Nanoparticle deposition during confined laser ablation

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Abstract

Confined laser ablation is used to form long lived dense plasma for single shot deposition of a metal nanoparticle film. Laser ablation of a silver target, using 1064 nm laser radiation at 1.5 J cm^{-2}, is performed in vacuum and the expansion of the plasma produced is restricted by placing a glass substrate over the target with a target-substrate distance of 50 μm. Time resolved optical emission spectroscopy shows that the confined plasma is sustained for longer than for free ablation. Electron microscopy revealed the presence of a silver nanoparticle layer deposited on the inside of the confining substrate. The nanoparticle layer formed by confined laser ablation is compared to films grown by conventional pulsed laser deposition (PLD). It is shown that a layer of nanoparticles, with similar surface coverage can be grown using a single shot in the confined geometry as opposed to the several thousand shots required for the PLD films.

Introduction

Laser ablation of solids is the removal of matter from a target under the action of a pulsed laser, this material can be deposited onto a substrate in a process known as PLD, which has been conducted in both vacuum and a gaseous background to produce metallic nanoparticle films [1, 2, 3].

In this paper we report on a new technique, known as confined laser ablation, whereby laser ablation is used for single shot synthesis of a nanoparticle film. In this technique, a transparent substrate is placed on top of the ablation target but separated by a gap of less than a mm [4] while conventional PLD the target-substrate distance is usually between 3-10 cm. The nanosecond laser pulse irradiates the ablation target through the substrate. Analogous to plume confinement in a background gas, the substrate will impede the plasma expansion and leads to plasma with very different characteristics and dynamics to other laser ablation based nanofabrication methods. Due to the confinement the plasma density decays at a much slower rate compared to a plasma which is allowed to expand freely.

Experimental and computational techniques

Spatially confined laser ablation of silver was carried out using a pulsed Nd:YAG laser operating at a wavelength of 1064 nm and pulse duration of 10 ns. The on target fluence was 1.5 Jcm^{-2}. A glass slide, transparent to the laser radiation, was placed 50 microns above the Ag target surface to spatially confine the ablation plasma. Ablation was carried out in vacuum at a pressure of 10^{-5} mbar. The ablation target setup was placed on a linear stage and moved after every shot. The ablation plasma was characterised using time and space resolved emission spectroscopy. An image ICCD camera with a gate time of 10 ns was coupled to 0.25 m asymmetrically configured Czerny Turner spectrograph. The spectral resolution was ~ 1 nm. Measured spectra were compared against spectra calculated using the collisional radiative spectral analysis code, PrismSPECT [5] to extract the plasma density and temperature. Deposited material was examined using electron microscopy and optical transmission spectroscopy.

Results and discussion

Fig. 1 shows the confined ((a), (b), (c)) and free ((e), (d), (f)) plasma emission for various times after the onset of plasma emission. It can be seen that a broad continuum exists in both cases early in time. The Continuum emission is primarily due to strongly Stark broadened bound-bound transitions of neutral Ag [4].

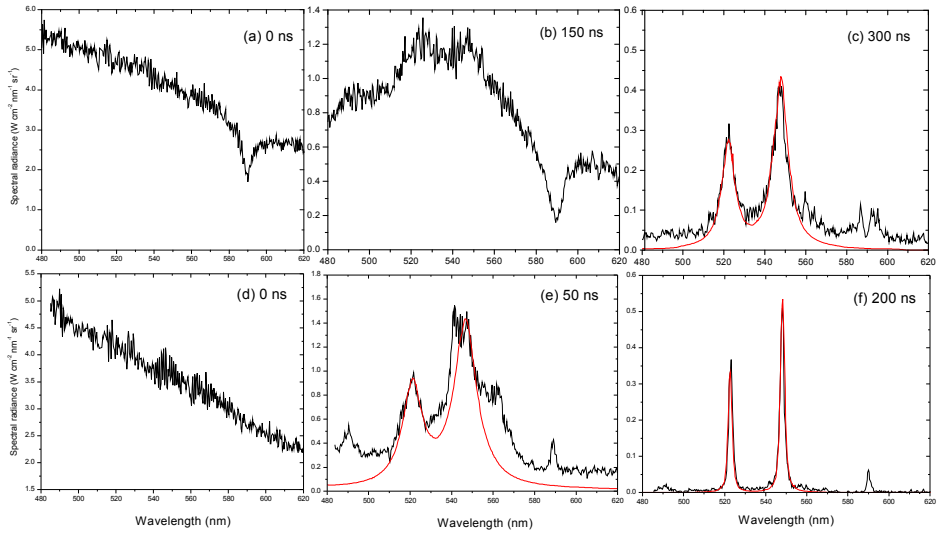

Figure 1 emission spectra at various delay times after the laser pulse; (a), (b) and (c) confined, (d), (e) and (f) free ablation.

In the free case, 50 ns after the beginning of the laser pulse, broadened spectral lines are evident and the spectral widths decrease with time indicating a drop in density. This is contrary to the confined ablation where the broadband emission is still present at 150 ns and only at ~ 250 ns two distinct, but broad, lines emerge. There is also a broad absorption feature centered at 589 nm which we could not attribute to any Ag transition. A previous study [4] indicates that during confined laser ablation modification of the interior surface of the confining substrate takes place. This leads us to believe the feature is due to the strong Na I 3s – 3p transition as Na is present in the confining glass substrate.

The spectra in fig. 1 have been fitted using the spectral code PrismSPECT [5] from which a plasma density and temperature can be found. For the confined plasma signal at 250 ns (not shown) the ion density and temperature used to fit the line shapes are $5x10^{18}$ cm^{-3} and 0.8 eV respectively. These values decrease to $3x10^{18}$ cm^{-3} and 0.75 eV for the spectrum at 300 ns. In contrast, the free ablation plasma density and temperature at 50 ns are $1.5x10^{18}$ cm^{-3} and 1.2 eV respectively. At 200 ns this has dropped to $5x10^{17}$ cm^{-3} and 0.65 eV. This shows that during confined ablation the density remains higher for longer. To estimate the initial density at the end of the laser pulse we can consider the following scenario. For ablation at a fluence of 1.5 Jcm^{-2} the ablation depth is ~ 10 nm. The solid density of Ag is ~ $5.9x10^{22}$ cm^{-3} and if we consider that 10 nm solid density Ag expands 1-dimensionally to occupy the 50 μm gap then this gives an approximate density of ~ 10^{19} cm^{-3}.

It is of interest to examine the material deposited on the confining substrate and compare with films deposited using conventional PLD. Figure 3 compares the deposition of a 1.4 nm film of silver with a target substrate distance of 9.5 cm, from a previous study [3] to the deposition using a single shot in the confined geometry.

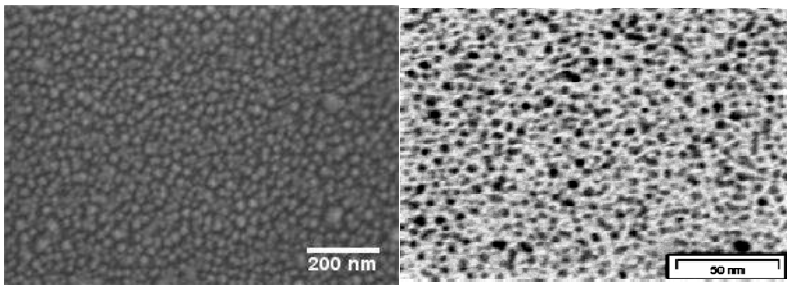

Figure 3 (a) SEM image of Ag nanoparticles deposited during confined laser ablation at 1 J cm^{-2} (b) TEM image of nanoparticles grown by PLD of Ag for 3000 shots at 1 J cm^{-2}[3].

From Fig. 3 (a) tightly packed nanoparticles of ≈ 25 nm in size are seen. The deposition is for one shot only so that the film equivalent thickness will be less than 4 nm which is the thickness of material ablated. It seems that in the confined geometry, single shot ablation is sufficient to deposit a nanoparticle layer with high surface coverage. Comparing this to unconfined PLD, several thousands of shots are required to produce a nanoparticle film of similar topography. The absorption spectrum of the confined ablation nanoparticles was measured and the surface plasmon resonance feature was observed at ~ 450nm indicating the presence of silver nanoparticles.

Conclusions

This paper presents a study on growing silver thin films by confined PLD. The presence of nanoparticles on the substrate was confirmed by both UV-Vis optical spectroscopy and electron microscopy measurements. Time and space resolved emission spectroscopy was used to characterise the plasma in this confined regime and compare it to a conventional laser produced plasma. It was found that the density decayed at a much slower rate in the confined case. There is a wide scope to use confined laser ablation for novel material synthesis as it represents a rapid nano - fabrication technique for any target material. There also exists the possibility to carry out confined laser ablation in a high pressure background gas to investigate formation of multi-component nanostructured materials.

Acknowledgements

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