Particulate Filtering Upon Pulsed Femtosecond Laser Deposition

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Pulsed femtosecond laser deposition has been shown to suffer from a severe particulate problem. However, in contrast to pulsed nanosecond laser deposition, particulates are not ejected as molten droplets, but as condensed clusters formed in the highly dense ablation plasma. In order to utilize the advantages of pulsed ultrashort laser deposition, three strategies for particulate avoidance are experimentally demonstrated: electrostatic filtering, scattering at a background gas, and magnetic filtering. Ultrathin layers prepared by these three techniques are characterized by scanning and transmission electron microscopy and promise for future developments are outlined.

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1. Introduction

When femtosecond lasers became commercially available, it was expected that the specific properties of these ultrashort lasers would also help improve pulsed laser deposition (PLD). This expectation was based on the fact that all solid materials can be readily ablated with femtosecond laser pulses (due to multiphoton absorption, excitation across the band gap can be accomplished even for laser wavelength not sufficient for ablation with “ordinary” laser pulses). Moreover, the absence of plasma shielding, a lowering of the threshold ablation fluence in comparison to ns-laser ablation, and the expected preservation of stoichiometry upon materials transfer was thought to prove beneficial. Eventually, droplet production was expected to be much reduced [1].

Over the years, however, the initial idea that fs-laser pulses would generate highly ionized plasmas virtually free of droplets was shown to not exactly meet what is observed. Instead, it was found that in the far field, laser ablation plumes generated by single femtosecond pulses consists of mostly neutral atoms, a certain percentage of ionized species, and very often, condensed clusters [2]. The latter clusters–likely resulting from a plasma-jet nozzle effect–have, except for their shape and size, nothing in common with molten droplets ejected upon ns-PLD [3]. Nevertheless, they certainly spoil the deposition of smooth, particulate-free thin films.

In the present contribution, we examine three means to keep the above-mentioned particulates off the thin films grown by pulsed femtosecond laser deposition (PfsLD), namely:

(i) scattering at a background gas,
(ii) electrostatic filtering, and
(iii) filtering using a transversal magnetic field just above the location of ablation.

2. Experimental

2.1. Pulsed femtosecond laser deposition

A 3D-Micromac micromachining workstation (micro-*PULSE* FS-150-1) featuring a Clark MXR CPA-2001 Ti:sapphire femtosecond laser (pulse length = 150 fs, repetition rate = 1 kHz, wavelength = 775 or 388 nm, via second harmonic generation) was complemented by a UHV chamber for pulsed laser deposition (Fig. 1). In this chamber, a base pressure of circa $2 \cdot 10^{-10}$ mbar is routinely achieved and assist gases (including nitrogen and argon) can be added to adjust for desired partial pressures to be used upon deposition within a background gas. Three targets of 1” diameter can be simultaneously taken up by a PVD target manipulator allowing for computer-controlled motion of the targets (revolution, toggling, and indexing). Opposite to the target manipulator, a VTS Createc substrate manipulator is located, being capable of rotating the substrate about its normal, eucentric tilting, biasing, and heating to about 1,100 °C. Both, 1” targets and 1 x 1 cm^2 substrates (mounted onto a dedicated carrier) can be exchanged via a load lock and a transfer rod equipped with a Bayonet tool. During deposition, the femtosecond laser beam hits the target under a glancing angle of 30°. By means of a focusing lens (focal length = 500 mm), an elliptical laser spot with half axes of 75 µm x 100 µm if formed (at the ablation threshold fluence of ca. 20 mJ/cm^2 (in the case of titanium); the size is increasing with fluence). By synchronized toggling and rotation of the target, the target surface is effectively and evenly rastered by the laser spot. The evolving plasma plume proved rather stationary and propagated essentially perpendicular to the target normal.

In the present contribution, the results of PfsLD experiments aiming at the deposition of particulate-free ultrathin metal films onto silicon substrates are discussed.

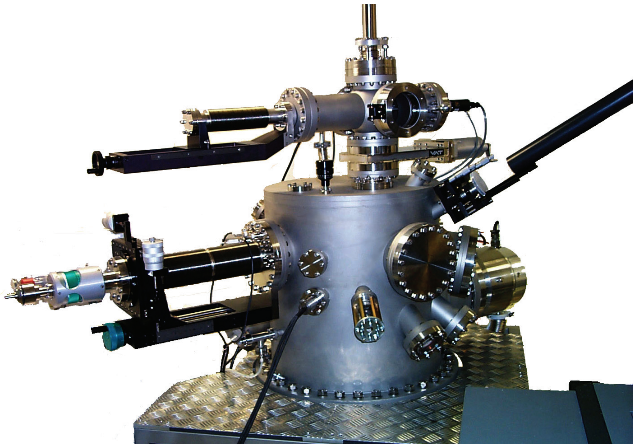


Fig. 1 PfsLD UHV chamber with load lock and transfer rod at the top, substrate manipulator on the left and laser port on the upper right.

2.2 Characterization of deposited thin films

The occurrence of particulates on thin films generated by PfsLD was studied in a field-emission environmental scanning electron microscope using typically 8 keV electrons under a water-vapour pressure of 140 Pa. The nanostructure of the thin films was imaged in a 400 kV JEM 4010 transmission electron microscope (point resolution 0.155 nm). For this, face-to-face glued cross-sections were embedded into alumina tubes [4], sliced, mechanically ground, one-sided dimpled, polished and ion-beam etched (Ar^+ ions, 2.5 keV, 5°). Electrostatic charging of the samples was avoided by selective carbon coating with the CoatMaster [5].

3. Results and Discussion

In Fig. 2, a typical result of an *unfiltered* PLD experiment using femtosecond laser pulses is depicted.

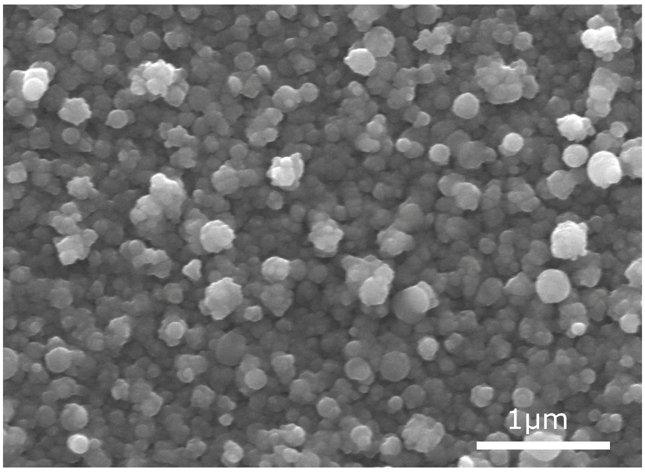


Fig. 2 Ti deposited at maximum fluence without filtering onto silicon.

The thin film is dominated by a huge number of particulates possessing diameters between 100 nm and 250 nm and the thickness of this film was estimated to several 100 nm. It could be shown that upon decreasing the fluence, the particulate size can be decreased by a factor of about four. According to literature [6], a reduction of the wavelength upon short-pulsed lasers deposition leads to a reduction of the particulate size. Similar finding, however, are not found for the ultrashort-pulsed femtosecond laser used here. The deposition of titanium thin films at laser wavelengths of 388 nm and 775 nm, respectively, proved to have virtually no impact on the both the size and shape as well as the number of particulates reaching the substrate. It can be hence concluded that the entire avoidance of those interfering particulates would require dedicated filtering techniques, three of which will be discussed in the following. In either of the techniques, it is attempted to separate the unwanted particulates (the latter are expected to be heavier and less charged than single-charged ions).

3.1 Electrostatic filter

If a negative bias is applied to the manipulator head carrying the substrate, positive ions can be redirected from inside the expanding plasma plume. A baffle positioned in the line-of-sight between the ablation position and the substrate (cf. Fig. 3) is intended to catch the less mobile, heavy particulates.

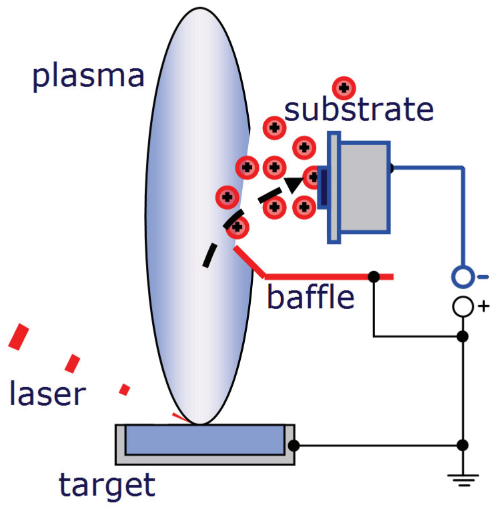
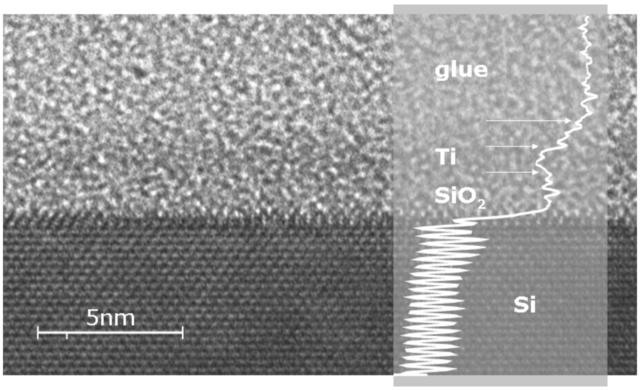


Fig. 3 Schematic of the electrostatic filter setup.

Voltages between -5 V and -400 V were applied and virtually particulate-free ultrathin films were deposited. The cross section of an electrostatically filtered, ultrathin titanium film (laser ablation wavelength = 775 nm, repetition rate = 1 kHz, fluence = 205 mJ/cm^2, bias = -300 V, deposition time = 15 min, UHV) is shown in Fig. 4. As an inset, a line scan across the micrograph, averaged over the entire width of the image, facilitates the discrimination of the different layers. It is hence easy to quantify the thickness of the native oxide film onto the silicon substrate to be between 1.5 nm and 2 nm, while the Ti film is just about 1 nm thick.

From this figure, it is obvious that the surface of the amorphous Ti film is not perfectly sharp and, even more importantly, the deposition rate can be estimated to be as low as ~ 2 pm/s.

Fig. 4 Cross-sectional transmission electron micrograph of an ultrathin titanium layer deposited onto silicon using electrostatic filtering in UHV.



3.2 Scattering at background gas

Lighter constituents of the ablation-plasma plume are more efficiently scattered at the molecules of a background gas than clusters or even particulates of larger diameter, and hence increased mass. Due to its high scattering power, argon was preferred over nitrogen in the experiment illustrated in Fig. 5, where again, light particles are redirected behind the line of sight by scattering at the background gas.

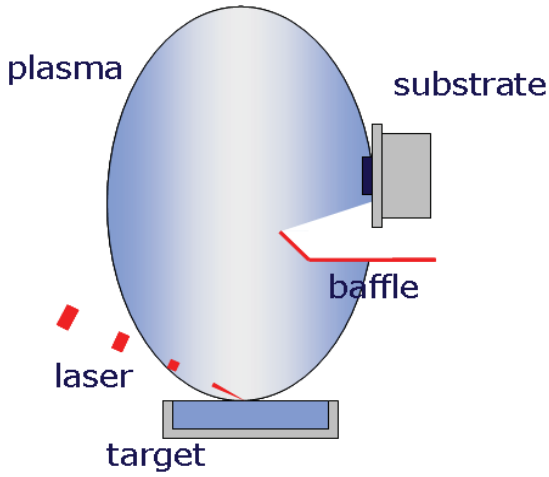


Fig. 5 Schematic of the setup used to filter out particulates by scattering at a background gas.

In Fig. 6, the surface of a thin titanium film deposited at a wavelength of 388 nm in an argon atmosphere ($3.3 \cdot 10^{-3}$ mbar) is depicted. Obviously, the particulate density is very low and the smoothness of the film is very good.

The cross-section of the same film is shown in Fig. 7, where on top of the native silicon oxide film, an about 7 nm thick, amorphous titanium film can be discerned. The deposition rate for this kind of particulate filtering is approximately 5 pm/s and hence – although still rather low – more than twice as high as for electrostatic filtering.

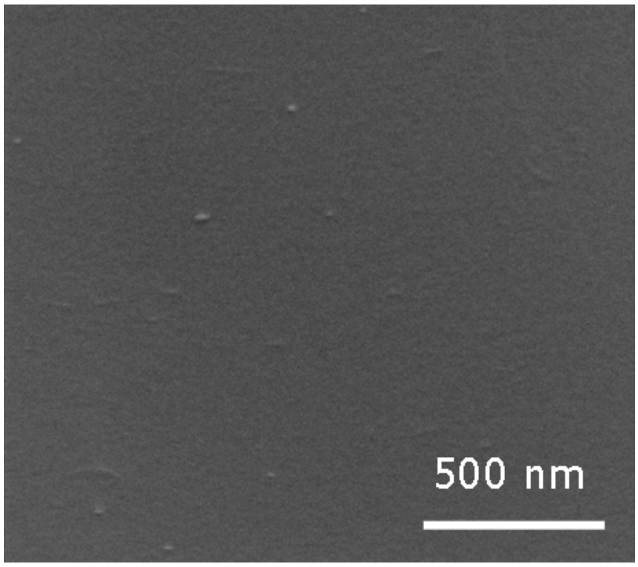


Fig. 6 Scanning electron micrograph of a titanium film (laser ablation wavelength = 388 nm, repetition rate = 1 kHz, fluence = 70 mJ/cm^2, deposition time = 25 min, argon atmosphere ($3.3 \cdot 10^{-3}$ mbar)). The micrograph was taken under a glancing angle of 10° and therefore the scale bar does only apply to the horizontal dimension.

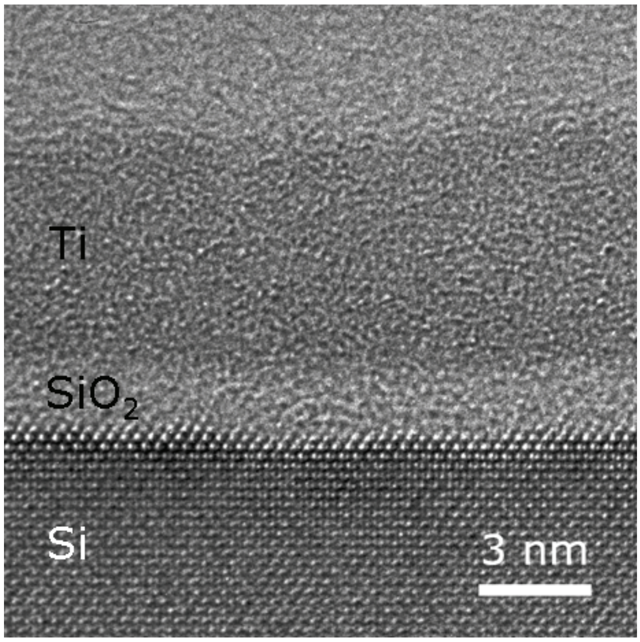


Fig. 7 Cross-sectional transmission electron micrograph of the titanium film depicted in Fig. 6.

3.3 Magnetic field perpendicular to expansion direction of the laser-plasma plume

In the last of the three particulate-avoidance approaches studied here, a static magnetic field is positioned just above the location where the laser hits the target. As illustrated by Fig. 8, upon entering the transversal magnetic field, the ejected positive ions are forced onto a circular trajectory redirecting them behind the baffle. The supermagnets used to generate the static magnetic field are fitted in a pole piece-type arrangement resulting in a rather homogeneous field strength valued 0.78 T at the position where the laser hits the target.

The magnetic field will have a much weaker influence on less charged/larger particles and the latter will hence not be able to reach the substrate hidden behind the baffle. Electrons, that are believed to become ablated slightly before ions are ejected, however, can even become trapped by the strong magnetic field and start gyrating within the pole-piece. Their fast motion in turn, might be capable of increasing the ionization of the expanding plasma.

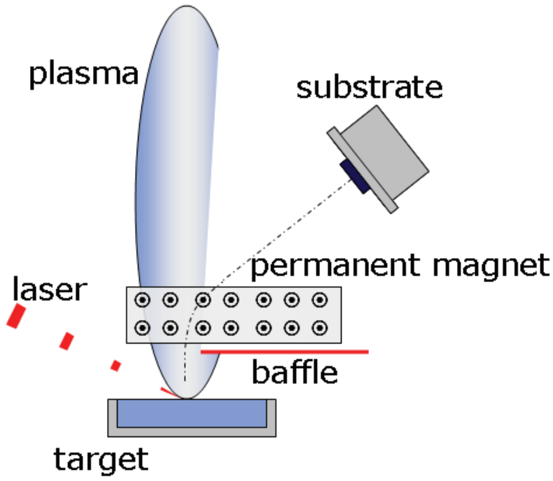


Fig. 8 Schematic of the setup used for particulate filtering using a transversal magnetic field.

With this approach, a Cr/Sc multilayer consisting of five Cr/Sc double layers was synthesized on a Si substrate. For this experiment, laser light of 775 nm wavelength was used and as shown in Fig. 9, even after a total deposition time of more than three hours, the number of particulates is as low as 0.15 μm^{-2}. Between the particulates, the surface roughness is essentially identical to the typical roughness of the epi-ready silicon wafer prior to deposition.

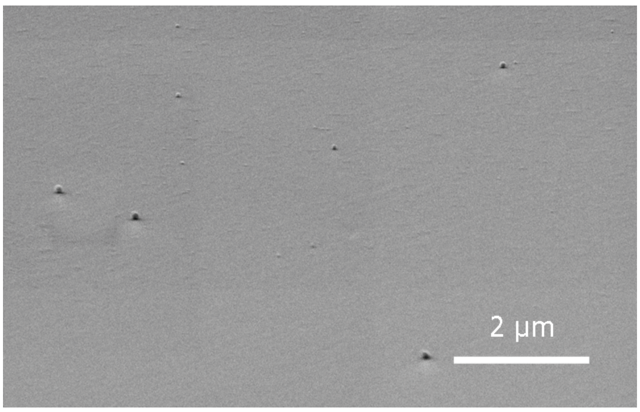


Fig. 9 Scanning electron micrograph of a multilayer consisting of five bilayers of Cr and Sc (laser ablation wavelength = 775 nm, fluence = 170 mJ/cm^2, total deposition time = 5 x (13 + 24) min, UHV). The micrograph was taken under a glancing angle of 10° and therefore the scale bar does only apply to the horizontal dimension.

From Fig. 10, depicting the TEM cross section of the multilayer, is it clear that the alternating Cr and Sc layers are amorphous but it is also evident that there must have been some variation in the laser power resulting in a certain scatter in the thicknesses of the individual layers. The total thickness of the film is about 10 nm and again, taking into account the total deposition time of 185 min, a fairly low deposition rate of just about 1 pm/s can be calculated. Here, the relatively long times required for deposition combine with a highly complex laser system to the critical issue of long-term stability of deposition rates.

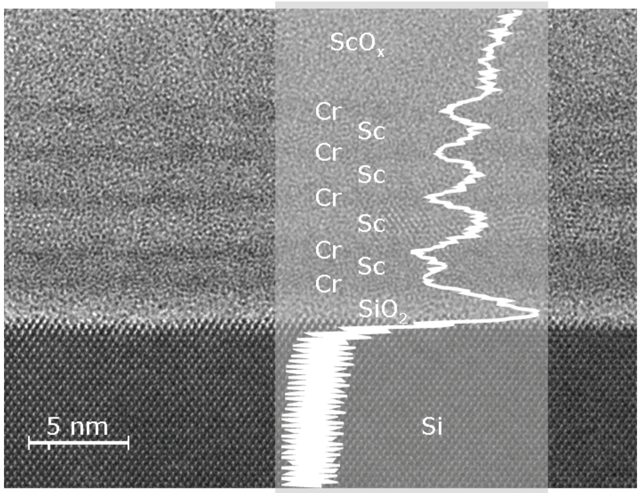


Fig. 10 Cross-sectional transmission electron micrograph of the Cr/Sc multilayer depicted in Fig. 9.

The sharpness of transitions between chromium and scandium layers and vice versa is remarkably good. However, even with a base pressure in the lower 10^{-10} mbar range, scandium is binding remarkable amounts of oxygen resulting in the preferred deposition of ScO_x rather than metallic scandium. The affinity of Sc towards oxygen is so high that in fact the oxygen partial pressure is decrease considerably upon ablation, ablated scandium acts as a getter pump. This must be considered a general problem (not restricted to PLD alone) encountered upon the deposition of Cr/Sc multilayers that are challenging candidates for multilayer mirrors in the so called water-window X-ray range [7].

Since in the present study, single-element thin films were deposited, stoichiometry preservation and the impact of any of the three particulate filtering strategies on the thin-film stoichiometry can hardly be assessed. Preliminary secondary ion-mass spectrometry data of thin films deposited from a Ca-rich SiAlON target, however, indicate that at least magnetic filtering in combination with scattering at an inert background gas does not significantly change the stoichiometry. This finding is believed to be caused by the fact that the majority of laser-ablated ions, more or less independent on the atomic number, is positively changed and hence elements with commonly strongly different oxidation states are not becoming spatially separated by the action of the magnetic field onto opposing charges. Similar findings are expected to apply for electrostatic filtering while particulate-mitigation by bare scattering at a background gas is more likely to reflect atomic-number dependencies of the scattering cross sections and hence deviation from genuine stoichiometry.

4. Conclusions

It must be summarized that the net deposition rates attainable by the three particulate filtering techniques studied here are too small for qualifying PfsLD as a widely usable, versatile deposition technique or even industrial application. With the relatively low ablation rates of femtosecond lasers, and relatively ineffective particulate-mitigation strategies, PfsLD is likely to remain an exotic thin-film deposition technique. However, future particulate filtering in PfsLD might use techniques developed for filtering arc plasmas [8], or other approaches based on an assist laser [2] to increase the ionization and improve the throughput.

Pulsed *picosecond* laser deposition may prove a valuable alternative to femtosecond systems since the much higher repetition rate and output power of currently available ps lasers can contribute to significantly increased deposition rates enabling the synthesis of well-defined ultrathin layers even with the three filtering techniques discussed in this paper. Due to slightly different mechanisms of picosecond laser radiation with matter (most likely also leading to higher ionization within the ablation plasma), picosecond laser pulses might prove better suited for pulsed ultrashort laser deposition than femtosecond laser pulses.

With the increased output power of future femtosecond lasers (several ten Watts will be available soon), it would be interesting to study PfsLD at wavelengths in the UV range. Whether a mere increase of the femtosecond laser pulse energy (for wavelengths in the visible or near infrared) would help to increase the thin-film growth rate is not clear since higher pulse energies might reduce the degree of ionization of the plasma and counterbalance the increased ablation volume. Independent of such future developments, all three filtering principles discussed here should prove beneficial for short-pulse (ns) excimer laser deposition as well.

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