PULSED LASER DEPOSITION OF THIN FILMS

M. JELÍNEK, V. TRTÍK, L. JASTRABÍK
Institute of Physics, Czech Academy of Sciences, Na Slovance 2, 18040 Prague 8, Czech Republic

Abstract

The principle of thin film deposition by laser ablation, a droplet problem, basic schemes for laser deposition of smooth thin films, creation of multilayer structures with YBaCuO, ferroelectric films and metals are discussed. Experimental results with deposition of YBaCuO on monocrystalline and polycrystalline substrates, buffer layers, ferroelectric films (PZT, PLZT, PMN) and some possible applications are presented.

1. Introduction

Creation of thin films by pulsed laser deposition (PLD) is known for a long time. Layers of wide scale of materials were deposited. But the main boom of the method started with the development of high temperature superconductors. It was necessary to find a method making possible to create high quality films of complicated material composition as YBaCuO, BiSrCaCuO etc. The main advantage of PLD is the possibility to transfer multicomponent target material stoichiometrically into the layer. Targets for PLD can be easily fabricated. Since 1987, when the first superconductive layers were created by PLD, the great experimental experiences were reached. In present experimental set-ups several different targets can be used for deposition and targets can be easily changed during the deposition process. It make possible to create multilayer systems. At first multilayers of superconductor-buffer layer-substrate were created and now very complicated multistructures of superconductors, dielectrics, ferroelectrics and metals are fabricated by PLD. In our contribution some problems of PLD thin film creation and multilayers application are presented and discussed.

2. PLD Method

The basic experimental apparatus for laser evaporation and ablation includes a vacuum chamber, a substrate holder with precise temperature control, and a source material (target). Laser, usually pulsed, is located outside vacuum chamber - see Fig.1. For low energy density of laser beam on the target, the evaporation process is dominating. Increase of density results in the generation of a plasma with ablation the target material perpendicularly to the target

R. Kossowsky et al. (eds.), Physics and Materials Science of High Temperature Superconductors, IV, 215–231.
© 1997 *Kluwer Academic Publishers. Printed in the Netherlands.*

surface. The amount of evaporated material per laser pulse and the minimum power densi needed for material ablation depends on the thickness of the target layer heated during th pulse. The absorbing target material is characterized by its optical and thermal propertie Laser energy absorbed by the target surface is wavelength dependent. For low power densit the dominant within the vapor cloud are neutral particles. As the density is increased, so i the total fraction of ions in evaporated plume.

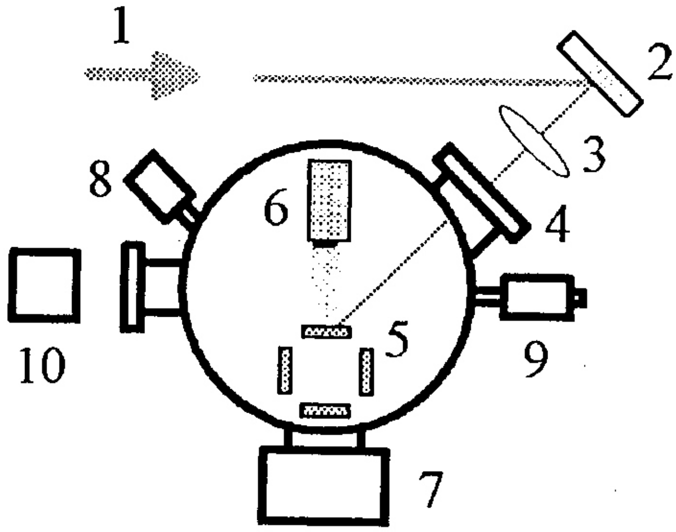

Fig. 1. Schema of PLD for creation of multilayers. 1. KrF excimer laser beam, 2. dielectric mirror, 3. focusing lens, 4. fused silica window, 5. targets, 6. heated substrate holder, 7. vacuum pump, 8. vacuum gauge, 9. oxygen filling, 10. CCD camera

Photographs of the deposition chamber are in Fig. 2 a,b. The shown system makes possible to change up to four targets during the deposition cycle.

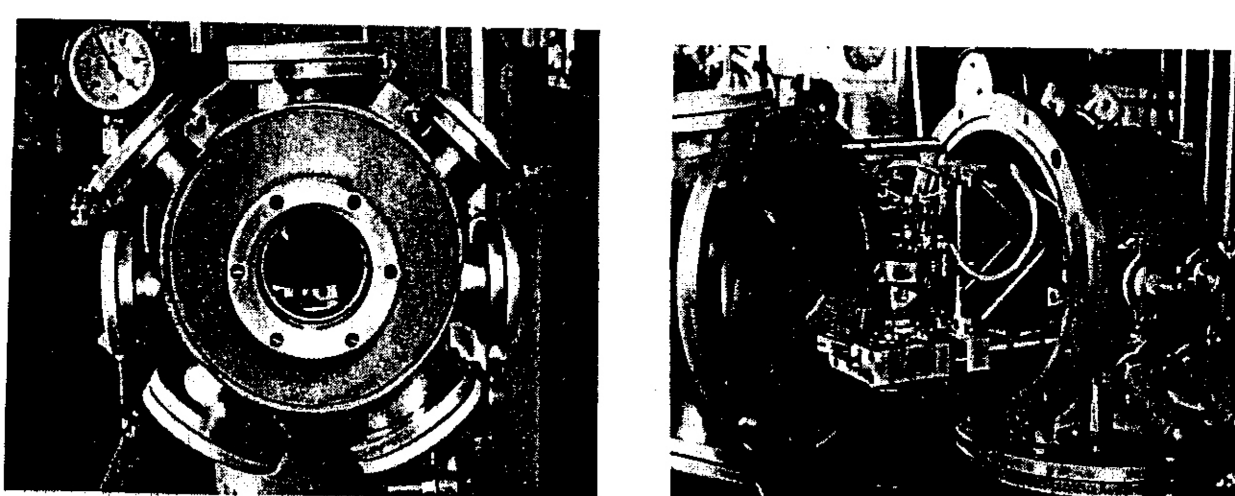

Fig.2. Photographs of the interaction chamber used for PLD experiments. a- front view, b - open chamber.

The quality, thickness and area of the deposited thin film is influenced by many parameters as:

- parameters of laser (laser wavelength, pulse length, repetition rate),
- interaction of laser radiation with a target (laser power density, spot size, target material properties, environment in the interaction chamber),
- interaction of plasma plume with the gaseous environment and substrate (gas pressure, target- substrate distance),
- parameters of the substrate (lattice parameters, thermal conductivity, thermal expansion coefficient, substrate temperature),
- regime of film growth (deposition rate, laser repetition rate, film thickness, time deposition regime).

Various deposition conditions are used for creation of films. For example - superconductive films are deposited in oxygen atmosphere (about 100 mTorr) meanwhile the substrate temperature (T_s) is held round 720°C [1], diamond-like films are created in vacuum and T_s is low (between room temperature and 100°C) [2], biocompatible ceramic (hydroxylapatite) is deposited in mixture of argon and water vapors at high T_s [3] etc. Laser power densities round 10^8 Wcm^{-2} and higher and pulse length of tens of nanosecond are usually used. Excimer laser radiation (short wavelength) is preferred. It heats only a very thin layer of target material. It can also photolytically break the molecular bounds of target material. During PLD the plasma plume having direction perpendicular to the target is observed. The PLD method incorporated into the scheme of laser applications [4] is shown in Fig.3.

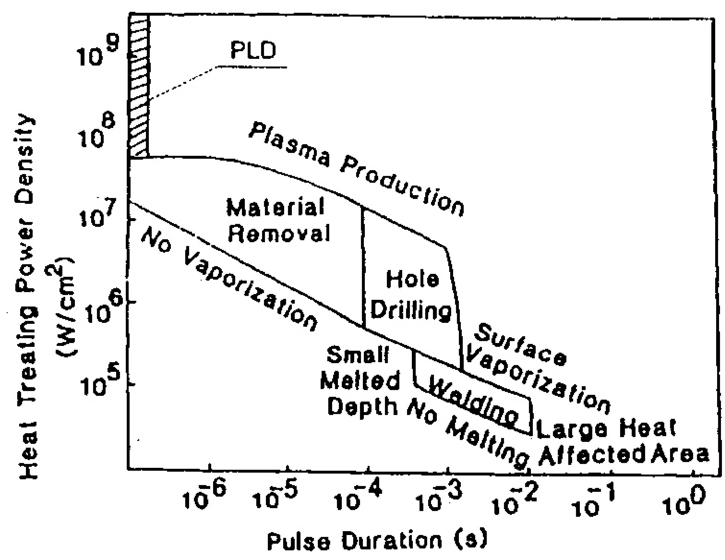

Fig. 3. Laser technology applications scheme (modified from [4])

Advantages and disadvantages of PLD can be summarized by the following way :

PLD - advantages

- stoichiometric deposition of even very complex materials,
- high instantaneous growth rate,
- simplicity and flexibility of engineering design, great experimental versatility.

- The equipment is relatively simple, inexpensive, with the laser outside the vacuum chamber,
- thin films have higher bulk density, better surface morphology and often highly preferential crystalline orientation,
- enhanced crystallinity owing to presence of high- energy atoms in incoming flux. The products of plasma plume are partly ionized and excited, have higher kinetic energy (in comparison to the other deposition methods) - it has influence on the atoms mobility in the substrate surface, on the reactions in gaseous environment, and results in film quality,
- it can be used to deposit thin films of almost any material,
- environment gas pressure can be changed from ultra- high vacuum to several hundreds of Pascal,
- PLD process is very clean- fast local heating of the target surface by focused laser beam minimalize the film contamination,
- very small consumption of target material, sharp definition of the boundaries of ejected material.

PLD - disadvantages, problems

- creation of droplets,
- small- area deposition, narrow angle of stoichiometric transfer of target material,
- dirty window after long time deposition,
- target degradation, target roughening,
- insufficient process characterization and optimization,
- much work has been performed in vacuum of too low quality [5].

3. Droplets Problem

One of the problem of thin films deposition and PLD especially is the roughness of film surface. In dependence on deposition conditions the nonuniformities *on* and *in* the film are created. These nonuniformities are usually called spherical inclusions, ball shaped particles, grains, microparticles, boulders, needles, clusters, pits, outgrowth, splashed molten material fragments etc. - shortly droplets and holes. Droplets and holes are the main obstacle in the development of multilayer structures.

Droplets and holes and their shape are influenced by:

a) Laser radiation- target interaction.

Laser radiation is absorbed by the target material. The temperature of the target surface exceeds the boiling point and subsurface material can be overheated. As a result the spherically shaped particles (diameter of 1- 5 μm for YBaCuO) are ejected from the target.

b) Laser-target-substrate configuration.

In the most deposition schemes the target and substrate are arranged in parallel. In such configuration the plasma plume is perpendicular to the substrate. To decrease the droplets density the configurations having various angles between the target and substrate, including off-axis ablation, were tested [6][7][8]. Another way how to decrease the droplets density is to use the second laser for heating, decomposition, fragmentation and excitation of plasma plume particulates [9][10] (see Fig. 4), or to use the method of two crossed laser beams - see Fig. 5. Such arrangement is some-what complicated, but the very smooth film surfaces were deposited [11][12].

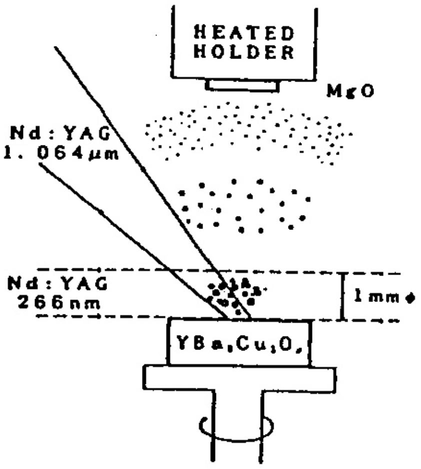

Fig. 4. Schematic diagram of the second laser irradiation on ablated particles induced by the first ablation laser [9].

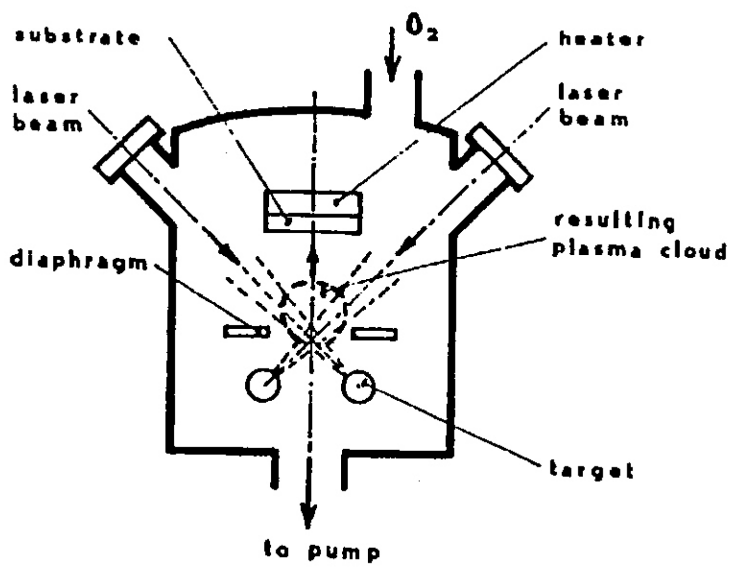

Fig. 5. Experimental set-up using two crossed laser beams [12].

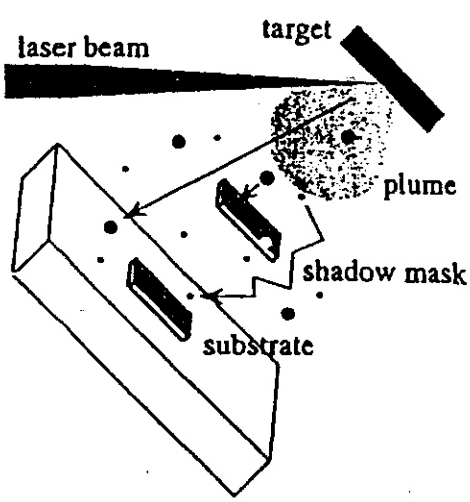

Fig.6. Schematic view of eclipse ArF-excimer PLD system [13]

Very smooth YBaCuO films were also created with the aid of shadow mask (eclipse method)[13][14]- see Fig. 6. As the ambient oxygen cannot be fully activated in front of the substrate the oxygen deficiency in the film can be observed. A very old method for decreasing the droplets density is to use the velocity filter for deflection of bigger particles in plasma plume [15].

c) Regime of film growth on the substrate.

This kind of nonhomogenities (droplets and holes) arise during the mechanism of film growth, have dimension smaller than 1um (for YBaCuO), and usually does not depend on the deposition method. Creation of droplets and holes is influenced mainly by improper choice of substrate temperature, oxygen pressure, deposition rate and by substrate imperfections.

One of the mechanism of creation of the droplets (usually called outgrowth) can be explained by different growth rates of YBaCuO in a-b plane and perpendicular to this plane [16]. The other theory suggests that the particles can arise during the expansion of plasma cloud in background gas [17].
We can conclude that the mechanism of droplets creation was not fully understood and explained till now. A droplets problem is usually mentioned and solved in connection with laser deposition of superconductive thin films (YBaCuO). The smoothness of ferroelectric, diamond-like and metallic films is usually much better.

From experimental experiences follows that the droplets density can be reduced mainly by:
* using freshly polished target [18],
* high density target (single crystal, glass, ceramic bulk) [6][19][20],
* choosing an appropriate laser wavelength [20],
* using the chopper synchronously triggered with the laser pulses [21],
* choosing an appropriate laser fluence (droplets emission from of metals decreases with increasing laser fluence- it is in contrast to the behavior of oxides targets; low laser beam fluences near the threshold of evaporation is preffered for YBaCuO) [22][23][24],
* using a high quality laser beam profile,
* varying the azimuthal angle of the incidence of the laser beam with respect to the target
* normal (not only the number of droplets is much smaller, but also their average size is reduced)[22],
* geometrical configuration of laser fluence- target- substrate [6][11][12][13][14],
* low temperature processing [25],
* thinner films,
* higher [26] or suitable [18] target- substrate distance,
* ablation from targets rotating at high speed,
* deposition in oxygen- argon gas mixture (for YBaCuO) [27],
* suitable substrate T_s, deposition rate and oxygen pressure (for YBaCuO) [28][29], larger spot size.

Usually, the droplets density of $10^6 cm^{-2}$ [30] or 2-5 x 10^5 [31] (for 100 nm thick film) can be reached by PLD. It is supposed that the density can be decreased to 10^2- 10^3 cm^{-2} in the future [32]. In our experiments with two crossed laser beams the density of $10^4 cm^{-2}$ was measured [12].

4. Deposition of Superconductive Thin Films

The experimental research is focused mainly on YBaCuO thin films, but also films of BiSrCaCuO, TlBaCaCuO etc. were created by PLD. In the early period of YBaCuO laser deposition (1987 - 88) the films were created in the so-called *ex-situ* arrangement. At first, the films were deposited in an evacuated chamber on the substrates having low T_s (300°C - 400°C). Then the films of correct stoichiometry of metallic constituents were annealed and oxygenated for a long time (several hours) in oxygen at high temperatures (~ 900°C). In the improved technological step (without long time, high temperature postannealing) the films

were deposited and annealed at the same time. In such *in - situ* deposition the deposition time is about 10 minutes and T_s ~ 700°C. Therefore the interdiffusion of substrate to the film is smaller, obtained films have crystalline structure, high zero resistance temperature T_z and high critical current density J_c.
As substrates for YBaCuO deposition the $SrTiO_3$, $NdGaO_3$, MgO, $LaGaO_3$ and yttria stabilized zirconia (YSZ) are usually used. For technological applications (microwave technique, semiconductor technology) the substrates as sapphire, $LiNbO_3$and silicon are preferred. On such kind of substrates the buffer layers (MgO, YSZ, $SrTiO_3$, ZrO_2, CeO_2) must be usually created. The buffer layer prevents the interdiffusion between the substrate and the film, prevents formation of cracks in the film (caused due to the difference of thermal expansion coefficients) and improves lattice constant match.
A typical set of PLD parameters (for YBaCuO) is the following :
- KrF excimer laser (λ = 248 nm); output energy 0.1- 1 J, pulse duration τ = 20 ns, repetition rate of 5 Hz,
- energy density on the target 1- 2 Jcm^{-2}, target-substrate distance 3 - 4 cm, deposition rate 1 A per laser pulse,
- T_s of 700°C - 750°C, oxygen pressure during the deposition 10 - 40 Pa with sharply increased oxygen pressure at the end of deposition,
- optically polished substrate surface, cleaned (in acetone, toluene, ethanol) and annealed in oven before the deposition.
High quality films show zero temperature resistance T_z of 89 - 91 K with sharp transition to superconductivity (ΔT = 0.5 K) and J_c (77 K) > 10^6 Acm^{-2}. Films are highly oriented grown with c-axis perpendicular to the substrate surface, resistance ratio Γ=R(300K)/R(100 K) ~ 3 and droplets density round 10^4 cm^{-2}.
One of the critical deposition parameter is T_s. To obtain a good temperature contact, the substrate is usually glued to the heating element by InGa or silver paste. Using the paste has however the undesirable influence on the thermocouple, which is usually welded to the surface of substrate holder near the contact place. To avoid such inaccuracy in temperature measurements, it is better to connect the thermocouple to the inner side of the holder bottom [33]. The influence of T_s on the shape of R(T) dependences and X- ray rocking curves is shown in Fig. 7 and Fig. 8.

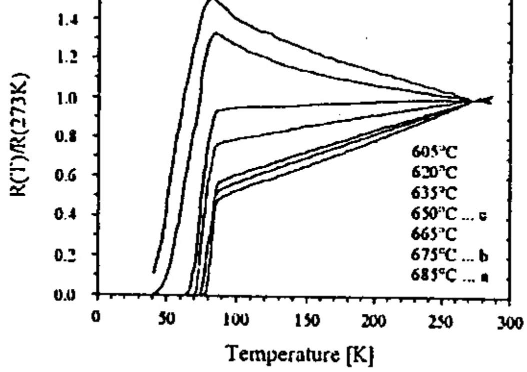

Fig. 7. Resistance vs temperature dependence of YBaCuO for different T_s. Sapphire substrate is coated by polycrystalline ZrO_2 [34].

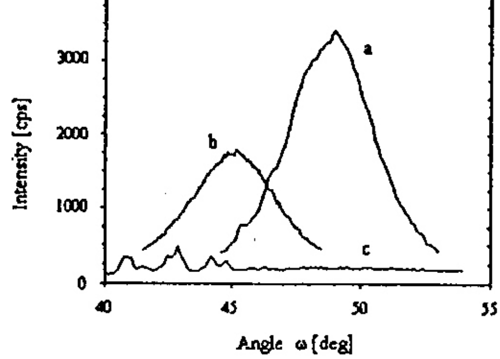

Fig. 8. X- ray measurement in ω- scan arrangement for YBaCuO on poly-ZrO_2/sapphire(for results in Fig. 7.) [34].

As was said, the quality of the film is influenced by many parameters. For example, the area and thickness homogeneity of the deposited film depend on the shape of plume and d_{t-s}. The change of the shape with laser power density and with the area of laser spot on the target is in Fig. 9.

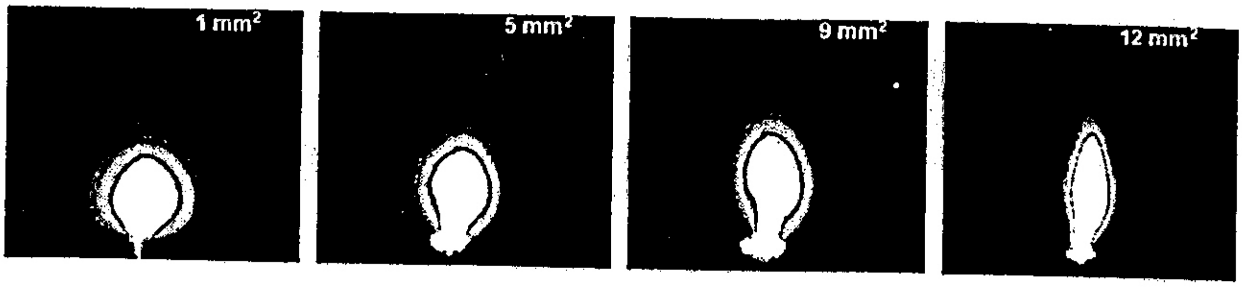

Fig. 9. The development of a plasma plume shape with laser beam spot area on YBaCuO target. The deposition was carried out in oxygen ambient of 200 mTorr. Laser energy was 150 mJ. (Power densities 5.5×10^7 Wcm^{-2}, 6.6×10^7 Wcm^{-2}, 1.2×10^8 Wcm^{-2}, 6.0×10^8 Wcm^{-2}). Colors of pictures correspond to intensity of light.

Shortly from our other results :

High quality films having T_c in region 89 - 90 K and Γ =3 were deposited on (100) $SrTiO_3$ (see Fig. 10) [34] and (100)$NdGaO_3$ substrates (XRD patterns - see Fig. 11) [1].

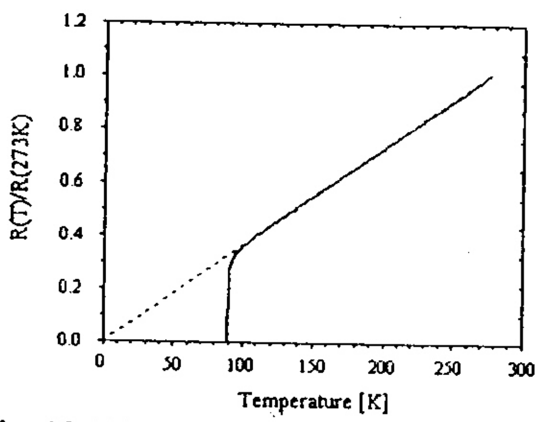

Fig. 10. R(T) dependence for YBaCuO on $SrTiO_3$ [34].

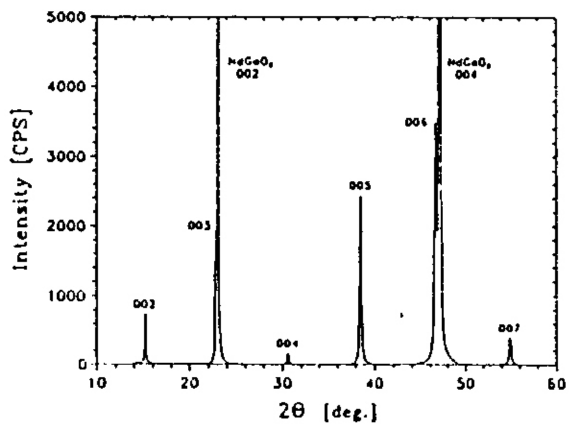

Fig. 11. X- ray diffraction pattern of YBaCuO on $NdGaO_3$ substrate [1].

High quality, highly oriented YBaCuO films were deposited on sapphire coated with a buffer layer. The buffer layers were also PLD deposited - seeTable I. and Fig.12.

Table I. Materials and responsible targets used for deposition of epitaxially grown buffer layers [35].

Material	Target
ZrO_2	metallic Zr
YSZ	sintered ceramic
CeO_2	sintered ceramic
$SrTiO_3$	monocrystalline

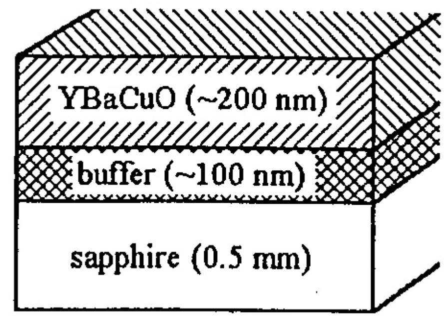

Fig. 12. Schema of YBaCuO/buffer/sapphire multilayer.

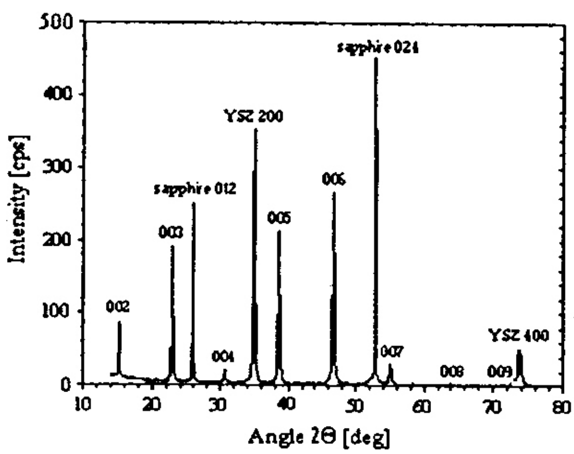

Fig. 13. The XRD spectra of YBaCuO deposited on a laser created buffer layer YSZ on sapphire.

The XRD spectra of YBaCuO/YSZ/(1102)sapphire are in Fig. 13. On the multilayer system YBaCuO/ZrO_2/(1102)sapphire the J_c(77 K) of 1.5 x 10^6 Acm^{-2} and microwave surface resistance R_s(77 K) = 2.4 mW for 8 GHz frequency were measured [36].

Major trends in PLD of superconductive films are the following :

- large area, homogeneous films (excellent film uniformity over an area of 20cm^2 were created [26][37],
- multilayer structures (DC SQUID with 15 epitaxial layers was fabricated [38]).

5. Deposition of ferroelectric films

Thin ferroelectric films with a diffuse phase transition and perovskite- like structure are developed for applications in electronic and optical devices due to its multifunctional properties:

* polarization switching,
* a high value of dielectric susceptibility,
* pyroelectricity,
* piezoelectricity,
* electro-optic effect.

Applications of ferroelectric thin films have been limited till now by the low quality of deposited films. This obstacle was overcome in the recent years by the development of new technological processes as PLD and sol-gel methods which make possible to create highly oriented, high quality films.

Overview of possible applications is in Fig. 14. Potential optical and electronic applications along with candidate ferroelectric materials, desired properties, required film thickness and critical integration issues are summarized in Tables II. and III.

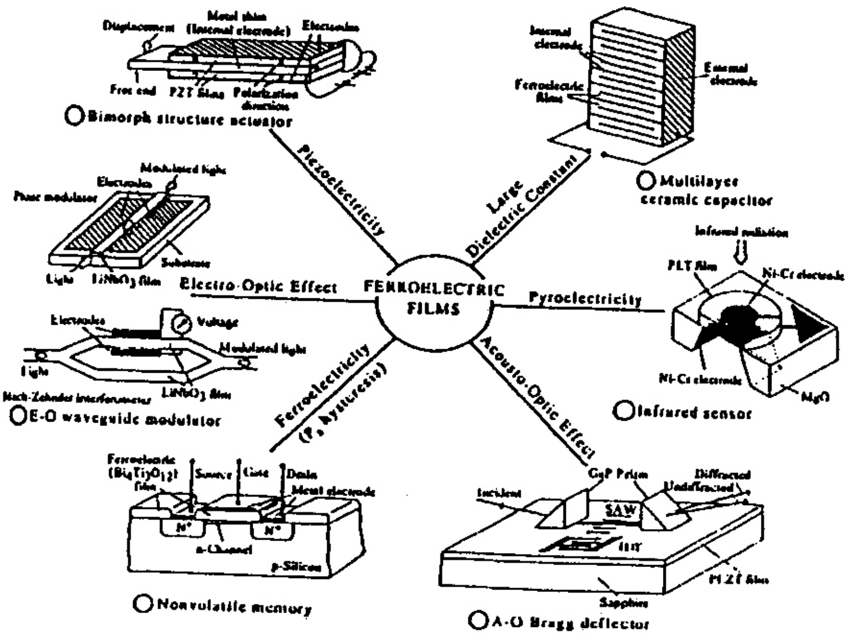

Fig.14. Applications of ferroelectric thin films [39]

Table II. Optical applications of ferroelectric films [40]

Application	Desired Properties	Candidate Materials	Required Film Thickness (μm)	Critical Integration Issues
Infrared Detectors	Pyroelectricity Low Dielectric Constant	$PbTiO_3$ $(Pb,La)TiO_3$ $Pb(Zr,Ti)O_3$ $K(Ta,Nb)O_3$	1-5	Epitaxial Film Deposition Substrate Compatibility Photolithography Silicon Micromachining
Optical Waveguides	Electro-Optic Effects	$LiNbO_3$, $KNbO_3$ $(Pb,La)(Zr,Ti)O_3$ $(Sr,Ba)Nb_2O_6$	0.2-2.0	Epitaxial Film Deposition Smooth Film Surfaces Substrate Compatibility Photolithography
Spatial Light Modulators	Photorefractive Effects	$(Pb,La)(Zr,Ti)O_3$	0.5-5.0	Substrate Compatibility Photolithography Device Design
Frequency Doublers	Efficient Second Harmonic Generation	$LiNbO_3$, $KNbO_3$	0.2-2.0	Epitaxial Film Growth Extreme Optical Quality Photolithography

Table III. Electronic applications of ferroelectric films [40].

Application	Desired Properties	Candidate Materials	Required Film Thickness (μm)	Critical Integration Issues
Nonvolatile Memories	Large Remanent Polarization Low Coercive Field Low Fatigue Rates	$Pb(Zr,Ti)O_3$ $Bi_4Ti_3O_{12}$ $BaMgF_4$	0.1-0.3	Compatibility with Silicon Electrode Materials Buffer Layers Photolithography
Dynamic RAMs	High Dielectric Constant High Breakdown Strength	$BaTiO_3$ $(Ba,Sr)TiO_3$ $Pb(Zr,Ti)O_3$	0.2-0.5	Compatibility with Silicon Non-Planar Surfaces Electrode Materials Photolithography
Thin-film Capacitors	High Dielectric Constant Low Dielectric Loss Temperature Insensitivity High Breakdown Strength	$(Ba,Sr)TiO_3$ $Pb(Zr,Ti)O_3$ $Pb(Mg,Nb)O_3$	0.1-0.5	Substrate Compatibility Electrode Materials Photolithography
SAW substrates	Piezoelectricity	$Pb(Zr,Ti)O_3$	2-10	Epitaxial Film Growth Substrate Compatibility Smooth Film Surfaces Photolithography
Microactuators	Piezoelectricity	$Pb(Zr,Ti)O_3$	1-10	Substrate Compatibility Photolithography Device Design

For measurement of electrical, electrooptical and optical properties of ferroelectric thin films the bottom and top electrodes have to be created. The usually used bottom metallic electrode, which is typically Pt, Ni or Al, is grown as a polycrystalline layer. The ferroelectric film grown on such a polycrystalline metallic electrode has the polycrystalline microstructure as well. The superconductive YBaCuO films have small resistance and metallic behavior at room temperature and grow highly oriented on substrates as (100) or (110) $SrTiO_3$. Ferroelectric materials and YBaCuO have the same perovskite structure, close matching in lattice constant and similar thermal coefficients [41]. As a result the ferroelectrics grow highly oriented on YBaCuO - see Fig. 15. and Fig. 16.

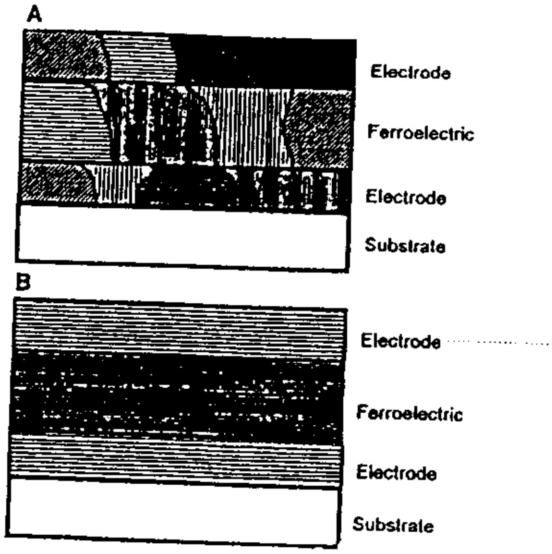

Fig. 15. (A)Schematic illustration of the ferroelectric thin films deposited onto Pt-coated substrates. (B) Schematic illustration of the epitaxial oxide superconductor electrode/ferroelectric heterostructure grown in situ by PLD [41].

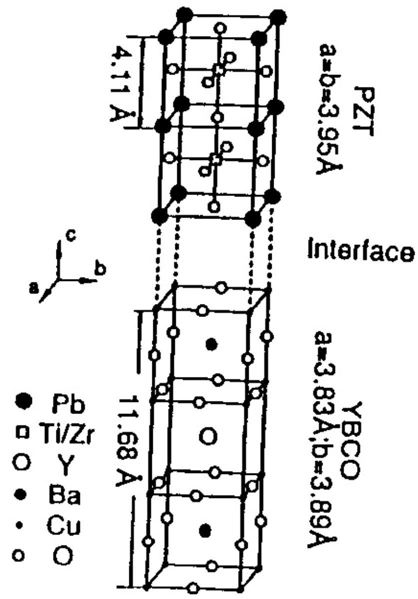

Fig. 16. A schematic illustration of the YBaCuO- PZT(0.2, 0.8) heterostructure showing epitaxial matching on the a-b planes of two lattices [42].

Summary of some of the recently PLD created multilayer structures (ferroelectrics, YBaCuO, metals) is in Table IV.

Table IV. The PLD created, ferroelectric-based multilayers.

Material	Bottom electrode	Substrate/Buffer	Top electrode	Ref
$PbZr_{0.52}Ti_{0.48}O_3$	YBCO	(100)$SrTiO_3$ (100)MgO (1102)sapphire	YBCO Pt	[43]
$PbZr_xTi_{1-x}O_3$	Pt	Si	Pt	[44]
$PbZr_{0.53}Ti_{0.47}O_3$	$La_{0.5}Sr_{0.5}CoO_3$	(100)Si	$La_{0.5}Sr_{0.5}CoO_3$	[45]
$Pb_{0.9}La_{0.1}(Zr_{0.2}Ti_{0.8})_{0.975}O_3$	$La_{0.5}Sr_{0.5}CoO_3$	$LaAlO_3$	$La_{0.5}Sr_{0.5}CoO_3$	[46]
$PbTiO_3$	Pt	(100)MgO	Al	[47]
$Bi_4Ti_3O_{12}$	YBCO	(001)Si/YSZ	Au	[48]
$Pb_5Ge_3O_{11}$	Pt	(111)Si (0001)sapphire	Pt	[49]
$Bi_2VO_{5.5}$	$LaNiO_3$	(100)$SrTiO_3$	$LaNiO_3$	[50]
$KTiOPO_4$	-	(100)Si (116)sapphire	-	[51]
$LiTaO_3$	-	(0001)sapphire	-	[52]
$LiNbO_3$	-	(1102)sapphire	-	[53]
$KTa_{0.55}Nb_{0.45}O_3$	-	(110)$SrTiO_3$	-	[54]
PMN	Pt	(111)Si	Pt	[55]

In our laboratory we have created and studied the following multilayers with PZT, PLZT, PMN and doped $SrTiO_3$ ferroelectric thin films [56][57][58] :
Ni/PZT(0.75, 0.25)/YBaCuO/(100)$SrTiO_3$
Ni/PZT(0.52, 0.48)/YBaCuO/(100)$SrTiO_3$
SnO_2/PLZT(0.09, 0.65, 0.35)/YBaCuO/(110)$SrTiO_3$
SnO_2/PMN/YBaCuO/(110)$SrTiO_3$
Ni/PMN/YBaCuO/(100)$SrTiO_3$
Pt/$SrTiO_3$:Cr/Pt/(1102)sapphire
Pt/$SrTiO_3$:Cr/Si-p,
where PZT = $Pb(Zr_xTi_{1-x})O_3$; PLZT= $Pb_{1-x}La_x(Zr_yTi_z)_{1-(x/4)}$; PMN= $PbMg_{1/3}Nb_{2/3}O_3$. The thickness parameters are in Fig. 17.

Example of dielectric hysteresis loops of PZT/YBaCuO/(100)$SrTiO_3$ measured by virtual ground Sawyer-Tower circuit (see Fig. 18) is in Fig.19. The hysteresis remanences of PZT(0.52, 0.48) and PZT(0.75,0.25) films deposited at temperature about 550°C were 42 and 24 μCcm^{-2} with coercive fields estimated at 55 and 80 $kVcm^{-1}$. For our best quality heterostructure, a drop of the P_r value of less than 20% was observed after about 10^9 cycles of polarization switching.

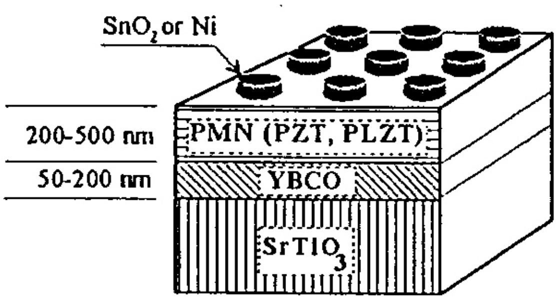

Fig. 17. Schema of multilayers with ferroelectric and superconductive film.

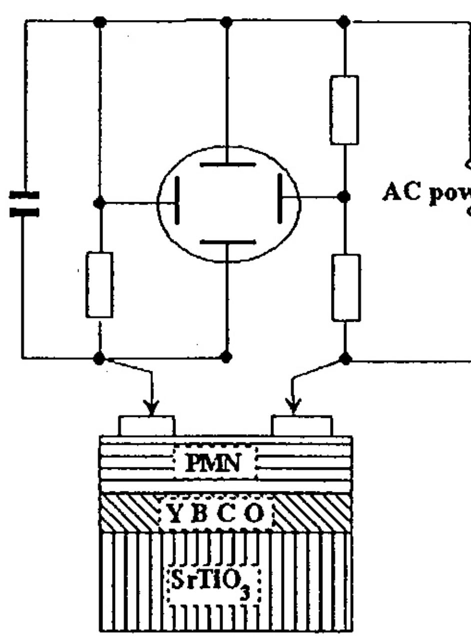

Fig. 18. Virtual ground Sawyer- Tower circuit. The two probes are placed in contact with two capacitor dots of equal area.

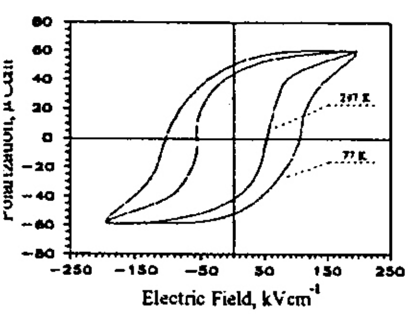

Fig. 19. The dielectric hysteresis loops of PZT (0.52, 0.48) film grown on the YBaCuO/(100)$SrTiO_3$ structure, at room temperature and liquid nitrogen temperature. PZT film thickness - 500 nm.

6. Conclusion

In this work we have tried to summarize practical information concerning the technology of deposition of thin films and multilayer structures by pulsed laser ablation. One of the main problems - droplets, is discussed and possibilities how to decrease the droplets density are presented. The PLD of superconductive films, buffer layers, experimental results and outlook is overviewed. The data about applications and experimental results of new direction in PLD thin film research - ferroelectric films and multilayers of ferroelectrics, superconductors and metals are collected.

The PLD technology is now well developed and seems to be very suitable mainly for fast creation of new kinds of high quality thin films of complicated materials and for creation and study of new kinds of multistructures, mainly in a laboratory scale and for requirements of basic research.

7. Literature

1. Jelínek, M., Jastrabík, L., Olšan, V., Soukup, L., Šimečková, M., Černý, R., Kluenkov, E., Mazo, L. (1993) Laser Deposited YBaCuO Thin Films, *Czechoslovak Journal of Physics* **6**, 661-669.

2. Jelínek, M., Olšan, V., Soukup, L., Charalabidis, D., Hontzopoulos, E., Georgiou, E. (1994) Some Properties of Carbon Films Deposited by Laser Ablation, *Diamond and Related Materials* **3**, 1128-1131.

3. Jelínek, M., Olšan, V., Jastrabík, L., Studnička, V., Hnatowicz, V., Kvítek, J., Havránek, V., Dostálová, T., Zergioti, Y., Petrakis, A., Hontzopoulos, E., Fotakis, C. (1994) Effect of Processing Parameters on the Properties of HA Films Grown by PLD, *Thin Solid Films* - in print.

4. Ready, J.F. (1978) *Industrial Applications of Lasers*, Academic, New York.

5. Dieleman, J., van de Riet, E., Kools, J.C.S. (1992) Laser Ablation Deposition: Mechanism and Application, *Jpn.J.Appl.Phys.* **31**, 1964-1971.

6. Holzapfel, B., Roas, B., Schultz, L., Bauer, P., Saemann- Ischenko (1992) Off-axis Laser Deposition of YBaCuO Thin Films, *Appl. Phys. Lett.* **61**, 3178-3180.

7. Lee S.H, Bae S.G. , Kang J.G., Lee H.J, Shin H.J., Ku J.K.. (1991) Substrate temperature effects on the preparation of YBaCuO superconducting films on (100) SrTiO by laser ablation, *J.Appl.Phys.* **70**, 5661-5666.

8. Usoskin, A.I., Chukanova, I.N .(1992) *High T_c Superconductor Thin Films*, Editor L.Correra, Elsevier Sci.Publ., 239.

9. Chiba, H., Murakami, K., Eryu, O., Shihoyama, K., Mochizuki, T., Masuda, K. (1991) Laser Excitation Effects on Laser Ablated Particles in Fabrication of High T_c Superconducting Thin Films, *Jpn. J. of Appl. Phys.* **30**, L732-L734.

10. Koren, G., Baseman, R.J., Gupta, A., Lutwyche, M.I., Laibowitz, R.J. (1990) Particulates Reduction in Laser- ablated YBaCuO Thin Films by Laser- induced Plume Heating, *Appl.Phys.Lett.* **56**, 2144-2146.

11. Gaponov, S.V., Gudkov, A.A., Fraerman, A.A. (1982), *Sov.Phys.Tech.Phys.* **27**, 1130.