Influence of burst pulses on the film topography in picosecond pulsed laser deposition of LaAlO₃

Erik Thelander¹ and Bernd Rauschenbach
Institute of Surface Modification, 15, Permoserstraße, 04318 Leipzig, Germany
E-mail: erik.thelander@iom-leipzig.de

Abstract. Using a commercial picosecond laser in a pulsed laser deposition setup for the deposition of LaAlO₃ thin films, we showed that it is possible to obtain a wide range of different surface topography just by altering the temporal output of the laser pulses. In single-pulse mode, a highly structured surface is obtained independent of the laser fluence. As the number of burst pulses is increased from 2 to 10, the surface roughness gradually decreases to almost atomically smooth as investigated with scanning electron and atomic force microscopy. Studies by X-ray photoelectron spectroscopy revealed no significant variation in the film composition indicating that the burst mode only tunes the topography without affecting other parameters. The surface roughness modification is independent of the background pressure in a wide range, which opens up the possibility of using different reactive atmospheres, which could be used to tune the properties of the material even further.

1. Introduction
The use of femtosecond (fs) laser pulses in pulsed laser deposition (PLD) has been thoroughly investigated in the last couple of years [1,2]. Since fs-pulses are of shorter duration than the electron-phonon coupling time, this is a cold ablation process, i.e. the ablated material is not melted. This was thought to be beneficial in the reduction of ejects of molten micrometer droplets, a typical contaminant in PLD processes. Instead, a new interesting feature was discovered; the deposited films showed a characteristic surface topography consisting of coalesced nanoparticles. This results in coatings with a high surface roughness, which is either desired or detrimental depending on the application in mind. The nanoparticles arise from the extreme material states that are induced when light of ultrashort duration interacts with matter at energy densities over the ablation threshold [3-5]. They therefore need to be considered as an inherent property of fs-PLD. Nevertheless, it has been shown that by adjusting the temporal output of the fs-pulses, in the so-called burst mode fs-PLD [6], it is possible to tune the surface topography and even to obtain epitaxial thin films. The reduction of nanoparticles in burst mode fs-PLD is attributed to the interaction of subsequent laser pulses with the slow moving part of the plasma plume which could further ionize or evaporate the particles in the plasma. Interestingly, the use of laser pulses with picosecond (ps) duration has not been extensively investigated even though it is known from micromachining that it is also a cold ablation process. From the few investigations available, one can distinguish two different regimes: when using a laser repetition rate < 4MHz the deposited films consists of nanoparticles and are identical to those deposited with

¹ To whom any correspondence should be addressed.
fs-pulses [7,8], but when using a repetition rate > 4MHz a new ablation mechanism is initiated, the so-called thermal ablation regime [9,10]. Here the laser pulses are delivered so fast that the heat cannot dissipate between the pulses and the material is heated to a critical temperature where it melts and, therefore, this is no more a cold ablation process. This, however, implies that there exists a possibility to alter the surface topography just by changing the repetition rate of the laser, something that is easier said than done since most lasers are optimized for a relatively narrow repetition rate range. A possible solution would be the use of burst pulses which take advantage of a very high instant repetition rate in combination with a lower pulse sequence repetition rate. In this paper, we report the use of ps-pulses in PLD of LaAlO₃. Specifically, we discuss the effect of the number of burst pulses on the surface roughness and film composition.

2. Experimental conditions
In the experiments, a Nd: YAG laser operating at 355 nm was used for pulsed laser ablation of LaAlO₃. The pulse duration was 9 ps with a pulse sequence repetition rate of 80 kHz. Pulse sequences with up to 10 burst pulses can be achieved by an internal Pockels cell. The burst pulses are delivered at 50 MHz and the burst sequences can be repeated with the repetition rate mentioned above. In the experiments, the number of burst pulses was varied between 1 and 10. The laser power was 1.80 W, yielding fluences in the range between 0.73 J/cm² and 0.073 J/cm² with losses in the beam path included. This is illustrated in figure 1 where 1, 5 and 10 burst pulses are shown schematically. An increase in the number of burst pulses within the pulse sequence group from 1 to 10 reduces the energy for each individual pulse by a factor 10, and, therefore, the fluence as well. The burst pulses have a 20 ns gap between each pulse, while the pulse sequence is repeated every 12.5 µs. The thin film deposition was carried out in a UHV-chamber with a base pressure of 10⁻⁸ mbar. During deposition, 1 sccm of O₂ was let into the chamber resulting in a pressure of ~10⁻⁵ mbar. A 1×1 mm² silicon wafer was used as a substrate, placed directly over the laser spot with a target to substrate distance of about 4 cm. The substrate was kept at room temperature and rotated to even out the inhomogeneities in the plasma plume. A LaAlO₃-target (99.99%) was used and scanned in a pre-programmed way to allow for a homogeneous ablation of the target. All samples were deposited for 20 minutes. The film topography was investigated by scanning electron microscopy (SEM) at 2.5 keV acceleration voltage and scanning force microscopy (AFM) in tapping mode. The composition of the films was investigated by XPS.
3. Results and discussion

In figure 2, SEM images are shown of LaAlO$_3$ films prepared by ps-pulsed laser ablation with burst pulse number 1, 5, and 10. The topography prepared with only 1 burst pulse, figure 2a, shows a very rough surface with particles ranging from 0.1 µm to 1 µm. At higher magnification, in figure 2b, it is seen that the film is built through coalescence of particles. The topography of the films highly resembles what is normally reported for fs-PLD of dielectrics [11]. For single-pulse experiments at lower fluencies (not shown here), the topography looks similar all the way down to the ablation threshold for single-pulse mode, showing that a reduction of the laser fluence in the single-pulse mode is not a possible route to obtain smooth thin films of LaAlO$_3$.

Although the laser fluence reduction has no beneficial effect on the film smoothness in single-pulse mode, a clear effect can be seen when applying burst pulses, as evidenced in figures 2c and d, where samples fabricated by 5 and 10 burst pulses are presented, respectively. As can be seen, as the number of burst pulses is increasing and, hence, the laser fluence is reduced, the surfaces get smoother. The samples are not free of nanoparticles, but the films look much more homogenous than in the sample with only one pulse. It should be noted that films prepared with 2, 3 and 8 pulses agree well with this general trend but are not shown here. This is in good agreement with PLD experiments using fs-burst pulses [6], where reduction of the nanoparticles is reported as the number of burst pulses is raised, and even epitaxial growth of TiO$_2$ is achieved using 19 burst pulses. However, a direct comparison is hard to do since a number of important parameters differ from the experiment presented in this paper (pulse energy and number, wavelength).

To quantify the surface roughness and hence the ability to tune the topography, the samples were investigated with AFM. Figure 3 shows an AFM image of a film deposited by 10 burst pulses. Individual nanoparticles can be clearly seen with particles sizes of 100 nm or less, yielding a root-mean-square (RMS) roughness of 8.3 nm. Identical measurements were carried out for all samples; the roughness obtained is plotted against the number of burst pulses in figure 3b. As can be seen, the surface roughness decreases by more than a factor 20 as the number of burst pulses increases from 1 to 10. Since the surfaces are rough and the AFM tip has a finite geometry, the measurements are probably underestimating the surface roughness in general, particularly so for the roughest surfaces. Therefore, the trend should hold even if the absolute values are underestimated.

![AFM image](image)

**Figure 3.** Typical AFM-measurement of a sample at 10 burst pulses (a). Surface roughness obtained by AFM displayed against the number of burst pulses (b). The dashed line is only intended as a guide for the eye.

The surface roughness reduction observed can be explained considering two different possibilities: heat accumulation in the target between subsequent burst pulses [9] leading to a change in the ablation...
mechanism, i.e. thermal ablation and plasma absorption of subsequent burst pulses [6]. The heat accumulation model is based on a step-wise temperature rise in the target when irradiated by laser pulses with high repetition rate. When the thermal conductivity is low, i.e. oxides, chalcogenide glasses, the heat absorbed cannot be dissipated and is accumulated. A critical temperature $T_c$ is reached after a certain number of laser pulses, so that the target enters a new ablation regime which could have effect on the deposited samples [10]. The number of laser pulses needed depends on the repetition rate and material, but is in general many tens of pulses for a bad thermal conductor. Therefore, it is plausible to say that heat accumulation in the target is not the dominant mechanism since a) the maximum number of burst pulses is only 10, i.e. the thermal ablation threshold is not fully reached and b) there is a relatively long pause (12.5 µs) between each burst sequence to allow for any accumulated heat to dissipate.

However, the effect of plasma absorption by subsequent pulses needs to be considered. A calculation reveals that the nanoparticles in the plasma plume travel a distance of around 20 µm from the target surface in the time between each burst pulse assuming a propagation velocity for the nanoparticles of around 10 000 m/s. Considering the dimensions of the laser beam (20 µm Gaussian beam radius and 60° incident angle) a large part of the nanoparticles can actually be in the area where absorption processes occur. Therefore, it is likely that a part of the plasma plume body is re-evaporated/ionized by subsequent burst pulses. Optical observation of the plasma plume also indicates plasma absorption due to a broadening of the plasma plume when the number of burst pulses increases (not shown here).

XPS measurements were carried out to determine the La/Al ratio in the deposited oxide films. A LaAlO$_3$ single crystal was used as a reference sample with a calibrated La/Al-ratio of 1; all other samples was normalized against it. The La/Al-ratio ranged between 0.92 and 0.81 for all samples with no apparent systematic dependency on the number of burst pulses. It is worth noting that all samples show a small La deficit, but in a first approximation the target transfer is near congruent. For picosecond pulses, it is known that a change of the ablation mechanism from a regime where the single pulse interaction dominates to a regime where thermal evaporation is dominant can alter the composition of the films produced [10]. Considering this, it is clear that the regime where thermal evaporation dominates was not reached even for the samples where a high number of burst pulses were used, since there is no compositional trend that supports this.

Conclusions
Pulsed laser deposition of LaAlO$_3$ using a picosecond laser oscillating at 355 nm was studied. Based on the experimental findings, the following conclusions can be drawn:

- Deposition with single pulses results in thin films covered with nanoparticles of size between 100 and 1000 nm and a surface roughness of more than 160 nm. The surface morphology is independent of the laser pulse energy and repetition rate.
- Deposition with bundled laser pulses in the so-called burst mode setup results in a reduction of the surface roughness. When the number of burst pulses is increased from 1 to 10, the surface roughness is reduced by more than a factor 20, demonstrating that the method could be used to modify the surface roughness of thin oxide films.

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