7}$,$10^{-8}$ mbar) and do not need to be replaced when the flange is opened.

Flanges are placed at 2 levels. The top level is the laser and deposition level. The bottom one

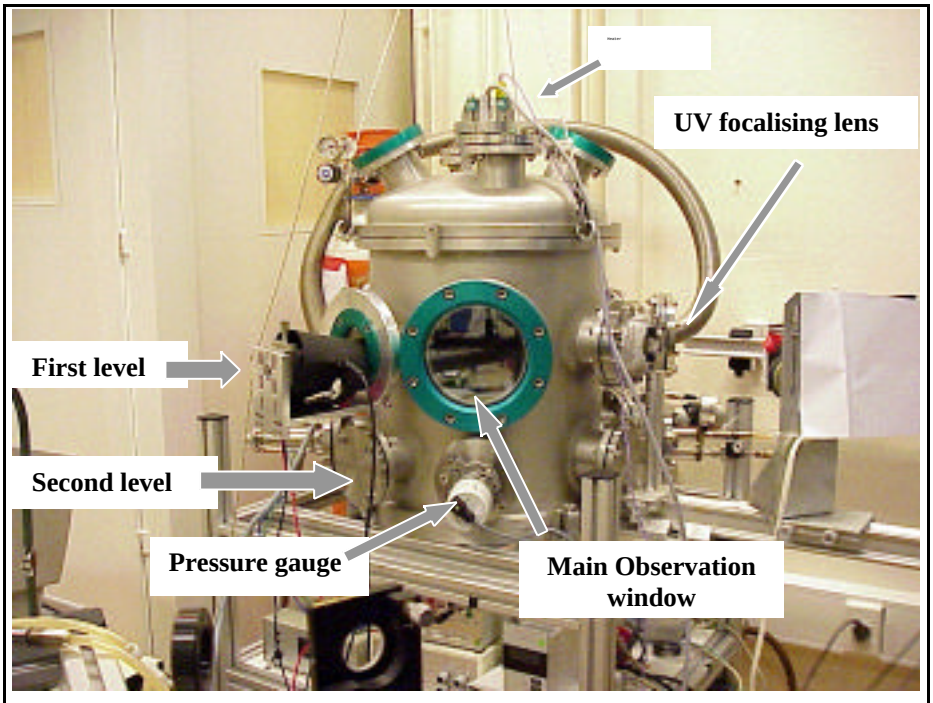



**Fig.A-13** *Photograph of the experimental set-up designed and built up in this work.*

is the instrument level (pumping, gas entrance, pressure gauges and mask manipulator,..).

The top cover consists in a curved cover designed to improve the contact to the O-ring when the chamber is pumped. It has four symmetrically disposed flanges, two of them are vertical and the other two are inclined pointing towards the substrate position. Two of them are provided of windows in order to control the horizontal movement of the plume when the deposition is taking place and the position of the red laser spot used for the thickness monitoring or for the UV laser alignment. In the centre of the top cover and in the axis of the chamber there is the flange for the heating system and temperature control. The top cover can be removed easily thanks to a pulley. However the substrate holder and heating system can be removed and changed without removing the top cover by just taking the heater flange out (Fig. A-13).


**Fig A-14***Photograph of the developed substrate holder*

The heating system consist in two resistive based ceramic bars which are kept together thanks to a ceramic (alumina) attachment system in the cold extremity. The ceramic bars are made of silicon nitride SN220 based on the scheme p1-01102-A and have been provided by the enterprise Kyocera[7]. The heating bars are mounted into a horizontal adjustable stainless piece which allows 4 cm movement in the horizontal direction. This part of the heating system is traversed by two bars which are connected to the top flange, and thanks to a screwing system, the hot part of the heating system can be adjusted vertically (Fig. A-14). In the top flange, an electrically protected passage permits the connection of the resistive bars to the power supply and there are also the thermocouples

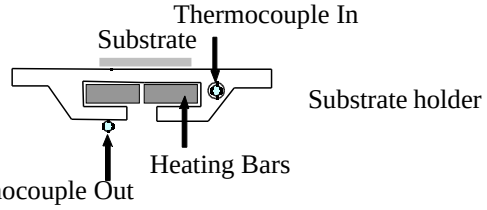



**Fig.A-15** *Schematic vertical view of the substrate heater*

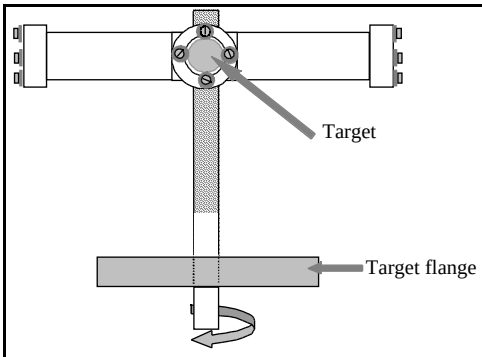



**Fig. A-16** *Schematic view of the rotating target holder*

connections. The thermocouples (K-type) measure the temperature at the substrate holder position. There are two thermocouples. The thermocouple “In” is inserted into the sample holder at the same distance from the heating bars as the substrate (Fig. A-15). The thermocouple “out” is in mechanical contact to the backside of the sample holder. The “In” thermocouple is considered as giving the substrate temperature while the second one allows to check the temperature given by the “In” thermocouple. The substrate holder has been performed in an special stainless alloy (HAYNES) cut by spark-erosion (Fig. A-15).

The heating bars are inserted inside the sample holder and are in mechanical contact. The temperature of the substrate is automatically controlled using a PID loop (temperature set-point, heating rate..) The heating power is about 100Watt (800°C)..

The target holder is shown in Fig.A-0-16, consists in four rings screwed into an aluminium cross connected to a rotating axis. Inside the rings a 1cm of diameter and up to 5mm thick target could be located. The vertical adjustment of the target is possible thanks to a threaded rod.

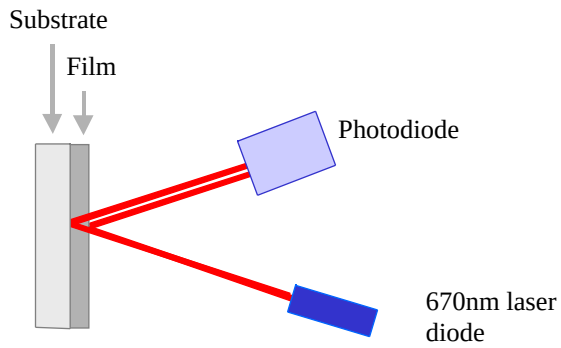



**Fig. A-17** *Optical interferometric system for film thickness monitoring during deposition.*

Two additional entrances have been performed to allow the introduction of a magnetron in the chamber for hybrid deposition. A flange for a turbo-molecular pump has been installed in the chamber in a 16cm flange. The limiting vacuum with primary pumping is about $10^{-3}$ mbar while secondary pumping allows about $5\ 10^{-8}$ mbar.

All the additional parts required to connect the pumping, gas entrance, high power laser window, heating system, rotating target and thickness measurement set-up were manufactured in the CNRS workshop following our drawings.

[7] Kyocera Fineceramics, S.A. Orlytech-Paray vieille poste. 4 Allee du commandant Mouchotte-91781 Wissous

## A.4.2Film thickness measurement

Real time thickness monitoring of the films is done by optical interferometry. A 670nm laser is modulated at a frequency $f \approx 63$Hz given by the lock-in. The laser reflects at both vacuum-film and film-substrate interfaces. Both signals interfere giving constructive interferences when optical path is

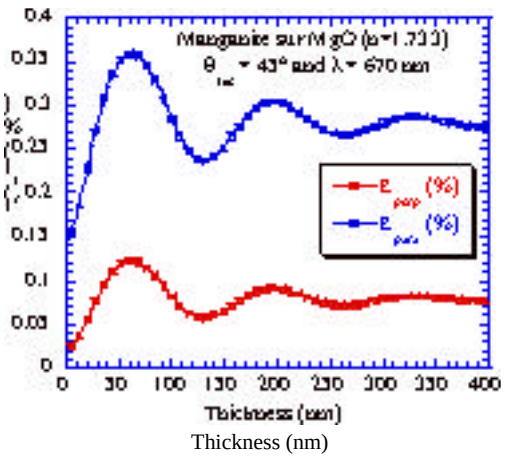



**Fig. A-18** *Calculated oscillations of the reflected intensity for a red laser at a incidence of 45° into a film of LCMO on MgO*

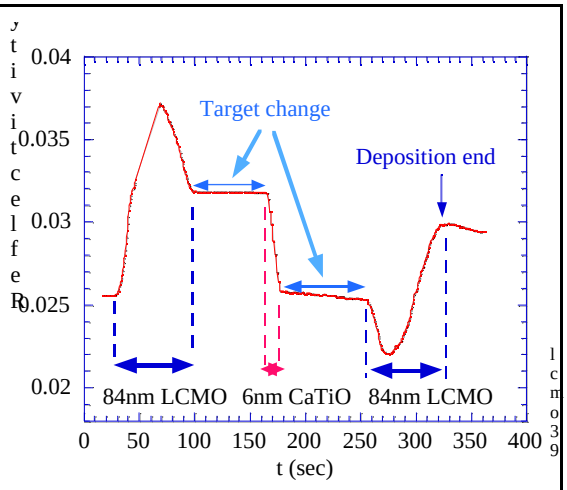



**Fig. A-19** *Experimental oscillations observed during the deposition of a trilayer of LCMO/$CaTiO_3$/LCMO/MgO*

an even number of times π (Fig A-17) which is proportional to the film thickness. The reflected light intensity is measured by a photodiode and the signal is sent to the lock-in. In Fig A-18 is displayed a calculation of the reflectivity as a function of the film thickness on a MgO substrate for the different components of the electric field. The first maximum corresponds to a LCMO film thickness of 60nm and after a film thickness of 400nm the oscillations become more and more damped so the film thickness is more difficult to determine. Thickness resolution depends on the difference of refraction indices between the films grown and the substrate. Experimentally we found about 1nm of thickness resolution for $CaTiO_3$ films on LCMO/MgO. In Fig.A-19 is displayed a reflectivity measurement performed during film deposition as a function of time, of a trilayer film of LCMO/$CaTiO_3$/LCMO on MgO. The given thickness are deduced from Rutherford Back Scattering measurements performed ex-situ which have an associated error of about 10%, and are in agreement with the experimental observation of the reflectivity measurements. In Fig.A-0-19 is also possible to observe the difference of growth rate between the insulating $CaTiO_3$ and LCMO which is probably caused by the different absorption of the UV light by the insulator and by the manganite and that allows a good control of the thickness of the insulating layer.

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