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# Pulsed Laser Deposition (PLD) - a Versatile Thin Film Technique

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**Summary.** Pulsed laser deposition (PLD) is for many reasons a versatile technique. Since with this method the energy source is located outside the chamber, the use of ultrahigh vacuum (UHV) as well as ambient gas is possible. Combined with a stoichiometry transfer between target and substrate this allows depositing all kinds of different materials, e.g., high-temperature superconductors, oxides, nitrides, carbides, semiconductors, metals and even polymers or fullerenes can be grown with high deposition rates. The pulsed nature of the PLD process even allows preparing complex polymer-metal compounds and multilayers. In UHV, implantation and intermixing effects originating in the deposition of energetic particles lead to the formation of metastable phases, for instance nanocrystalline highly supersaturated solid solutions and amorphous alloys. The preparation in inert gas atmosphere makes it even possible to tune the film properties (stress, texture, reflectivity, magnetic properties...) by varying the kinetic energy of the deposited particles. All this makes PLD an alternative deposition technique for the growth of high-quality thin films.

## 1 Introduction

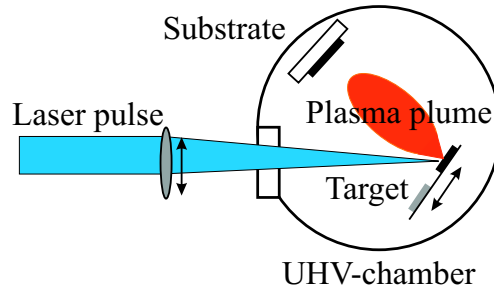
With the pulsed laser deposition (PLD) method, thin films are prepared by the ablation of one or more targets illuminated by a focused pulsed-laser beam.

This technique was first used by Smith and Turner [1] in 1965 for the preparation of semiconductors and dielectric thin films and was established due to the work of Dijkkamp and coworkers [2] on high-temperature superconductors in 1987. Their work already showed main characteristics of PLD, namely the stoichiometry transfer between target and deposited film, high deposition rates of about 0.1 nm per pulse and the occurrence of droplets on the substrate surface (see also [3]). Since the work of Dijkkamp et al., this deposition technique has been intensively used for all kinds of oxides, nitrides, or carbides, and also for preparing metallic systems and even polymers or fullerenes.

The aim of this paper is to give a brief sketch on the versatility of the pulsed laser deposition method and to give some examples of where it is needed. Differences compared to conventional thin film techniques like thermal evaporation and sputtering will be discussed, too.

## 2 Typical Experimental Set-ups

A typical set-up for PLD is schematically shown in Fig. 1. In an ultrahigh vacuum (UHV) chamber, elementary or alloy targets are struck at an angle of  $45^\circ$  by a pulsed and focused laser beam. The atoms and ions ablated from the target(s) are deposited on substrates. Mostly, the substrates are attached with the surface parallel to the target surface at a target-to-substrate distance of typically 2–10 cm.



**Fig. 1.** Schematic diagram of a typical laser deposition set-up

In our case, an UHV of about  $10^{-9}$  mbar, an excimer laser LPX110i (Lambda Physik) with KrF radiation (wavelength 248 nm, pulse duration 30 ns), Si or  $\text{Al}_2\text{O}_3$  substrates, and a target-to-substrate distance of 3–7 cm are used. In order to obtain a steady ablation rate from the target, the laser beam is scanned (in our case by eccentric rotation of the focusing lens and by additionally sweeping and/or slightly turning the target under the laser beam) over a sufficiently large target area (at least  $1 \text{ cm}^2$ ). By adjusting the number of laser pulses on each target, multilayers with desired single layer and

bilayer thicknesses can be created. Two ways for growing alloy systems were applied, using a bulk alloy target or elementary targets of the constituents. In the latter case, the pulse number on each target is supposed to be low enough to obtain a thickness of less than one monolayer from each element.

Under these deposition conditions, in addition to atoms and ions, in most cases some droplets of target material are also deposited on the substrate surface, too. In most systems, the formation of large droplets or the tearing-off of target exfoliations can be reduced by using dense and smooth targets [4, 5]. However, the ablation of smaller droplets originating from the fast heating and cooling processes of the target, which is due to the pulsed laser illumination cannot completely be avoided. In the literature, the corresponding mechanisms are called “hydrodynamic sputtering” [6] or “subsurface heating” [7]. These droplets can only be prevented from reaching the substrate surface, for instance by using the so-called “off-axis” geometry, firstly described by Holzapfel et al. [8] during PLD of high-temperature superconductors, or by using special laser ablation facilities, for instance the “dual-beam” ablation technique [9], where the substrate is shadowed from the material ablated simultaneously from two targets.

### 3 Versatility of the PLD Technique

During PLD, many experimental parameters can be changed, which then have a strong influence on film properties. First, the laser parameters such as laser fluence, wavelength, pulse duration and repetition rate can be altered. Second, the preparation conditions, including target-to-substrate distance, substrate temperature, background gas and pressure, may be varied, which all influence the film growth. In the following sections, we focus on the most interesting of these parameters.

#### 3.1 UHV and Different Gas Atmospheres

The PLD technique allows preparing all kinds of oxides, nitrides, carbides, but also polymers, Buckminster fullerenes or metallic systems. In Tab. (1), a non-comprehensive list of materials deposited for the first time after 1987 is given.

In order to obtain all these different kinds of materials, one has to work in ultrahigh vacuum (UHV) or reactive gas atmosphere during deposition. This is possible with PLD, because the energy source is *outside* the deposition chamber. During growth of oxides, the use of oxygen is often inevitable for achieving a sufficient amount of oxygen in the growing oxide film. For instance, for the formation of perovskite structures at high substrate temperatures in a one-step process, an oxygen pressure of about 0.3 mbar is necessary [2].

Also, for many other oxide or nitride films, the necessity of working in a reactive environment makes it difficult to prepare such samples vice thermal

Material		Literature	
High-temperature superconductors	YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	Dijkkamp et al. (1987)	[2]
	BiSrCaCuO	Guarnieri et al. (1988)	[10]
	TlBaCaCuO	Foster et al. (1990)	[11]
	MgB <sub>2</sub>	Shinde et al. (2001)	[12]
Oxides	SiO <sub>2</sub>	Fogarassy et al. (1990)	[13]
Carbides	SiC	Balooch et al. (1990)	[14]
Nitrides	TiN	Biunno et al. (1989)	[15]
Ferroelectric materials	Pb(Zr,Ti)O <sub>3</sub>	Kidoh et al. (1991)	[16]
Diamond-like carbon	C	Martin et al. (1990)	[17]
Buckminster fullerene	C <sub>60</sub>	Curl and Smalley (1991)	[18]
Polymers	Polyethylene, PMMA	Hansen and Robitaille (1988)	[19]
Metallic systems	30 alloys/multilayers	Krebs and Bremert (1993)	[20]
	FeNdB	Geurtsen et al. (1996)	[21]

**Table 1.** List of some materials deposited for the first time by PLD after 1987 and references

evaporation, using electron guns. In the case of sputtering, where commonly argon is used as the background gas, a larger amount of oxygen or nitrogen can only be added in special oven facilities close to the substrate surface.

### 3.2 Small Target Size

The PLD technique is also flexible, because the spot size of the focused laser beam is small and, therefore, the target area may even be less than 1 cm<sup>2</sup>. This allows to prepare complex samples with enrichments of isotopes or isotopic markers within the deposited film. Being able to easily prepare samples for research purposes or for application tests is especially interesting, if the sample or one component is extremely expensive or impossible to prepare with other techniques. Here, the flexibility of the PLD technique pays off, due to the possibility of easily exchanging and adjusting the targets.

In our case, for instance Fe-Ag thin films and multilayers were prepared with <sup>57</sup>Fe contributions to make special areas of the samples sensitive for Mössbauer spectroscopy and to investigate intermixing effects between the two components [22].

### 3.3 Stoichiometry Transfer

In many cases, one takes advantage of the fact that during PLD the stoichiometry of the deposited film is very close to that of the used target and, therefore, it is possible to prepare stoichiometric thin films from a single alloy bulk target. This so-called “stoichiometry transfer” between target and substrate has made the PLD technique interesting for the growth of complex systems, for instance of high-temperature superconductors, piezoelectric

and ferroelectric materials with perovskite structure, and also for technical applications (sensors, capacitors, ...).

Stoichiometry transfer between target and substrate is difficult to obtain with evaporation or (magnetron) sputtering by using a single target, because in general the partial vapor pressures and sputtering yields of the components are different from each other which gives rise to a different concentration of the thin film growing on the substrate. In the case of PLD, with most materials a stoichiometry transfer between target and substrate is obtained, which can be explained as follows.

The fast and strong heating of the target surface by the intense laser beam (typically up to temperatures of more than 5000 K within a few ns [23], corresponding to a heating rate of about  $10^{12}$  K/s) ensures that all target components irrespective of their partial binding energies evaporate at the same time. When the ablation rate is sufficiently high (which normally is the case at laser fluences well above the ablation threshold), a so-called Knudsen layer is formed [6] and further heated (for instance by Inverse Bremsstrahlung) forming a high-temperature plasma [24], which then adiabatically expands in a direction perpendicular to the target surface. Therefore, during PLD, the material transfer between target and substrate occurs in a material package, where the separation of the species is small. The expansion of the whole package can be well described by a shifted Maxwell-Boltzmann center-of-mass velocity distribution [25]

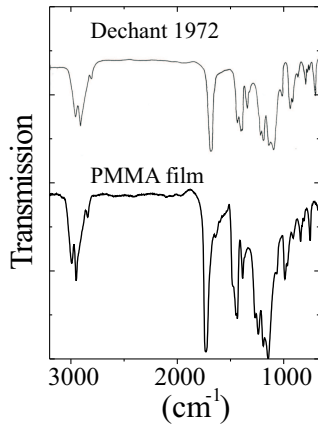
$$f(v_z) \propto v_z^3 \cdot \exp[-m_A(v_z - v_{cm})^2/(2kT_{\text{eff}})]. \quad (1)$$

with a center-of-mass velocity  $v_{cm}$  and an effective temperature  $T_{\text{eff}}$ . Then, adiabatic collisionless expansion occurs transferring the concentration of the plasma plume towards the substrate surface.

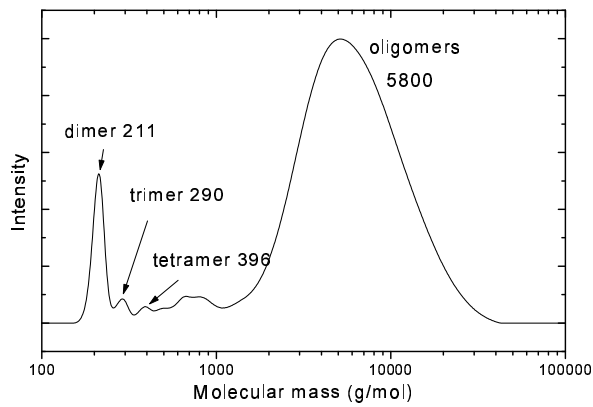
Thus one can understand that complex structures such as oxides or perovskites are built up again at the substrate surface, when the substrate temperature is high enough, because all components are transferred from target to substrate at the right composition.

But also in the case of polymers, the preparation of films from single bulk targets is possible, as was first shown by Hansen and Robitaille in 1988 [19]. In the case of polymers, chemical structure and chain length strongly depend on the applied laser wavelength and fluence (see for instance [26]). In Fig. 2, an infrared spectrum (FTIR) of poly-(methyl methacrylate) (PMMA) laser deposited at a fluence of  $300 \text{ mJ/cm}^2$  is compared with a literature spectrum [27]. As can be seen, apart from small intensity differences all absorption lines are seen also in the PLD film indicating that the reorganization at the substrate surface leads to a chemical structure very close to the bulk structure. Nevertheless, using a laser wavelength of 248 nm, the chain length of the grown PMMA films is reduced when depositing the film at room temperature. This is known from gel permeation chromatography (GPC) measurements performed after dissolving the PMMA films in tetrahydrofuran (see Fig. 3, note the logarithmic scale on the x-axis). The obtained average molecular mass  $M_n$

obtained is about 5800 g/mol. Details of these experiments are described elsewhere [28].



**Fig. 2.** FTIR spectrum of laser deposited PMMA films in comparison to bulk material [27]

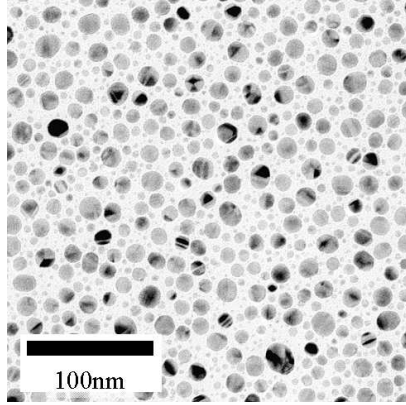


**Fig. 3.** GPC measurements on laser deposited PMMA

### 3.4 Pulsed Nature of PLD

The *pulsed* nature of the PLD process allows for strongly changing the laser conditions for each target. Therefore, it becomes possible producing complex composite materials like polymer-metal systems, where completely different

laser fluences are necessary for the deposition of polymer and metal, respectively. In Fig. 4, a transmission electron microscope (TEM, Philips EM-420) image of a polycarbonate (PC) film with a layer of Ag grains is shown. For production of such a sample, the PC has to be prepared at low laser fluence of about  $60 \text{ mJ/cm}^2$  to optimize the chemical structure, while the Ag crystals were deposited at an about 80 times higher fluence of  $5 \text{ J/cm}^2$ . By this technique, even PC/Ag-multilayers were grown for the first time with low interface roughness as will be described in [29].



**Fig. 4.** TEM image of a polycarbonate film with nanocrystalline Ag grains

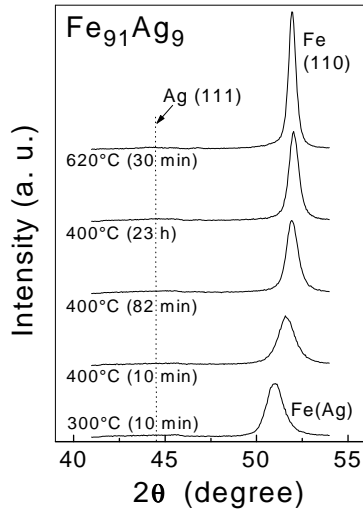
### 3.5 Energetic Particles

To obtain sufficiently high ablation rates (on the order of  $0.01 \text{ nm}$  per pulse) for the deposition of metallic systems in UHV, high laser fluences of more than  $5 \text{ J/cm}^2$  are necessary [20, 30]. Under these conditions, the film deposition occurs with energetic particles.

At a laser fluence of  $8 \text{ J/cm}^2$  the velocities of the plasma plume expansion correspond to average kinetic energies of the ablated ions of more than  $100 \text{ eV}$  [23] in agreement with results of Lunney [31]. The mean energy of the atoms is much lower, on the order of  $5\text{--}10 \text{ eV}$  [32]. In the literature, an acceleration of the ions in the strongly increasing space charge field incurred by the more mobile electrons, collectively moving away from the ions [33], is made responsible for the higher energies of the ablated ions.

The deposition with energetic particles allows for the formation of metastable phases, for instance nanocrystalline highly supersaturated solid solutions or amorphous films over a wide composition range. For instance, in the Fe-Ag system, which is almost immiscible in thermodynamic equilibrium, the bcc Fe(Ag) single phase can be supersaturated much higher than with conventional deposition techniques, namely up to  $13 \text{ at.}\%$  or up to  $40 \text{ at.}\%$  at room temperature and  $150 \text{ K}$ , respectively [34, 35]. In Fig. 5, x-ray measurements

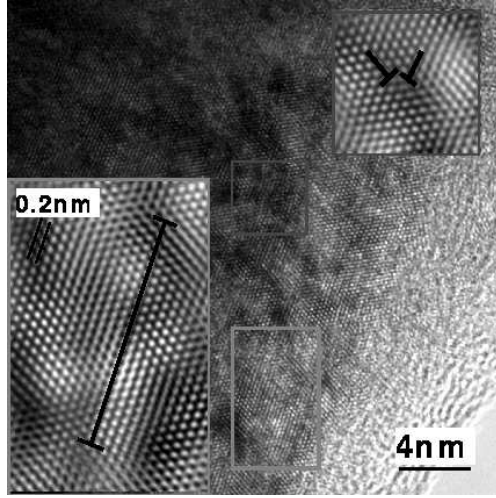
(Philips X'Pert MRD) of a  $\text{Fe}_{91}\text{Ag}_9$  thin film are shown after annealing at different temperatures. From the absence of an Ag peak at about  $44.5^\circ$  and from the width of the  $\text{Fe}(\text{Ag})$  peak it can directly be seen that the sample is supersaturated homogeneously and nanocrystalline with a grain size of about 6 nm (as deduced from the Scherrer formula [36]). With annealing temperatures up to  $620^\circ\text{C}$ , the peak shifts to higher scattering angles, but no Ag peak occurs, indicating that Ag diffuses out of the  $\text{Fe}(\text{Ag})$  grains into the grain boundaries, where wetting and stabilizing occurs up to high temperatures without Ag grain formation.



**Fig. 5.** High-angle x-ray diffraction of a laser deposited  $\text{Fe}_{91}\text{Ag}_9$  thin film after annealing at different temperatures

For mixing effects leading to homogeneous films, implantation of the energetic ions, intermixing with the already deposited material, and film growth below the surface (so-called “subsurface growth”) were made responsible. The implantation of particles (with energies above the displacement threshold) below the substrate surface also induces defect formation, at least for high laser fluences above  $6\text{ J/cm}^2$ . Using high resolution transmission electron microscopy (HRTEM, Philips CM200) in cross-section, dislocation densities of more than  $10^{12}\text{ cm}^{-2}$  were obtained in  $\text{Fe}(\text{Ag})$  thin films (Fig. 6).

The implantation of additional material into the already grown film, which is fixed to the substrate, leads to high compressive stress on the order of GPa. This compressive stress can be detected from peak shifts to lower scattering angles in conventional high-angle x-ray diffractometry [30]. Due to intermixing effects at the substrate surface, in general a strong adhesion of PLD films exists to all substrates used in our case (Si,  $\text{Al}_2\text{O}_3$ , W) and no tearing off the substrate was observed up to film thicknesses of  $1\ \mu\text{m}$ .



**Fig. 6.** HRTEM image of a supersaturated Fe(Ag) film showing a dislocation loop and dislocations (enlarged in the insets)

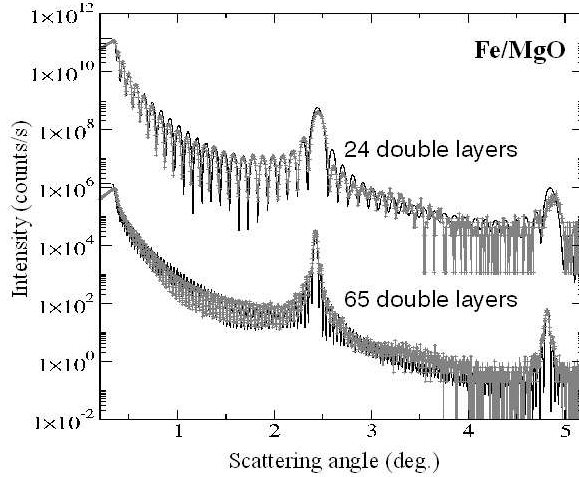
In the case of Fe/MgO and  $\text{Ni}_{80}\text{Nb}_{20}$ /MgO, the interface roughness of multilayers laser deposited in UHV is very small (typically about 0.35 nm for layer periodicities of up to 5 nm), as can be deduced from a fit to the x-ray reflectivity measurements (using  $\text{Co-K}_{\alpha}$  radiation) depicted in Fig. 7 (for details of the fit procedure see [37]). This is an indication for high surface mobility of the deposited particles and low intermixing effects in this system [37, 38].

### 3.6 Tunable Particle Energy

The kinetic energy of the deposited particles can be systematically varied from an average energy of about 50 eV to about 150 eV by increasing the laser fluence from 2 to about 10  $\text{J}/\text{cm}^2$  for metallic systems. This only slightly changes the film properties [39]. A much stronger influence on the film properties occurs, when the particle energy is lowered by an inert gas pressure. Then, the energy can be reduced to thermal energies below 1 eV.

In an Ar atmosphere, well below about 0.1 mbar, the reduction of the average energy of the ablated particles can be described by scattering of a dense cloud of ablated material moving through a dilute gas [39]. On the way towards the substrate, mainly the energetic ions are scattered out of the deposition path, while the slower atoms reach the substrate surface without any hindrance. At higher gas pressures, the plasma expansion leads to a shock front between plasma plume and surrounding gas, which hinders the plasma expansion and induces a further velocity reduction [40].

A decrease of particle energy is accompanied by systematic changes in texture and microstructure. With conventional thin film techniques usually the substrate temperature has to be varied to change texture. This shows



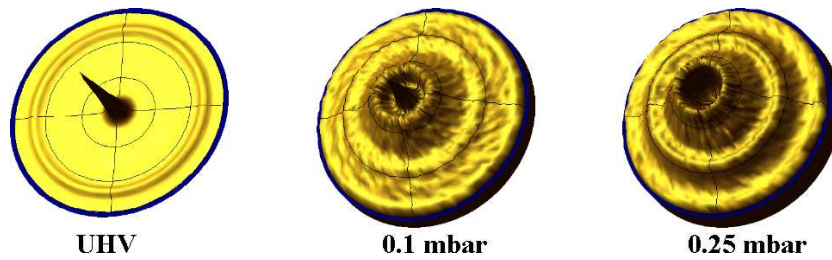
**Fig. 7.** X-ray reflectivity measurements and fit of laser deposited Fe/MgO thin films with a layer periodicity of 2.1 nm for different numbers of bilayers

that during PLD, where energetic particles exist, the particle energy is an additional parameter to play with.

As an example, in Fig. 8 texture measurements (using a conventional four-circle diffractometer with Co- $K_{\alpha}$  radiation) are shown for Permalloy ( $\text{Ni}_{80}\text{Fe}_{20}$ , Py) deposition in different Ar gas atmospheres at room temperature. These are 3-dimensional plots, where the angles  $\psi$  and  $\varphi$  are used as usual and the “height” is the measured intensity. For Py deposited in UHV, the films exhibit a strong (111) fibre texture typical for fcc metals with a full width at half maximum (FWHM) of  $5^{\circ}$ . For higher pressures during deposition, the sharpness of the peaks is reduced and the FWHM rises, before a complete change in the texture occurs. For 0.1 mbar, besides the (111) fibre texture also traces of the (200) and (321) fibre texture are seen. For even higher pressures the (111) direction completely vanishes and only the (200) and (321) directions remain.

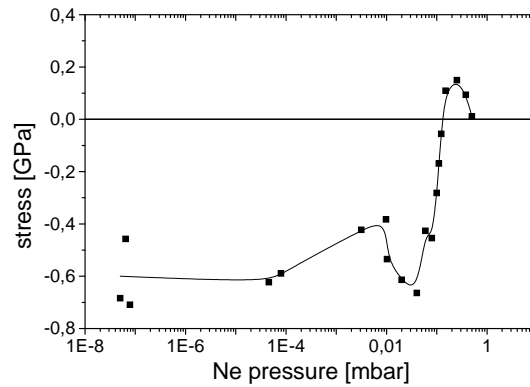
The reduction of kinetic energy is also accompanied by a lowering of intermixing and resputtering effects [39, 41], and by a stress transition from compressive to tensile [42].

As a further example, stress values obtained for Ag under different Ne gas pressures are shown in Fig. 9. Details of the used *in-situ* bending beam technique are described in ref. [42]. Under UHV conditions and at low Ne pressure, the film stress is about  $-0.6$  GPa. With increasing pressure a steep compressive-to-tensile transition occurs at about 0.1 mbar and tensile stress of  $+0.15$  GPa is reached. One can see that depending on the desired condi-



**Fig. 8.** Change of the Permalloy thin film texture, depending on the Ar gas pressure during PLD at room temperature

tions, films with compressive or tensile stress, or even stress-free films can be grown by PLD by simply changing the background inert gas pressure during deposition.



**Fig. 9.** Change of stress of Ag films laser deposited at different Ne gas pressures

It is also possible to reduce bulk defects and intermixing at interfaces, if desired. The kinetic energy of the deposited particles has to be reduced by the inert gas to such an extent that it is below the threshold for bulk atom displacements (about 25 eV in the case of most metals). Under such conditions, implantation of particles into the growing film is minimized while at the same time having enough energy for structural displacements at the film surface and increased surface mobility. This can be achieved with Ar gas using a pressure of about 0.04 mbar and with He at about 0.1 mbar. Under these conditions, multilayers with much sharper interfaces can be prepared, as has been tested in the case of the Fe/Ag system [39].

The change of interface roughness strongly influences the properties of multilayers. As was shown earlier, for instance the giant magneto resistance of Py/Ag multilayers [43] and the x-ray reflectivities of Ni<sub>80</sub>Fe<sub>20</sub>/MgO multilayers [37] are drastically changed, when preparing the samples in UHV and in Ar gas atmosphere, respectively.

## 4 Conclusions

Since the breakthrough of the PLD technique due to the work of Dijkkamp in 1986 all kinds of materials were prepared by this method. The stoichiometry transfer between target and substrate and the possibility of working in UHV as well as in different reactive and inert gas atmospheres are particularly attractive features of PLD. That the kinetic energy of the deposited ions lies in the range of about 100 eV, is also of interest due to the possibility of preparing new systems far away from equilibrium (supersaturated binary systems, nanocrystalline materials, metastable alloys, ...). Furthermore, using an inert gas pressure makes this method versatile, because the energy of the deposited particles is a free parameter to play with. Energy may be reduced and adjusted for special purposes. For instance, an adjustment of texture, stress or interface roughness can be obtained. The possibility of additionally changing laser features, such as wavelength, repetition rate, pulse length, fluence and target-to-substrate distance, and the deposition conditions, such as substrate temperature and substrate orientation with respect to the deposited material, further demonstrates the enormous versatility of PLD.

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## References

1. H. M. Smith and A. F. Turner, *Appl. Opt.* **4**, 147 (1965).
2. D. Dijkkamp, T. Venkatesan, X. D. Wu, S. A. Shareen, N. Jiswari, Y. H. Min-Lee, W. L. McLean, and M. Croft, *Appl. Phys. Lett.* **51**, 619 (1987).
3. D. B. Chrisey and G. K. Hubler: *Pulsed laser deposition of thin films*, (Wiley, New York 1994).
4. C. Scarfone, M. G. Norton, C. B. Carter, J. Li, and H. W. Mayer, *Mat. Res. Soc. Symp. Proc.* **191**, 183 (1991).
5. S. Fähler, M. Störmer, and H. U. Krebs, *Appl. Surf. Sci.* **109/110**, 433 (1997).
6. R. Kelly, and J. E. Rothenberg, *Nucl. Instrum. Methods Phys. Res. B* **7/8**, 755 (1985).
7. R. K. Singh and J. Narayan, *Phys. Rev. B* **41**, 8843 (1990).

8. B. Holzapfel, B. Roas, L. Schultz, P. Bauer, and G. Saemann-Ischenko, Appl. Phys. Lett. **61**, 3178 (1992).
9. A. A. Gorbunov, W. Pompe, A. Sewing, S. V. Gaponov, A. D. Akhsakhalyan, I. G. Zabrodin, I. A. Kaskov, E. B. Klyenkov, A. P. Morozov, N. N. Salaschenko, R. Dietsch, H. Mai, and S. Völlmar, Appl. Surf. Sci. **96-98** 649 (1996).
10. C. R. Guarneri, R. A. Roy, K. L. Saenger, S. A. Shivashankar, D. S. Lee, and J. J. Cuomo, Appl. Phys. Lett. **53**, 532 (1988).
11. C. M. Foster, K. F. Voss, T. W. Hagler, D. Mihailovic, A. J. Heeger, M. M. Eddy, W. L. Olsen, and E. J. Smith, Solid State Comm. **76**, 651 (1990).
12. S. R. Shinde, S. B. Ogale, R. L. Greene, T. Venkatesan, P. C. Canfield, S. L. Budko, G. Lapertot, and C. Petrovic, Appl. Phys. Lett. **79**, 227 (2001).
13. E. Fogarassy, C. Fuchs, A. Slaoui, and J. P. Stoquert, Appl. Phys. Lett. **57**, 664 (1990).
14. M. Balooch, R. J. Tench, W. J. Siekhaus, M. J. Allen, A. L. Connor, and D. R. Olander, Appl. Phys. Lett. **57**, 1540 (1990).
15. N. Biunno, J. Narayan, S. K. Hofmeister, A. R. Srinatsa, and R. K. Singh, Appl. Phys. Lett. **54**, 1519 (1989).
16. H. Kidoh, T. Ogawa, A. Morimoto, and T. Shimizu, Appl. Phys. Lett. **58**, 2910 (1991).
17. J. A. Martin, L. Vazquez, P. Bernard, F. Comin, and S. Ferrer, Appl. Phys. Lett. **57**, 1742 (1990).
18. R. F. Curl and R. E. Smalley, Scientific American, October 1991, 32.
19. S. G. Hansen and T. E. Robitaille, Appl. Phys. Lett. **52**, 81 (1988).
20. H. U. Krebs and O. Bremert, Appl. Phys. Lett. **62**, 2341 (1993).
21. A. J. M. Geurtsen, J. C. S. Kools, L. de Wit, and J. C. Lodder, Appl. Surf. Sci. **96-98**, 887 (1996).
22. R. Gupta, M. Weisheit, H. U. Krebs, and P. Schaaf, Phys. Rev. B **67**, 75402 (2003).
23. S. Fähler and H. U. Krebs, Appl. Surf. Sci. **96-98**, 61 (1996).
24. C. R. Phipps, T. P. Turner, R. F. Harrison, G. W. York, W. S. Osborne, G. K. Anderson, X. F. Corlis, L. C. Haynes, H. S. Steele, K. C. Spicochi, and T. R. King, J. Appl. Phys. **64**, 1083 (1988).
25. J. C. S. Kools, T. S. Baller, S. T. De Zwart, and J. Dieleman, J. Appl. Phys. **71**, 4547 (1992).
26. S. Nishio, T. Chiba, A. Matsuzaki, and H. Sato, J. Appl. Phys. **79**, 7198 (1996).
27. J. Dechant: *Ultrarotspektroskopische Untersuchungen an Polymeren*, (Akademie Verlag, Berlin 1972).
28. E. Süske, T. Scharf, H. Kijewski, P. Schaaf, D. Nelke, E. Panchenko, M. Buback, and H. U. Krebs, in preparation.
29. J. Faupel and H. U. Krebs, in preparation.
30. H. U. Krebs, J. Non-Equilibrium Processing **10**, 3 (1997).
31. J. Lunney, Appl. Surf. Sci. **86**, 79 (1995).
32. P. E. Dyer, Appl. Phys. Lett. **55**, 1630 (1989).
33. W. Demtröder and W. Jantz, Plas. Phys. **12**, 691 (1970).
34. M. Störmer and H. U. Krebs, J. Appl. Phys. **78**, 7080 (1995).
35. S. Kahl and H. U. Krebs, Phys. Rev. B **63**, 172103 (2001).
36. B. D. Cullity: *Elements of x-ray diffraction*, (Adison-Wesley, Reading, Massachusetts 1967).
37. S. Vitta, M. Weisheit, T. Scharf, and H. U. Krebs, Optics Lett. **26**, 1448 (2001).

38. C. Fuhse, H. U. Krebs, S. Vitta, and G. A. Johansson, in preparation.
39. K. Sturm, S. Fähler, and H. U. Krebs, *Appl. Surf. Sci.* **154-155**, 462 (2000).
40. T. Scharf and H. U. Krebs, *Appl. Phys. A* **75**, 551 (2002).
41. K. Sturm and H. U. Krebs, *J. Appl. Phys.* **90**, 1061 (2001).
42. T. Scharf, J. Faupel, K. Sturm, and H. U. Krebs, submitted.
43. J. Faupel, H. U. Krebs, A. Käufler, Y. Luo, K. Samwer, and S. Vitta, *J. Appl. Phys.* **92**, 1171 (2002).