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Particulates-free Ta thin films obtained by pulsed laser deposition: the role of a second laser in the laser-induced plasma heating

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Abstract

The presence of various types of particulates on the surface of the thin films deposited by pulsed laser deposition (PLD) is a strong limitation in key technological applications of this method. We investigated the morphology of the Ta thin films obtained by a two laser system technique. The first UV laser was used for the target ablation, and the second IR laser, propagating parallel with the target surface, intercepted the particulates present in the ablation plasma. We chose the second laser wavelength in IR because of its much higher absorption by plasma and liquid particles. The particulates density on the surface of the films was studied as a function of the time delay between the UV and IR laser pulses. Depending on the ablating laser experimental parameters, we succeeded to obtain a delay time regime 10–300 μs for which completely particulates-free films were deposited. For these delay values, the second laser intercepted the slow component of the ablation plasma consisting on micrometer sized particulates with propagation velocity within the range of 10^3 to 10^4 cm/s.

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Keywords: Pulsed laser ablation; Thin films; Second laser irradiation; Particulates

1. Introduction

Pulsed laser deposition (PLD) of thin films has been described as a three-step process: (i) interaction of the laser radiation with the target; (ii) transport of the ablated material from the target to the collector; and (iii) its subsequent deposition onto the collector surface [1–4]. The main advantages of PLD include the high reproducibility, the control of the film thickness and stoichiometry, the high deposition rate, the purity of the deposited film, the possibility to use different substrate materials and the low substrate temperature. Nevertheless, the limitation of PLD is related to the presence of various types of particulates both on the surface of the films as well as in their bulk. These micrometer and submicrometer sized particulates can be droplets, expelled in liquid phase from the target surface, or irregular shaped solid target material fragments. They represent the most important shortcoming for the application of the synthesised thin films in technological fields, since in high performance electronic, optical and optoelectronic devices particulates-free films are required.

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The origin of these particulates was associated with different physical mechanisms that are initiated during the laser radiation-target material interaction [1–6], such as: (i) explosive dislocation of the substance caused by the subsurface overboiling of the target; (ii) gas phase condensation (clustering) of the evaporated material; (iii) liquid phase expulsion, under the action of the recoil pressure of the ablated substance (vapour and plasma); (iv) blast-wave explosion at the liquid (melt)–solid interface; and/or (v) hydrodynamic instabilities developing across the liquid target's surface.

The study and complete understanding of these formation mechanisms is a mandatory step in reducing the particulates density, aiming to their complete elimination. Accordingly, many attempts have been conducted to decrease the density of the particulates [7–11]. We mention among them the following ones: employing smooth target surface and uniform target ablation, combined rotation and scanning of the target with respect to the laser beam, optimisation of the separation distance between the target and the substrate surface, variation of the substrate orientation with respect to the direction of the plasma-plume expansion, use of shadow masks, introduction of electromagnetic shutters, fragmentation of particulates by means of an additional laser beam propagating parallel to the substrate surface, or dual-laser beam ablation from a single target. We stress however that the deposition of completely particulates-free thin films was to our knowledge not yet reported.

In previous studies, we investigated the formation mechanisms of particulates, present on the surface or embedded into the bulk of SiC, TiC, TiN, and C_xW thin films, as well as their structure and composition [12–17]. In the present work, we report new scanning electron microscopy (SEM) studies performed on Ta thin films, obtained by UV laser irradiation of Ta targets. The ablation plume was irradiated with a second, pulsed IR laser, propagating parallel with the target surface. The IR laser pulses were sent with different controlled time delays after the ablating UV laser pulses. We expected that the IR laser pulses fragment and evaporate the conglomerates that are emitted from the target surface and therefore are responsible for the presence of particulates on the surface or inside the deposited films. The variation of particulates density on the films surface was studied as a function of the time delay between the two laser pulses.

2. Experimental

The experimental set-up is presented schematically in Fig. 1. The irradiations were performed in a stainless steel vacuum chamber. Before each deposition the chamber was evacuated down to a residual pressure of 7×10^{-4} Pa. Two different laser systems were employed. For the ablation of the Ta target material we used the pulses generated by a Lumonics excimer laser, operated either with KrF^* ($\lambda = 248$ nm, $\tau_{FWHM} \sim 12$ ns), or with ArF^* gas mixture ($\lambda = 193$ nm, $\tau_{FWHM} \sim 10$ ns) at a repetition rate of 10 Hz. The laser beam incidence angle onto the target surface was approximately 45°.

The KrF^* laser beam was focused by a quartz lens placed at 45 cm in front of the Ta target and just outside the entrance window. The laser fluence at the target position had a value of 3.3 J/cm^2 for a first set of samples. The targets were submitted to the action of 12000 laser pulses.

The ArF^* pulse energy was two times lower than that of the KrF^* laser. Therefore, a focusing quartz lens with 10 cm focal length was placed inside the vacuum chamber. For a second set of samples deposited by this wavelength, the laser fluence was set at 3 and 11 J/cm^2. This was obtained changing the laser pulse energy while maintaining the same focusing conditions. Moreover, the number of laser pulses incident on the target for the deposition of one film was increased to 23300 for this set of samples.

The second, IR beam was generated by a controllable, time delayed Quantel Nd:YAG ($\lambda = 1.064$ μm, $\tau_{FWHM} \sim 10$ ns) laser, propagating parallel to the target surface. It was crossing the flux of the ablated substance at a distance of 2 mm above the focus of the first ablating laser beam. The IR laser pulse energy values were chosen in the range 190–230 mJ. An FL 10 cm cylindrical lens vertical on the axis of the emitted Ta plume focused the IR laser beam. The estimated fluence was in the range 3.8–4.6 J/cm^2. The time delay between the two UV and IR laser pulses could be changed continuously in a broad range (0–1500 μs).

The controlled delay between the UV and IR laser pulses was set with a stable and high precision digital

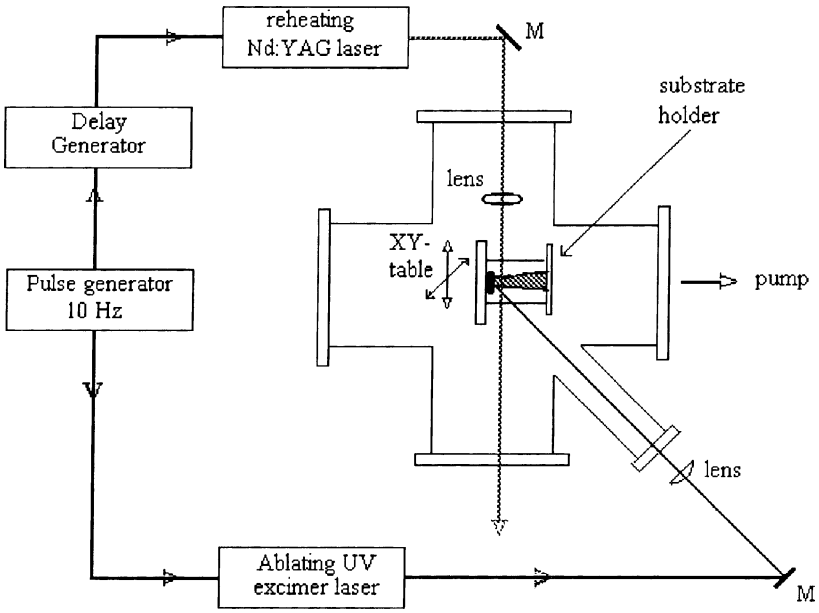

Fig. 1. Experimental set-up.

delay generator (EG&G Mo. DDG 9650). The two laser pulses were recorded by a fast photodiode (rise time <1 ns) and monitored on a 350 MHz Tektronix oscilloscope. On the other side, the time jitter between the laser trigger and light pulses generated by the two laser systems was of a few nanoseconds. By this method, the delay time range of interest in our experiments, from 10 μs to 1 ms, could be determined with a relative accuracy of 5×10^{-2} to 5×10^{-4}. We emphasize that no long term drift was observed during the deposition time.

Each set of samples above consisted of a reference sample, that is of a film deposited by the UV laser without the presence of the IR laser beam and a number of samples obtained with both laser beams with different time delays between them. Then the morphology of the samples obtained with both laser beams were compared with that of the corresponding reference within each set.

The ablated substance was collected onto the surface of glass slides placed plan-parallel with the target surface. The distance between the target and collector was 35 mm. During the depositions, the collectors were kept at room temperature. To avoid fast drilling, the targets were mounted on a vacuum-compatible XY translator that was computer controlled and performed a meander-like movement, both vertically and horizontally. This resulted to a scanned surface of a 10 mm × 10 mm square on the target. The movement was selected such that every target point was irradiated by five laser shots before the translator moved to the next point 0.5 mm apart. The substrate holder was also connected to the XY translator, performing a similar movement as the target. We notice that the deposited films exhibit large thickness uniformity.

The morphology of the deposited films was investigated by scanning electron microscopy (SEM) with a Cambridge S120 and JEOL TEM Scan 200 CX instrument.

3. Results and discussion

In order to delimit the role of the various deposition parameters, all samples in each particular set were prepared under identical conditions, with a given UV–IR laser beams configuration, and the same fluence, focusing conditions as well as number of applied laser pulses. We only modified, under a high accuracy control, the delay time between the UV and IR laser pulses. Furthermore, we did not attempt to compare the morphology of films deposited with the KrF^* or

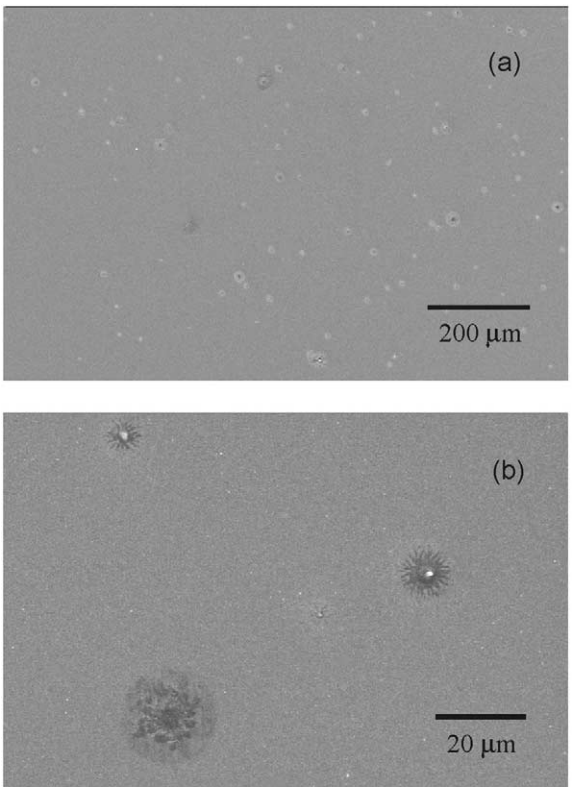

Fig. 2. (a) SEM image of a thin film deposited by KrF^* laser irradiation with a fluence of 3.3 J/cm^2; and (b) SEM image at higher magnification of the same thin film.

ArF^* lasers used for ablation because of the different target absorbtivities at the two laser wavelengths.

Fig. 2 shows the SEM image of a Ta film deposited by the multipulse irradiation of the Ta target with the aid of the KrF^* laser source. In order to have a first view of the surface morphology, this sample was deposited with the UV KrF^* laser only (reference sample) at a fluence of 3.3 J/cm^2. We observe particulates with a density of approximately 10^4 cm^{-2} (Fig. 2a). At higher (10-fold) magnification, structural modifications of the film surface become visible in the close vicinity of the particulates (Fig. 2b). These modifications are due to a slow crystallisation process, most probably induced by the energetic particulates incident onto the film surface during deposition.

In the first set of depositions performed with the two (UV) KrF^* and (IR) Nd:YAG laser system, the UV laser fluence was kept at a value of 3.3 J/cm^2. For the second, IR laser pulses, different delay times in respect to the ablating UV pulses were selected within the range 0–1500 μs. At 1000 μs delay time, a significant decrease of the particulates density to about 4×10^3 cm^{-2} was observed (Fig. 3a), as compared to the reference sample (Fig. 2).

Reducing the time delay between the two laser sources led to a further gradual decrease of the particulates density, until 10^2 cm^{-2} at 230 μs (Fig. 3b). However, the most interesting and rather unexpected result which validates the hypothesis of this work is that completely particulates-free thin films were deposited with time delays between the UV and IR laser pulses of 100 μs (Fig. 3c), or 10 μs (Fig. 3d).

Similar observations were made for the second set of samples, when the irradiations were performed with the ArF^* laser source at a laser fluence of 11 J/cm^2. The optimum delay time between the UV and IR laser pulses was found to be 300 μs (Fig. 4a). In this case, we observed the complete elimination of the particulates. The decrease of the delay time to 210 μs (Fig. 4b) and 100 μs (Fig. 4c) resulted in the appearance of micrometer and sub-micrometer sized particulates on the obtained films surface. We compared two reference samples obtained only under the action of the ArF^* laser pulses, but at two different laser fluences, 3 and 11 J/cm^2 (Fig. 5), by changing the pulse energy while keeping all geometric parameters constant. In the case of the higher laser fluence we observed more, and larger particulates, a fact which is indicative, to our opinion for higher laser plasma recoil pressure for the higher fluence depositions.

Recently, Hopp et al. [18] reported the suitability of multipulse ArF^* 193 nm excimer laser irradiation for the destruction of solid particulates by heating and evaporation. The number of particulates decreased after laser irradiation and the efficiency of their breaking depended on the laser fluence. In PLD, it was previously proved by light emission observations [19], or by spatial separation using rotating target holders [20] that the particles in the ablated material can be classified in respect to their propagation velocity. The fast components, with a velocity of about 10^5 to 10^6 cm/s consist of radiative particles, whereas the slower components with velocities of about 10^3 to 10^4 cm/s include larger, micrometer sized particulates. It was shown that these large particulates affect the quality of the deposited thin films. The role of a second UV 266 and 248 nm laser, directed perpendicularly on

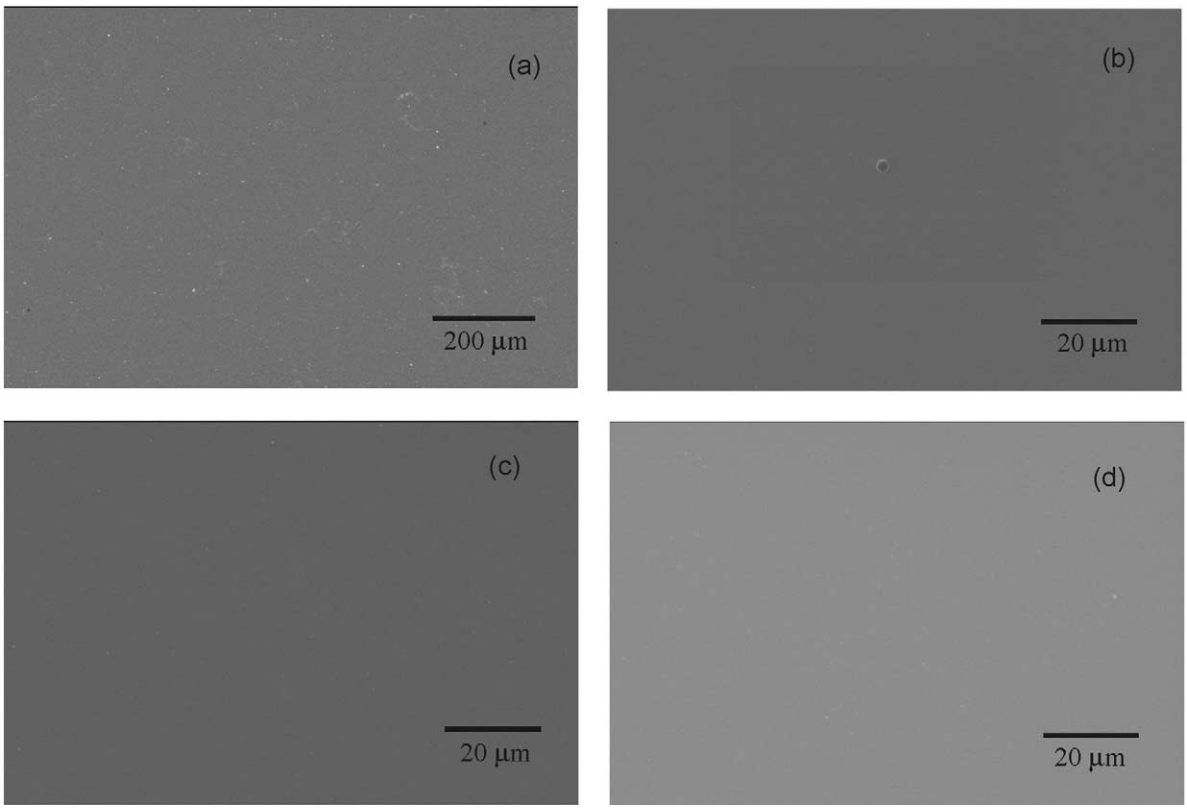

Fig. 3. SEM image of a thin film deposited by KrF^* laser irradiation with a fluence of 3.3 J/cm^2. The time delay of the IR laser pulses from the UV pulses was (a) 1000 μs, (b) 230 μs, (c) 100 μs, and (d) 10 μs.

the ablation plume, was investigated first by Chiba et al. [19], as well as Koren et al. [21], respectively. In [19] the laser irradiation of the fast components did not caused significant changes in the studied electrical characteristics of the films. Improvement of films surface morphology was observed, when the slower, about 10^5 cm/s velocity particulates were irradiated with the second UV laser. The absorption of the laser radiation by the ablated particulates resulted in their fragmentation. However, the complete elimination of the particulates in the experimental conditions studied in [19] was not fully demonstrated. Similarly, only a reduction of particulates density on the deposited films surface was reported in [21] which was the most probably the effect of the application of a fixed delay of 1 μs between the IR ablating and the UV reheating lasers. This resulted to the evaporation of a very narrow velocity class of particulates ejected from the target.

In our experimental conditions, the second IR laser pulses were delayed in respect with the ablating UV laser pulses with an optimum time delay in the range 10–300 μs. We succeeded in this way to intercept the last parts of the ablated material that have propagation velocities in the range 10^3 to 10^4 cm/s. These last parts of the ablated material consist, as it is known, of large micrometer sized non-radiative particulates, expulsed from the target surface in liquid, or solid phase. The films surface morphology was considerably improved by laser heating and breaking during their transit from the target toward the collector surface.

The main absorption mechanisms in laser-generated plasmas are inverse bremsstrahlung and single- and multi-photon ionisation. The absorption coefficient for inverse bremsstrahlung is proportional to $n_e n_i \lambda^2$, where n_e and n_i are the electron and ion densities, and λ is the laser wavelength. Since this absorption process is largely enhanced for IR radiation, we used an IR

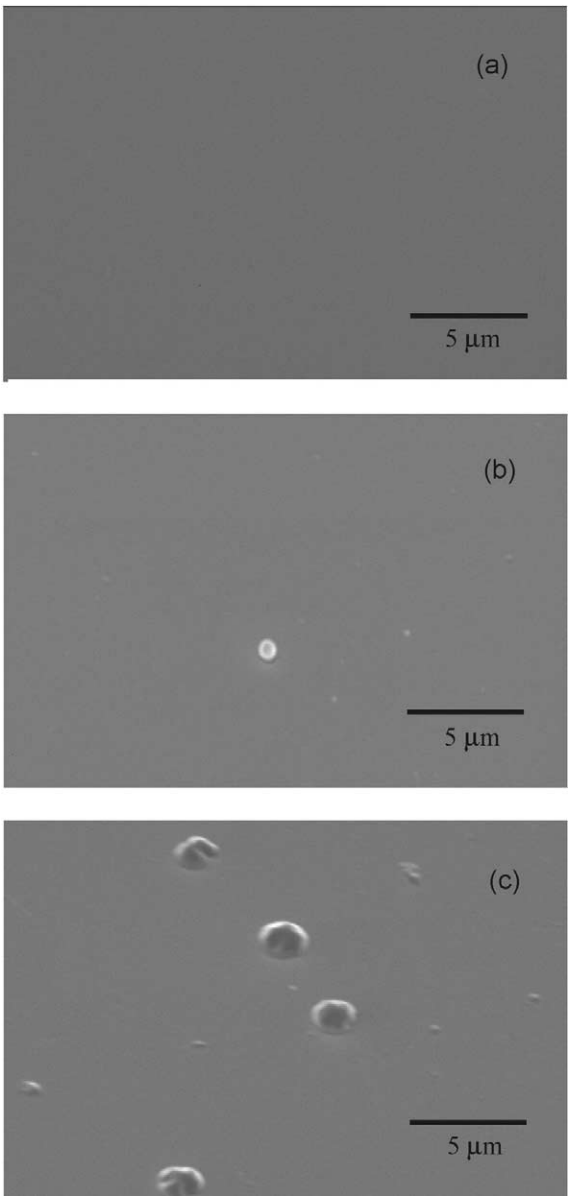

Fig. 4. SEM image of a thin film deposited by ArF* laser irradiation with a fluence of 11 J/cm^2. The time delay of the IR laser pulses from the UV pulses was (a) 300 μs, (b) 210 μs, and (c) 100 μs.

Nd:YAG ($\lambda = 1.064$ μm) laser to heat the plume and break the ablated particulates into smaller species. On the other hand, we note that the IR radiation is very efficiently absorbed in liquid and solid phases [22,23]. This way the particulates, in liquid or solid phase, are heated and evaporated. Consequently, we obtained an

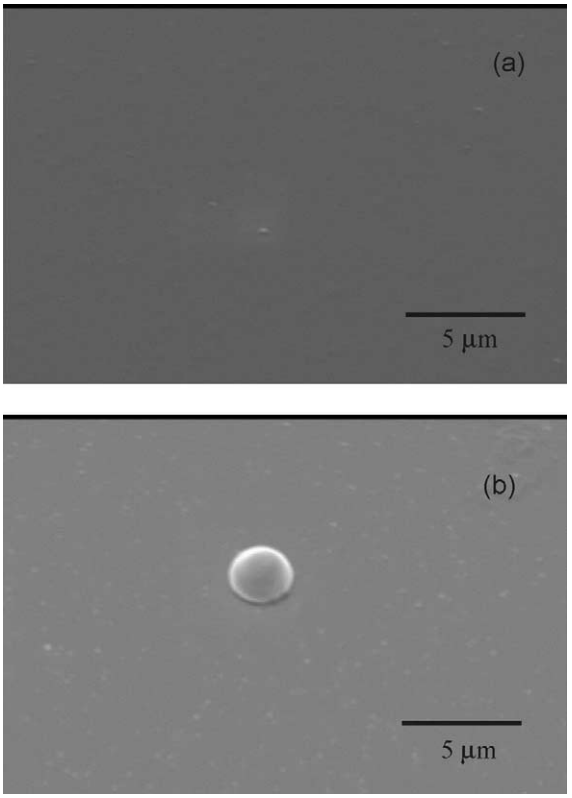

Fig. 5. SEM image of a thin film deposited by ArF* laser irradiation with (a) 3 J/cm^2, and (b) 11 J/cm^2 laser fluence.

essential improvement of films surface morphology by laser irradiation of the tail of the ablated material that consists on large molecular fragments and micrometer sized particulates.

4. Conclusions

We observed particulates on the surface of the Ta thin films obtained by UV pulsed laser ablation with dimensions in the micrometer and sub-micrometer range and having a density of about 10^4 cm^{-2}. These particulates modify locally the films surface morphology, probably by inducing a slow crystallisation process. In order to reduce the particulates density in PLD/RPLD, we used two synchronised laser systems for deposition of the thin films: the first UV laser was used to ablate the target material, while the second IR laser to reheat and evaporate the particulates by

intercepting the laser-generated plasma. By choosing a proper value for the time delay between the two laser pulses, we succeeded to find the suitable experimental conditions, for which particulates-free films were obtained. This confirms the basic idea of this work. The process optimisation proved to depend on the wavelength and fluence of the UV laser pulses applied for the ablation of the target material. Moreover, we observed that the ability to select the delay time between the two lasers in a broad range of delay values allows us to find the appropriate experimental conditions for any target material–laser system.

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