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Pulsed laser ablation and deposition of niobium carbide

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ABSTRACT

NbC crystalline films have been deposited in vacuum by ultra-short pulsed laser deposition technique. The films have been characterized by transmission and scanning electron microscopies and by X-ray diffraction. To clarify the ablation–deposition mechanism, the plasma produced by the ablation process has been characterized by optical emission spectroscopy and fast imaging. A comparison of the results with those obtained by ns pulsed deposition of the same target has been carried out.

1. Introduction

The carbides of the group 5 are very important due to their high melting temperature and their enhanced hardness [1]. In particular, niobium monocarbide (NbC), in the form of thin film, is a promising material for tribological applications [2,3]. Many different techniques have been used to produce both NbC powders and coatings. The most important techniques for micro and nano powders production are high and low temperature chemical reactions which include direct combination of metallic niobium with carbon [4], self-propagating high-temperature reactions [5,6], reaction between niobium oxides and carbon [7], carburization of niobium in a H_2–CH_4 atmosphere [8], reaction of metallic Mg powders with NbO_5 and $MgCO_3$ [9]. High temperature reactions have also been used to produce NbC coatings by chemical vapor deposition technique, through carburization of the metal substrate or hydrogen reduction of niobium pentachloride in the presence of methane [10,11]. Other techniques used to obtain NbC films include thermo-reactive deposition/diffusion [3], reactive and non-reactive magnetron sputtering [12,13], and pulsed laser deposition (PLD). In particular, reactive-PLD has been used to produce NbC coatings by the ablation of metallic niobium in the presence of gaseous hydrocarbons [14–16] while conventional PLD, utilizing a NbC target in vacuum and the presence of a buffer gas, has been described by Duhalde et al. [17]. These last experiments have been carried out by ns laser pulses and no data have been reported about the composition and dynamics of the laser induced plasma, even if it is well known that its characteristics determine those of the deposited films. Moreover, no data at all are available in literature about PLD performed on NbC by ultra-short laser pulses. In this work, a NbC target has been ablated in vacuum by both a Nd:YAG laser with a pulse duration of 10 ns and a Nd:glass laser with a pulse duration of 250 fs. The plasmas produced by the laser–target interaction have been characterized by time and space resolved optical emission spectroscopy and ICCD fast imaging. The results obtained in the two different laser temporal regimes have been compared and related to the different laser–matter interaction mechanisms and to the characteristics of the thin films deposited on suitable substrates.

2. Experimental

The ablation and deposition experiments were performed by using an experimental apparatus already described [18]. It consists of a stainless steel vacuum chamber, evacuated to a pressure of 1.5×10^{-4} Pa, equipped with a rotating target support and with a heatable substrate holder. A Light Conversion frequency

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doubled Nd:glass laser ($\lambda = 527$ nm, $\tau = 250$ fs, 10 Hz repetition rate) and a Quanta System frequency doubled Nd:YAG laser ($\lambda = 532$ nm, $\tau = 10$ ns, 10 Hz repetition rate) were used as radiation sources for the ablation and deposition experiments. Both laser beams were incident at an angle of 45° on the target surface, while the laser fluences were 15.0 J cm^{-2} and 30.0 J cm^{-2} respectively. We used these fluences, the highest fluences available for both lasers, for obtaining the highest deposition rates of the material on the substrate. Anyway, we have verified that the characteristics of the deposited films and those of the laser-induced plasmas did not vary with the laser fluence in the range 3–15.0 J cm^{-2} for the fs laser source and 5–30.0 J cm^{-2} for the ns one. The ablation targets were crystalline NbC hot pressed powders (Goodfellow, 99.0%) and the deposition substrates were (1 0 0) oriented silicon sheets from Goodfellow. In transmission electron microscopy analyses, the deposition substrates were carbon–formvar films on copper grids. The distance between the target and the substrate was kept at 2.0 cm and the films were deposited at three different temperatures (25, 300 and 500 C°).

Optical emission spectroscopy (OES) was carried out by a Princeton ICCD device (1024 × 1024 pixels). The width of the entrance spectrograph slit was 80 μm while the gratings employed were of 1200 and 150 grooves/mm, for the acquisition of the spectra of the primary and secondary plumes respectively. The gated system had a time resolution of 2 ns and each acquisition was integrated on 50 laser shots in order to increase the signal to noise ratio. Varying the position of the optical elements by a micrometric translation stage, it has been possible to obtain space-resolved emission spectra. The same ICCD system equipped with 105/35 mm quartz Nikkor lenses was used for acquiring gated images of the lateral view of the plasma plume emission induced by a single laser pulse, in the 200–800 nm range. The spatial resolution was 25 μm and all acquisitions were carried out by accumulating up to 20 shots, thereby avoiding previously irradiated surfaces.

The morphology of the deposits was studied by scanning electron microscopy (SEM, Philips-FEI ESEM XL30), while their composition and crystallinity by X-ray diffraction (XRD, Siemens D-5000 with Cu Kα radiation). High resolution transmission electron microscopy (HR-TEM, Fei-TECNAI G2 20 TWIN) has been used to characterize the nanoparticles forming the films deposited by fs PLD. Even if non-defective NbC is Raman inactive, micro-Raman spectroscopy (HORIBA LabRam HR 800) has been used to evidence the possible presence of carbon phases in the films.

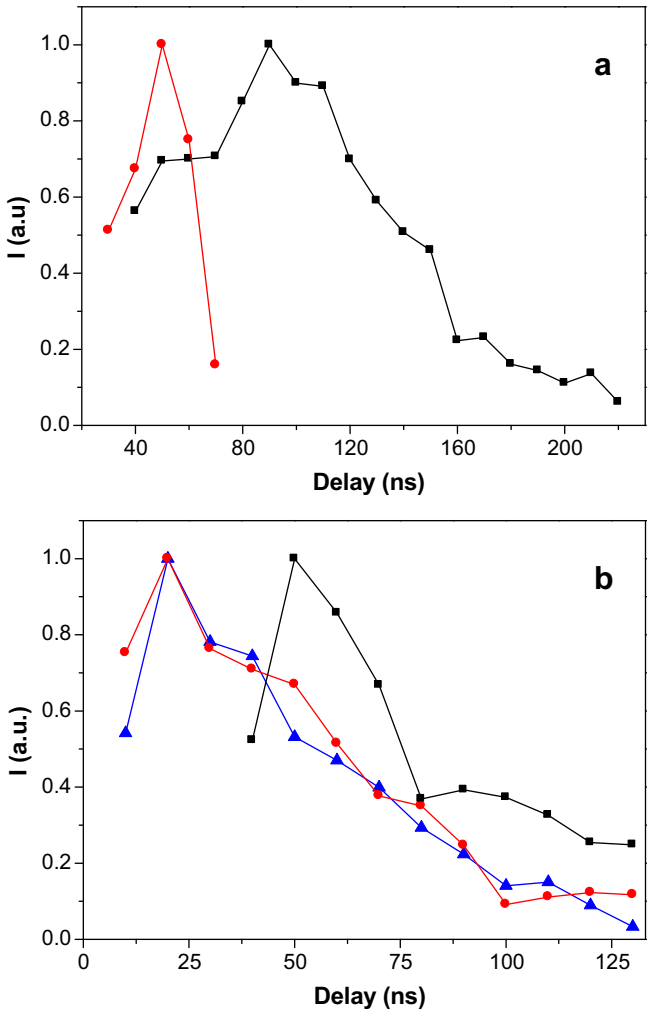

Fig. 1. Normalized time-resolved emission plots. (a) Emission from C II (426.7 nm) and Nb I (405.9 nm), recorded at 0.5 mm from the target, from the primary plume produced by fs ablation of NbC; (b) emission from C II, Nb II and Nb I, recorded at 0.5 mm from the target, from the plume produces by ns ablation of NbC; ■ Nb I, ● C II, ▲ Nb II. The laser fluences were 15.0 J cm^{-2} for fs ablation and 30.0 J cm^{-2} for ns ablation.

3. Results and discussion

3.1. Plasma characterization

ICCD Imaging of the plasma produced by fs ablation of NbC target evidence the presence of two different emissions of material, clearly separated in time, as already seen for many other systems ablated with ultra-short laser sources and firstly evidenced by Albert et al. [19,20]. The first emission of material (primary plume), staring after the end of the laser pulse, shows a temporal duration of about 600 ns. This plume was characterized by a front velocity of about 1.6×10^6 cm/s and an anisotropic angular distribution parameter $n = 4.4$. The n parameter is related to the plume angular distribution by the relation $I(\theta) = I_0 \cos^n \theta$, where $I(\theta)$ is the flux intensity along a direction forming an angle θ with the normal to the target surface and I_0 is the intensity corresponding to $\theta = 0$. After the quenching of the primary plume, a secondary plume has been observed. This second emission of material has a front velocity of 5.2×10^4 cm/s and an n parameter of 4.1. All these results are in good agreement with those obtained for fs ablation of other transition elements carbides [21–23]. A third emission of material, in the form of large fragments, has been detected 100 μs after the laser pulse.

Optical emission spectroscopy of the primary plume shows many spectral lines assigned to neutral Nb and to singly ionized C. From the time and space resolved spectra it has been possible to calculate the species velocity: Nb I = 1.0×10^6 cm/s and C II = 3.7×10^6 cm/s. In Fig. 1a, the normalized time-resolved emission plots for C II (426.7 nm) and Nb I (405.9 nm), recorded at 0.5 mm from the target, are reported. By the same technique, a black body like continuous plasma emission from the secondary plume has been detected, indicating, as usual for fs ablation, that it is formed by particles. In order to estimate the temperature of the front of the plume, the Wien's equation in the form $I_\lambda \propto \varepsilon(1/\lambda^4)e^{-hc/\lambda k_B T}$ (I_λ is the radiation intensity, ε the particle emissivity, λ the wavelength, T the temperature and k the Boltzmann constant) and considering, in the Mie approximation, $\varepsilon \propto 1/\lambda$ [24] has been applied. An initial temperature (500 ns after the laser pulse, with a gate of 500 ns) of about 3500 K, which decreases up to 1940 K after 9 μs, has been obtained.

On the other hand, the plume produced by ns laser ablation shows the typical features of the plasma obtained by short pulse ablation. ICCD imaging evidences that the plume front velocity is