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Detailed studies of aluminum thin films morphology deposited by pulsed laser ablation

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ABSTRACT

In the present paper we report the investigations by scanning electron microscopy of Al thin films prepared by pulsed laser ablation deposition experiments in vacuum. Laser parametric studies show that the poor thickness uniformity of Al films arises from surface roughening and structure formation on the irradiated Al target surface. Moreover, it has been confirmed that the plume deflection effect, the morphological changes of the irradiated target surfaces and of the deposited films strongly depend on the laser fluence (4.6–14.7 J/cm^2). At low laser fluence, plume deflection angles up to 12° and columnar structures on the target surface have been observed. The variation in the target morphology and in the droplets density of the deposited films can be associated with competitive ablation processes related to different values of local incident laser fluence.

Systematic profilometric investigations of the deposited Al films revealed a strong asymmetry during the deposition process. These results confirm once again our previous achievements obtained with Si laser ablation experiments.

1. Introduction

Pulsed laser ablation deposition (PLAD) has become a competitive deposition technique to grow thin film of any material [1]. Nevertheless, in spite to its many advantages, the presence of particulate on the film surface and the inhomogeneities in the film thickness prevent PLAD from emerging as technology for the deposition of high quality thin films. The poor thickness homogeneity of the deposited coatings has been reported by several authors for different materials [2–5]. This shortcoming is due mainly to the well known and extensively studied "plume deflection effect" [6–9]. Our previous investigations on laser ablation deposition of Si [10] and present studies on Al have showed that, contrary to expectations, a considerable deposition rate is achieved along the incident laser beam direction (45°, as in the typical PLAD experiments). The morphological investigations by scanning electron microscopy (SEM) show high concentration of droplets along the direction of the incident laser beam (45°). Furthermore, profilometric analyses reveal that measured thickness profiles as a function of the angle with respect to the target normal are characterized by two different distributions peaked respectively at about 0° (i.e., normal to the target surface) and about 45° (i.e., direction of the laser beam). These results can be explained by the changes of morphology and topography observed on the irradiated target surfaces at different laser fluences.

2. Experiments

Our PLAD experiments were carried out in high vacuum stainless-steel system (reported elsewhere) pumped to a base pressure of 10^{-5} Pa by a turbomolecular pump [11]. The used laser source was an UV XeCl excimer laser (Lambda-Physik, LPX 315i, $\lambda = 308$ nm, $\tau = 30$ ns, repetition rate of 10 Hz). The laser beam was focused with an incident angle of about 45° on high purity Al targets by an MgF_2 lens having 30 cm focal length. Series of 15,000 pulses (550 pulses/site) were directed at the Al target surface. Target was rotated with frequency of 3 Hz to avoid drilling and to obtain irradiation conditions as uniform as possible. The plume expansion and the deposition rate of the ablated material were studied by a special deposition configuration. In this non-conventional geometrical configuration, a sequence of 1 cm × 1 cm silicon substrates was arranged around the laser spot onto a hemi-cylindrical holder at a distance of 4 cm from −25° to 85° with respect to the target normal (Fig. 1). In order to measure the thickness value of the deposited films, silver paste droplets were placed on the surface of each Si substrate in three points along a horizontal line. After the deposition, the silver paste was removed by ultrasonic bath in acetone and a profilometer (Tencor Alphastep) was used to measure the

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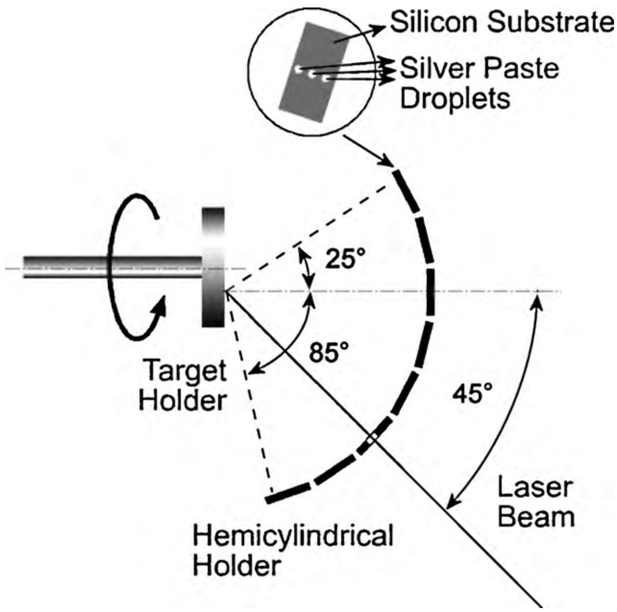

Fig. 1. Schematic of the hemi-cylindrical geometrical configuration.

thickness of films scanning through these areas. Thickness value for each position was obtained as the average value of four measurements performed scanning with the profilometer tip from the silicon substrate towards the Al film along four different directions as shown schematically in Fig. 2.

The morphology of deposited films and target surfaces was studied by a scanning electron microscope (mod. JEOL-JSM-6480LV).

3. Results

The average thickness values of the deposited films versus the angle to the target normal at various fluences are depicted in Fig. 2. For all graphs it is noted that deposition rate distributions are peaked not only along the target surface normal but also along the incident laser beam direction. The common characteristic of thickness profiles is thus the presence of double-peak mass distribution: one peak in the incident laser beam direction and another peak in the normal direction of the target surface. This trend is observed to be the same at all the laser fluences used in the present study (4.6–14.7 J/cm^2).

The best fit reported in Fig. 2 is easily achieved by using a $\cos^p(\theta)$ distribution centered around the normal to target surface and with a lorentian distribution centered at about 45°. It is also interesting to note that as in our experiment with Si, the peaks of the $\cos^p(\theta)$ distribution around 0° move from positive towards negative angle as the laser fluence increases as reported in Fig. 3. This figure also reports the maximum plume deflection angle measured for different used laser fluences. It is evident that the trend of the two datasets is similar as shown in Fig. 3.

In order to characterize qualitatively the coatings, the surface of the Al films deposited at different angles (−25° to 85°) and at seven different laser fluences (4.6–14.7 J/cm^2) was analyzed by SEM. Images of the films surface, reported in Fig. 4, clearly show that droplets and fragments distribution is peaked along the direction of the incident laser beam with a density distribution of droplets and fragments depending with the laser fluence. Starting from the lowest fluence used (4.6 J/cm^2), the droplets and fragments appear to cover the film at any angle reaching a maximum both in density and size at the laser fluence value of 7.2 J/cm^2. Starting from the fluence value of 8.5 J/cm^2, droplets distribution appears to become narrower with respect to previous cases and the particulate density looks to present a local minimum for a laser energy density of 10.6 J/cm^2. Intensifying the energy density of the laser beam and reaching the values of 12.5 and 14.7 J/cm^2, droplets and fragments density increases again covering the film surface around all directions.

SEM images of the irradiated targets are reported in Fig. 5. At low and medium laser fluences, the formation of columnar structures can be observed, which grew aligned with the laser incoming direction. Similar morphological structures were observed also in case of laser ablation of Si target [12,13]. At the highest fluences, the morphology of the irradiated area drastically changes appearing flat, except for the presence of a crater-like structure near the external border of the laser generated track.

4. Discussion

Some of the peculiar aspects of the ablation of Al target, as the plume deflection and existence of a second component, have been also observed with other materials [14]. However, these new experimental results give us the opportunity to draw a more detailed scenario of the different phenomena involved during the ablation when different energy densities are used. It is evident that the results here reported for Al and also those reported for Si in our previous experiments [10] reflect the existence and competition of different phenomena during the laser ablation. The aspects that we wish to discuss here are mainly related to the results obtained in the thickness profiles and surface morphology of the deposited films and to their relationship with the laser fluence. The origin of the plume deflection effect has been linked in our earlier studies to the target surface topography modification induced by laser irradiation [6].

The qualitative interpretation that we give of these new experimental observations is based on the assumption that the ablation process with nanosecond laser pulses can be described by the heat diffusion mechanism: the heating of the areas exposed to the laser beam leads to a vaporization of the layers near the surface, to the melting of the intermediate layers and to the heating of the deepest layers of the bulk target. When asperities are present over the irradiated area, each local surface experiences different energy densities depending on the local angle of the incidence radiation. Such local energy density may reach 1.4 times the nominal laser fluence, for a nominal laser angle of incidence equal to 45°. Due to the deflection process of the luminous plume, the thickness profile was expected to present a maximum shifted along the maximum deflection angle. As the maximum deflection angle reaches, for the fluences used in our experiments, values less than 12° (see Fig. 3), we expected to find the maximum thickness value between 0° and 12°. Contrary to expectation and confirming again our previous finding on PLAD experiments on Si, we found that another peak on the thickness profile is located at about 45°, i.e. along the direction of the incoming laser beam. The deconvolution of the thickness profiles revealed that in effect the superposition of two different distributions easily fit the experimental data. It is interesting to note that while one of these distributions has always its maximum at about 45°, the $\cos^p(\theta)$ distribution has its center that shifted from approximately 9° for the lowest laser fluence towards the −7° for the highest laser fluence (Fig. 3). After further and deepest SEM investigations (Fig. 4) we realized that the maximum thickness at about 45° is due to the strong emission of fragments and liquid droplets that we believe to be related to the phase-explosion mechanism that has been described elsewhere [10,15].

As the laser fluence exceeds the ablation threshold level (that we found to be around 4.0 J/cm^2 for Al and our XeCl* excimer laser), a decrease of the maximum plume deflection angle is accompanied with a strong increase of the ablation yield (here not reported

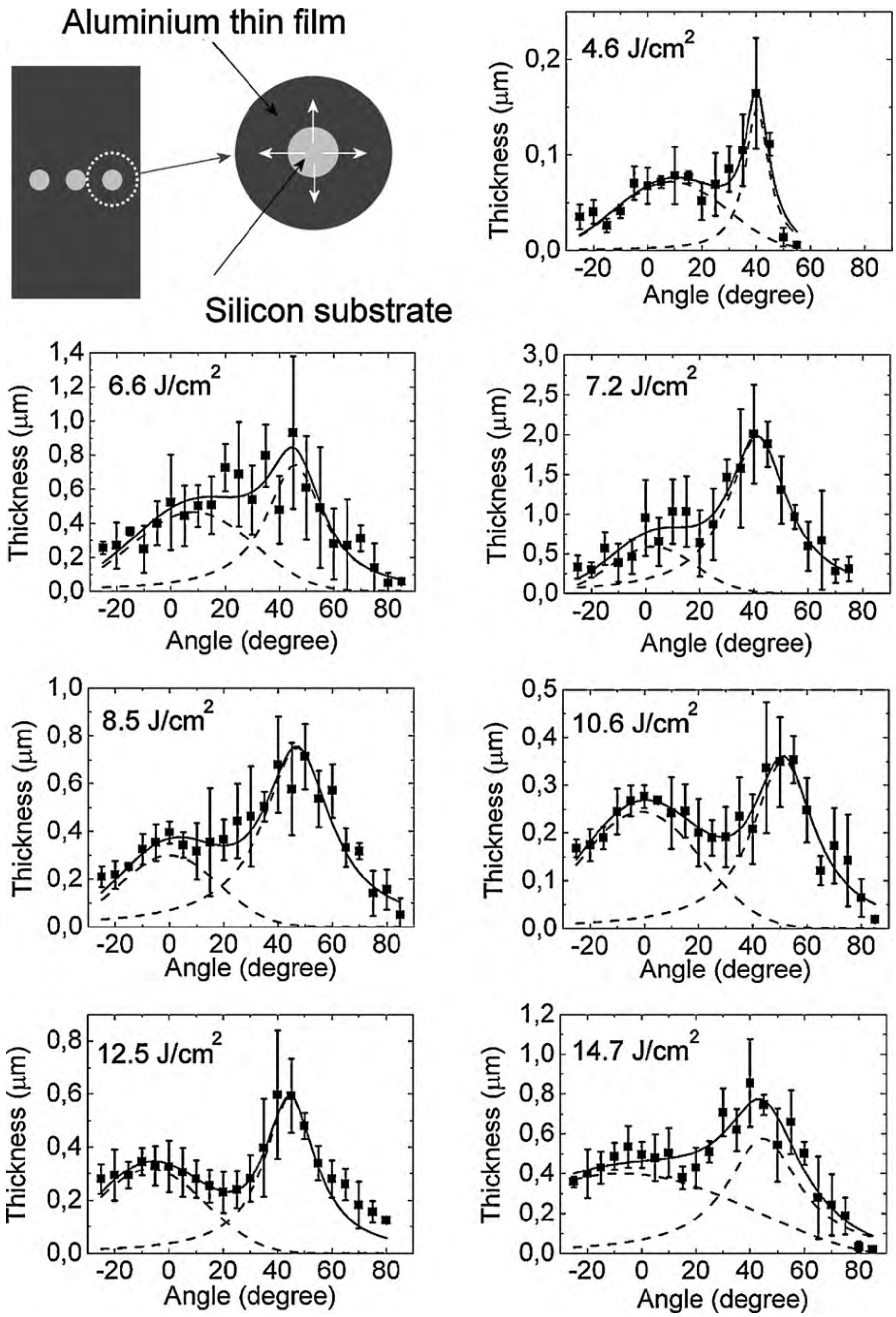

Fig. 2. Thickness profiles of the films deposited at different laser fluences.

for sake of brevity) that reaches a maximum at 7.2 J/cm^2. The target surfaces irradiated with fluences that range between 4.6 and 7.2 J/cm^2 present the growth of columnar structures on the irradiated areas (Fig. 5). These structures on the irradiated surfaces are at the origin of strong plume deflection effect that originate the shift of the center of the $\cos^p(\theta)$ thickness distribution shown in Fig. 3.

When the laser fluence overcomes the 7.2 J/cm^2 value, the columnar structures on the target surface disappear (Fig. 5) and the plume deflection effect becomes negligible. The vanishing of the plume deflection effect outcome as consequence that the center of the $\cos^p(\theta)$ distribution moves closer and closer to the target normal. Is not yet clear why for the highest fluence levels (12.5 and 14.7 J/cm^2) the center of this distribution reaches negative angular value and we undertake to investigate in more detail the ablation with such high energy density. These strong morphological changes observed on the target surface and the noticeable decay on the ablation rate can be explained by taking in account the well known "plasma shielding" effect [16,17]. In laser ablation with laser pulses in nanosecond range, the initial plume formation and expansion typically occurs in a few nanoseconds, so also during the irradiation process. Ablated material may absorb a part of the laser beam radiation so that the whole energy of the laser pulse will not longer reach the target surface participating to the heating of the target surface. The presence of such effect extensively reported in literature justifies the drastic lowering of the ablation rate at the high nominal fluences used in our experiments. Intensifying laser irradiance, the temperature and the degree of ionization of the vapor increases, this leads to additional plasma absorption. The plasma progressively behaves like an optically thick medium and effectively shields the target surface from the trailing part of

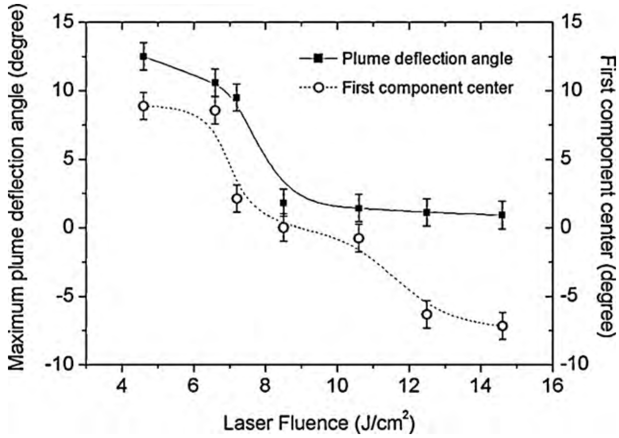

Fig. 3. Maximum plume deflection angle and first component center as a function of laser fluence.

the laser pulse. Most of the laser absorption occurs in a vapor layer confined close to the target surface. During this process, a self-regulating regime exists: absorption in the plasma will decrease the evaporation rate and then the density of the expanding plasma. The plasma is thus expected to transmit just enough laser radiation to the target surface in order to sustain itself. Under such conditions the excess of energy responsible for the phase explosive regime, that originates fragments and droplets, is limited by plasma absorption, and a decrease in droplets density is observed on the film surfaces.

This scenario may look to be in contrast with the SEM micrographs reported in Fig. 4. In fact, it can be easily observed that the droplet density at 45° and 0° with respect to the laser fluence reaches a local minimum for a value of 10.6 J/cm^2. A possible explanation can be found on the geometric arrangements used; however, additional experiments should be carried out to verify this hypothesis. When the laser beam impinges with an angle of incidence of approximately 45° as in our experimental conditions and assuming that the expansion of the plasma plume occurs mainly along the

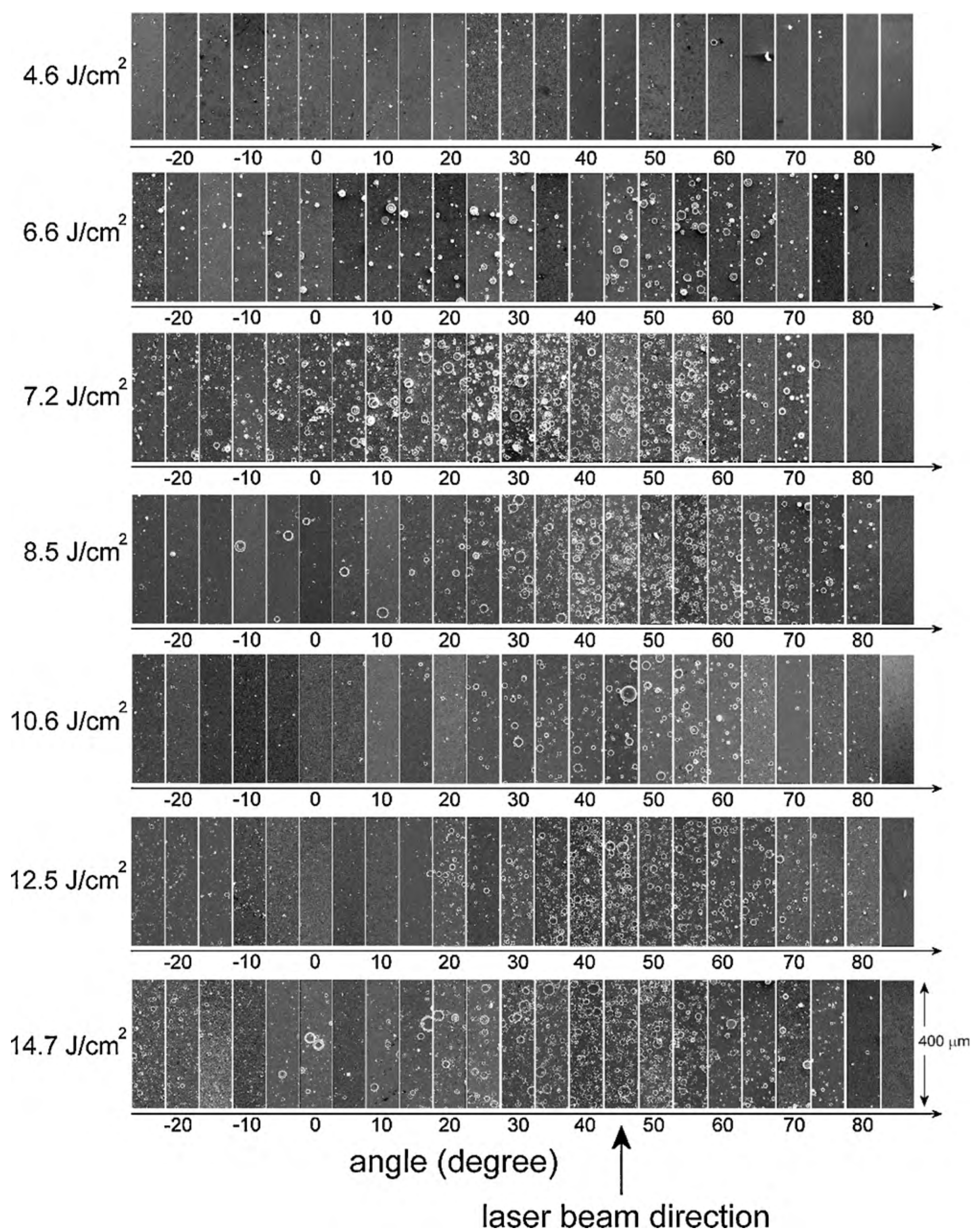

Fig. 4. SEM micrographs of the films deposited at different laser fluences (length of scale marker is 400 μm).

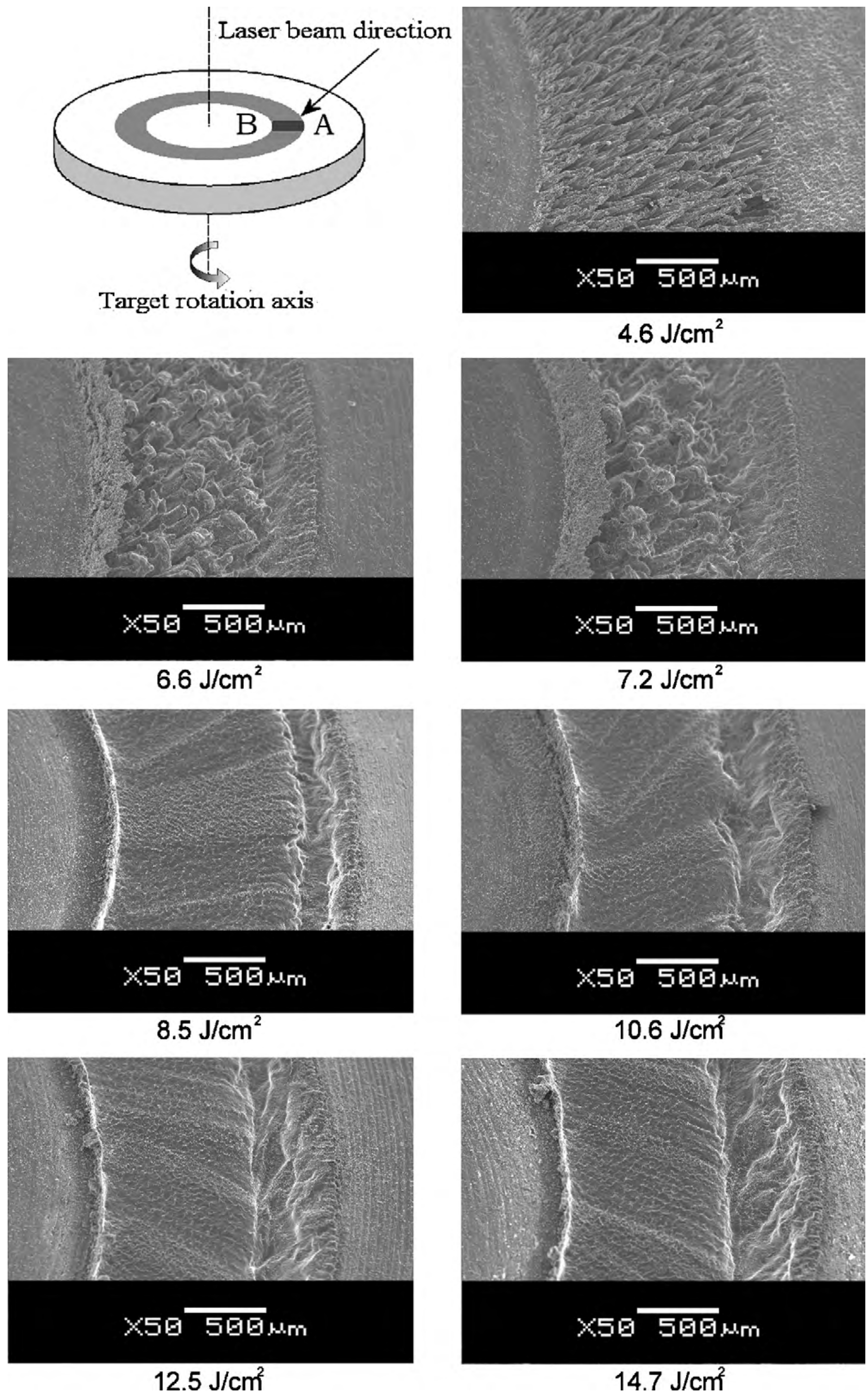

Fig. 5. SEM micrographs of the target surface irradiated with different laser fluences (length of scale marker is 500 µm).

normal direction it becomes evident that the shielding effect cannot be uniformly distributed inside the whole irradiated area. In fact, assuming that the plasma absorption coefficient is uniform inside the plasma plume, the fraction of the laser energy shielded from the plume is lower in the region that lies close to points A, while linearly increases towards the point B (see Fig. 5). This hypothesis looks to be reasonable because allows us to explain both the presence of a crater near the external part of the laser generated track on the target surface (see Fig. 5) and the growth of ablation rate and droplets density at the highest values of laser fluences used in our experiments. In fact, while in the internal region of the laser generated track droplets and fragments emission is limited by the low fluence level determined by the plasma absorption, in the external part, where the plasma absorption of the laser beam decreases, the ablation processes on local surfaces, if the energy density exceeds the threshold, becomes explosive. From these surfaces droplets and fragments emission becomes favorable with respect to that of monomers, and, as droplets and fragments have no emission in the visible spectral range, a decrease of the plume deflection effect and a strong increase of the ablation rate are detected at the same time.

5. Conclusions

In summary, we have shown the presence of a mass-abundant plume component containing droplets and fragments (in agreement with the phase-explosion model) having the laser beam direction at fluences appropriated to PLAD experiments. Furthermore, we realized that the phase-explosion process occurs on all the irradiated areas when the local laser fluence overcomes the threshold value even if the nominal laser fluence does not. The angular-dependent morphology of the deposited films suggests that the plume expansion, in terms of highest droplets density, occurs mainly in the direction of the laser beam, giving rise to a strong asymmetry of the film thickness profiles. Therefore, the deposition rate measured in the direction of laser beam (45°) is always higher than that measured in the target normal direction (0°). These parametric studies together to those carried out with Si laser ablation suggest that good quality Al films can be obtained at relatively high laser fluence (10.6 J/cm^2) with respect to that of ablation threshold, that is when droplet density reaches a local minimum and at the same time the center of the first component on thickness distribution is very close to the 0° value.

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