Picosecond and subpicosecond pulsed laser deposition of Pb thin films

F. Gontad,[1,*] A. Lorusso,[2] A. Klini,[3] A. Loufardaki,[3] M. Panareo,[1,2] C. Fotakis,[3] and A. Perrone[2]

[1]*Istituto Nazionale di Fisica Nucleare (INFN), 73100 Lecce, Italy*

[2]*University of Salento, Department of Mathematics and Physics "E. De Giorgi," 73100 Lecce, Italy*

[3]*Institute of Electronic Structure and Laser (IELS), Foundation for Research and Technology-Hellas (FORTH) P.P. 1385, Vassilika Vouton, GR-711 10 Heraklion, Greece*

(Received 11 June 2013; published 3 September 2013)

Pb thin films were deposited on Nb substrates by means of pulsed laser deposition (PLD) with UV radiation (248 nm), in two different ablation regimes: picosecond (5 ps) and subpicosecond (0.5 ps). Granular films with grain size on the micron scale have been obtained, with no evidence of large droplet formation. All films presented a polycrystalline character with preferential orientation along the (111) crystalline planes. A maximum quantum efficiency (QE) of 7.3×10^{-5} (at 266 nm and 7 ns pulse duration) was measured, after laser cleaning, demonstrating good photoemission performance for Pb thin films deposited by ultrashort PLD. Moreover, Pb thin film photocathodes have maintained their QE for days, providing excellent chemical stability and durability. These results suggest that Pb thin films deposited on Nb by ultrashort PLD are a noteworthy alternative for the fabrication of photocathodes for superconductive radio-frequency electron guns. Finally, a comparison with the characteristics of Pb films prepared by ns PLD is illustrated and discussed.

DOI: 10.1103/PhysRevSTAB.16.093401 PACS numbers: 52.38.Mf, 79.60.−i, 81.07.Bc, 81.15.Fg

I. INTRODUCTION

During recent years, lead has been proposed as an interesting photocathode material for superconductive radio-frequency guns (SRF guns), due to its reasonably high quantum efficiency (QE) [1–4]. Another interesting characteristic is its superconducting transition temperature ($T_c = 7.2$ K), very close to that of niobium, the material typically used for superconductive cavities [5]. In addition, the quality factor of the superconductive cavity can be preserved by introducing a lead cathode, as has been already demonstrated by Sekutowicz *et al.* [5].

To date, the fabrication of lead photocathodes based on thin films has been investigated through the use of different deposition techniques, such as electroplated deposition, arc deposition, sputtering, evaporation, and pulsed laser deposition (PLD) in the nanosecond ablation regime [1,6]. PLD seems to be one of the best techniques due to the excellent adherence of the deposited films to the substrate, a necessary characteristic of a photocathode in a SRF gun, because of the extreme working conditions. However, in ns PLD, because of the relatively long laser pulse length, the ablation mechanism involves heating the target surface to its melting point, and then further heating to the vaporization temperature [7]. Such a mechanism promotes the ejection of molten material from the target surface and the appearance of micrometric droplets on the substrate surface [8]. Moreover, in the case of materials with a low melting point, such as lead, this effect can be further aggravated.

In the picosecond and subpicosecond regimes, however, the electron-lattice interaction can be neglected because the laser pulse duration is shorter than the electron cooling time [7]. This avoids the formation of a molten pool and, therefore, the consequent ejection of molten material. As a result, the ablation process in these regimes can be considered a direct solid-plasma transition [7]. Consequentially, the use of subnanosecond pulsed lasers could be the key to improving the morphological quality of the deposited films.

In previous work [6,9], we deposited lead films by PLD in the nanosecond regime at two different wavelengths, 266 and 1064 nm. The films obtained had similar granular structure with some micrometric droplets. The size of the grains was larger for the UV wavelength. Moreover, the grains were polycrystalline with preferential orientation along the (111) plane. In this work, we study the morphological features of Pb films deposited with 0.5 and 5 ps laser pulses, and the crystallinity of the films as a function of the laser fluence. In addition, we analyze the photoemission performance of the films in a dedicated photodiode cell.

II. EXPERIMENTAL DETAILS

All Pb thin films were deposited in a typical PLD system, described in a previous report [10]. Nb substrates were placed parallel to and in front of the pure Pb targets at a distance of 5 cm. Prior to every experiment, the system was pumped down to a pressure of 6×10^{-6} Pa. A dye laser, which generated 0.5 and 5 ps pulses pumped by a KrF excimer laser ($\lambda = 248$ nm), was focused onto the target

*fgontad@le.infn.it

TABLE I. Experimental parameters.

Base pressure (Pa)	6×10^{-6}								
Cleaning laser shots	2000								
Deposition laser shots	20000								
Repetition rate (Hz)	10								
Wavelength (nm)	248								
Spot area (mm^2)	4.4								
Target-substrate distance (cm)	5								
Pulse length (ps)			0.5				5		
Energy density (J/cm^2)	0.03	0.09	0.27	0.45	0.58	0.12	0.27	0.52	0.86
Pulses per site	1583	1502	1199	1118	1206	1286	1212	1212	1128

surface at an angle of 45°. Prior to Pb deposition, 2000 laser pulses were used to remove contaminants from the target surface. The depositions were carried out with the cumulative effect of 20000 laser pulses, with an energy density between 0.12 and 0.86 J/cm^2 for the pulse length of 5 ps, and between 0.03 and 0.58 J/cm^2 for the pulse length of 0.5 ps. The energy density was changed for every experiment using a dielectric attenuator, while trying to avoid subsequent changes to the laser spot size. Table I shows the experimental parameters used in this work.

The morphology of the deposited films was studied by scanning electron microscopy (SEM, model JEOL-JSM-6480LV). The crystallinity of the films was analyzed by x-ray diffraction (XRD, model D/MAX ULTIMA) using Cu Kα line. Finally, the QE of the films was obtained in a dedicated photodiode cell, a schematic of which is shown in Fig. 1. QE measurements and laser cleaning were carried out with the fourth harmonic of a Nd:YAG laser (266 nm) under high vacuum conditions (2×10^{-6} Pa), obtained by ionic and turbomolecular pumps. The quality of the vacuum was evaluated by a quadrupole mass spectrometer (model AMETEK MA100).

III. RESULTS AND DISCUSSION

Figure 2 shows the surface morphology of the film deposited with 0.09 J/cm^2 energy density in the 0.5 ps ablation regime, where a granular structure with grain size on the micron scale can be observed. Despite the granular structure of the film, the substrate surface seems to be fully covered with a thin Pb film with an approximate thickness of one micron and no signs of droplets. This could be attributed to the absence of evaporated material from a molten phase, because of the ultrashort pulse length [7]. Moreover, the structure of the films deposited with 0.12 J/cm^2 energy density and pulse duration of 5 ps (Fig. 3) is very similar, even though the pulse length is 10 times longer and the laser intensity is therefore 10 times lower. This film structure presents, to a certain extent, similarities with the film deposited on an Nb substrate with the ns-pulsed laser, shown in Fig. 4. All films show a granular structure with grain size in the micron range independent of the laser pulse duration, as has been observed for other deposition techniques, such as sputtering or evaporation [1]. The granular structure seems to be an inherent property of Pb thin films. However, for the

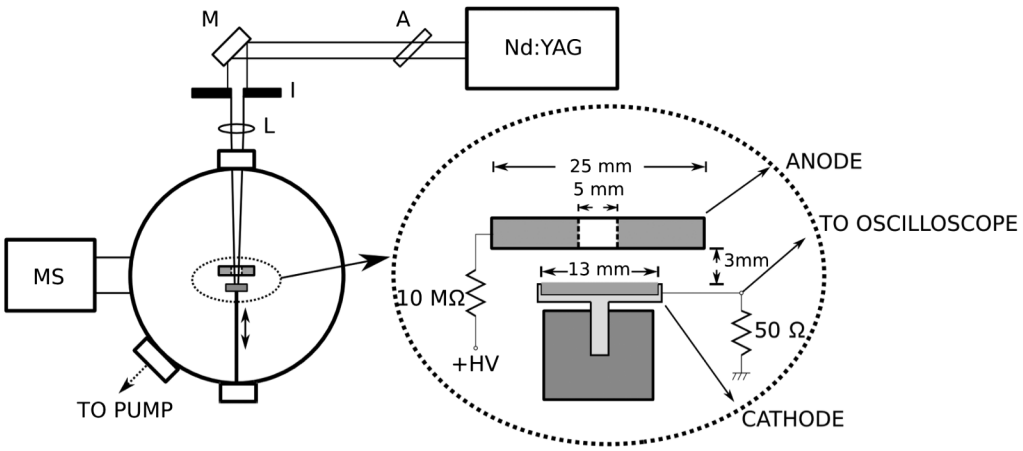

FIG. 1. Schematic of the photodiode cell used for measuring the QE of the films. M: mirror; A: attenuator; I: iris; L: lens; MS: mass spectrometer.

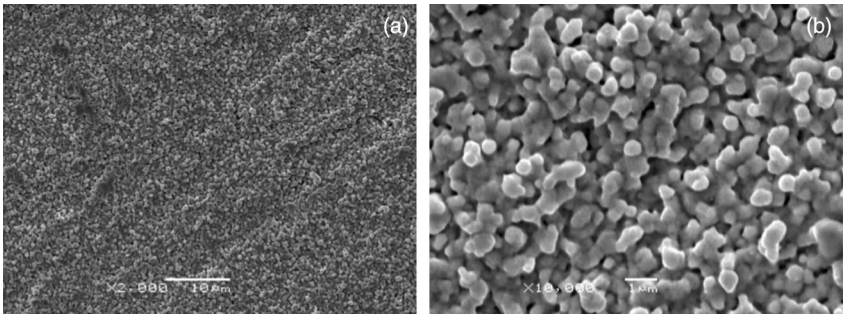

FIG. 2. SEM micrographs of a Pb film deposited on Nb, with energy density 0.09 J/cm^2, pulse duration of 0.5 ps, and a wavelength of 248 nm: (a) low magnification; (b) high magnification.

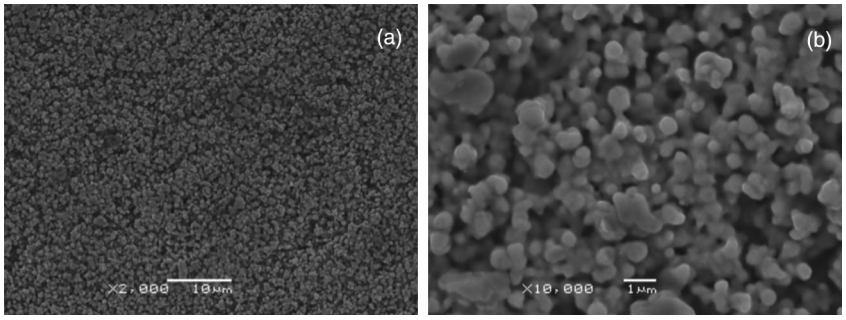

FIG. 3. SEM micrographs of a Pb film deposited on Nb, with energy density 0.12 J/cm^2, a pulse duration of 5 ps, and a wavelength of 248 nm: (a) low magnification; (b) high magnification.

films deposited in the nanosecond regime, the appearance of droplets (shown in Fig. 4 by arrows), around a few microns in size, cannot be ignored. As a consequence, the morphology of the Pb thin films deposited in the picosecond and subpicosecond regimes seems to be more suitable for application in actual SRF guns.

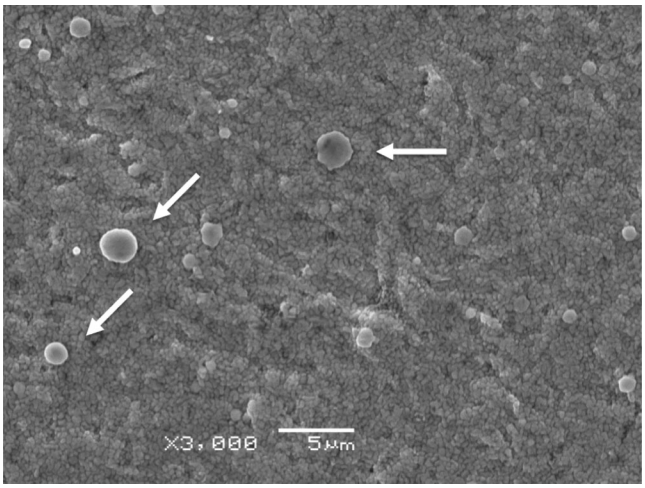

FIG. 4. SEM micrograph of a Pb film deposited on Nb, with an energy density of 1.0 J/cm^2, a pulse duration of 7 ns, and a wavelength of 266 nm. The biggest droplets are indicated by arrows.

The XRD pattern of the film deposited with pulse duration of 0.5 ps and an energy density of 0.09 J/cm^2 is shown in Fig. 5(a). The most intense peak, located at 32.28°, can be attributed to the (111) crystalline plane of Pb, as expected [9]. Moreover, the peaks associated with the (200), (220), (311), and (222) crystalline planes of Pb are also observed in the patterns [11]. The appearance of peaks located at 38.5°, 55.6°, and 69.7°, which can be attributed to Nb, implies that the substrate surface is not perfectly covered. This can be seen on the SEM images of the films, where, due the presence of small voids between the grains, very small areas of the Nb substrate could be accessible through the film. The XRD patterns of all deposited films present a similar shape (and are not shown here for the sake of brevity), indicating that the crystalline structure of the deposited films is very similar, regardless of the pulse duration or laser energy density.

Preliminary studies on the photoemission performance of the Pb films deposited by PLD with ultrashort pulses have been carried out in the photodiode cell shown in Fig. 1. A QE of 1.2×10^{-5} was estimated for the sample deposited with pulse duration of 0.5 ps and an energy density of 0.09 J/cm^2 (see Fig. 6), which was calculated by taking the ratio between the number of electrons and the number of photons that strike the target surface. If the exposure of the samples to air is very long (many months), a thick PbO layer is formed on the surface and the photoelectron emission process can occur not only by absorption

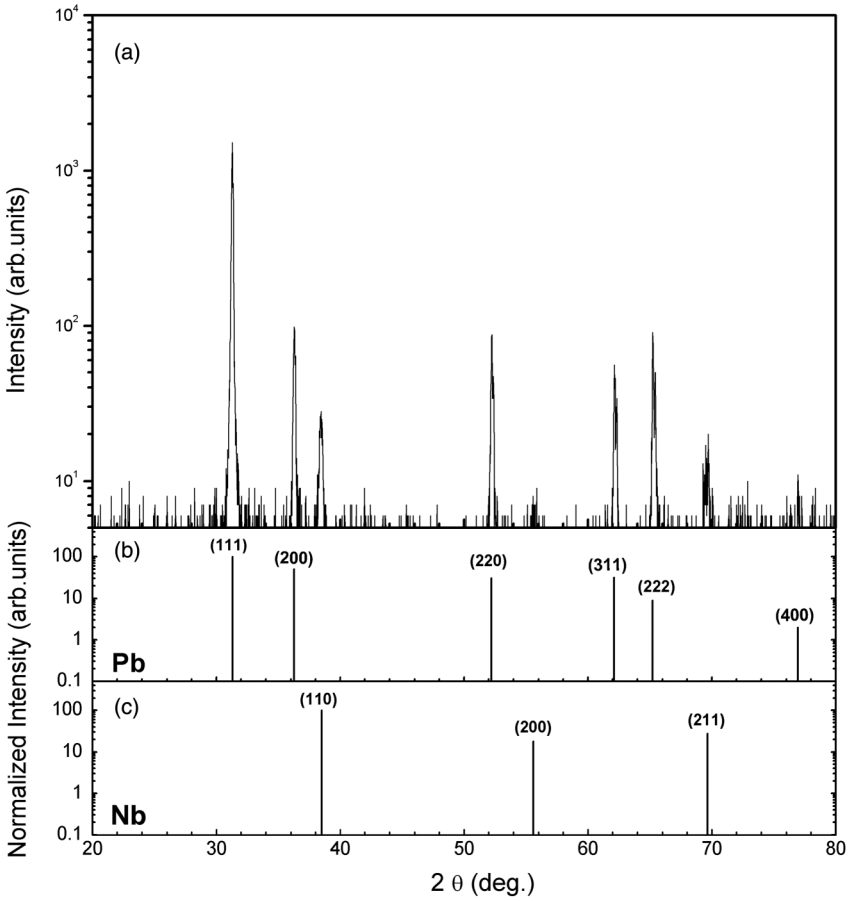

FIG. 5. XRD pattern of the Pb film deposited with a pulse duration of 0.5 ps and an energy density of 0.09 J/cm^2 (a); normalized patterns of pure Pb (b), and Nb (c) powders [11].

of a single photon, but also by absorption of two photons. In the latter case, the collected charge vs the laser energy shows parabolic behavior (inset of Fig. 6).

When the target surface was cleaned with 6000 laser shots at an energy density of 0.04 J/cm^2, the QE increased to 7.3×10^{-5}, as can be seen in Fig. 6. This QE was found to last for days, demonstrating the chemical stability of Pb photocathodes under high vacuum conditions. The measured QE of the deposited film is higher than the Nb bulk value ($\sim 1 \times 10^{-5}$ at 250 nm), and similar to the Pb bulk QE ($\sim 7 \times 10^{-5}$ at 250 nm) [1]. Another interesting feature of the photoemission performance of the PLD deposited Pb films is that the photoemission is characterized by a single-photon absorption, as previously reported for Pb films deposited with a pulse duration of 7 ns. The QE value obtained for those films (6×10^{-5} at 266 nm) is comparable with that obtained in this work [9]. However, the relationship between the collected charge on the anode and the laser energy used for the photoemission process is not perfectly linear; at higher laser energy a parabolic dependence is observed. This behavior has already been reported in literature and can be explained by the space charge effect [12]. Even though Pb has been shown to have good

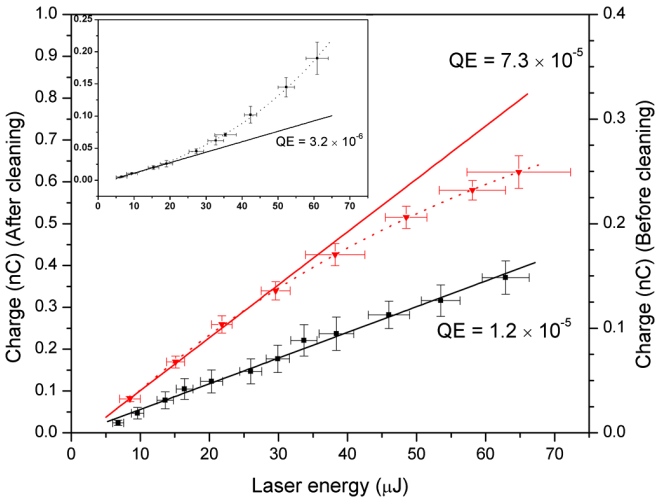

FIG. 6. Collected charge on the anode as a function of the laser energy striking the cathode, for the film deposited with 0.5 ps pulse duration and 0.09 J/cm^2 energy density: before (squares) and after (triangles) laser cleaning. Solid lines correspond to the linear fit of the data for low energy. Inset: the collected charge of the film exposed in open air for some months, before laser cleaning.

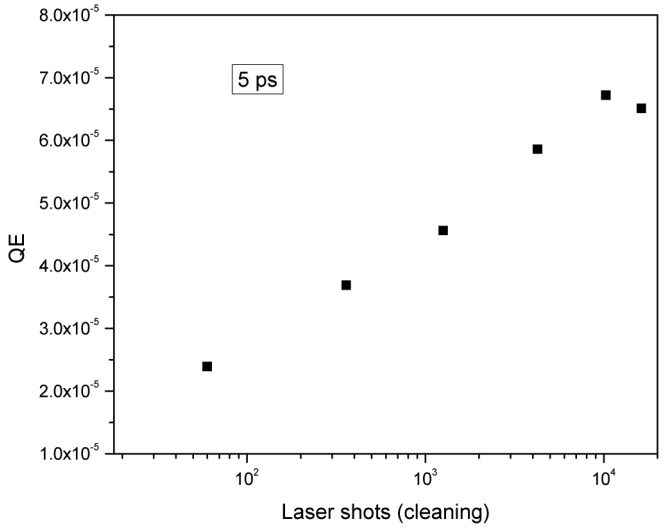

FIG. 7. QE of the film deposited with 5 ps pulse duration and 0.12 J/cm^2, as a function of the number of cleaning pulses with an energy density of 0.04 J/cm^2.

chemical stability under vacuum conditions, the preservation of the sample under atmospheric conditions provokes the oxidation of the upper monolayers and, therefore, degradation of the photoemission performance.

The importance of laser cleaning can be clearly observed in Fig. 7, where the QE of Pb improves considerably with the number of pulses until it reaches a maximum. Moreover, the repetitive effect of 6000 laser shots at an energy density of 0.01 J/cm^2, used to clean the cathode, promotes the formation of a smoother surface, as shown in Fig. 8, which further contributes to enhancing the photoemission performance. Therefore, choosing the correct number of laser pulses can result in both cleaning and smoothing of the film surface, producing a combined effect that considerably increases the photoemission performance of the film.

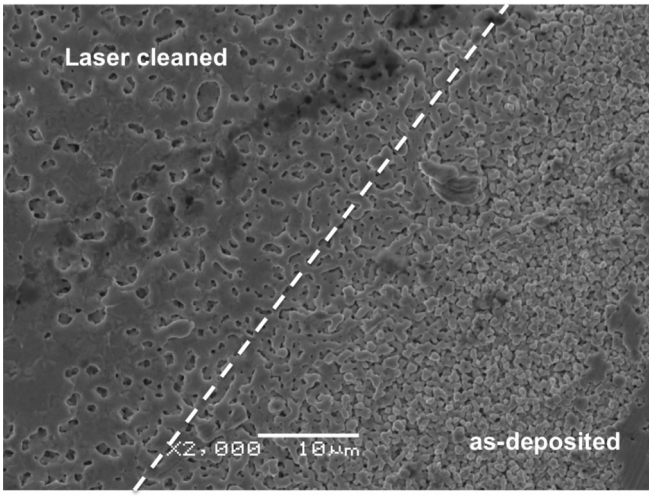

FIG. 8. SEM micrograph of the as-deposited Pb film, deposited on Nb at 0.12 J/cm^2 with pulse duration of 5 ps, before and after laser cleaning.

IV. CONCLUSIONS

The use of ultrashort pulses for the PLD of Pb thin films avoids the formation of significantly large droplets on the film surface. The films have a granular structure with grain size on the micron scale, as has also been reported for the PLD of Pb thin films in the nanosecond regime. The grains have a crystalline structure with preferential orientation along the (111) planes, as shown by XRD.

The QE of the films deposited in the picosecond and subpicosecond regimes is comparable with that of bulk material. The high chemical stability of Pb under vacuum conditions, demonstrated by the constant QE over a period of several days, makes it an excellent candidate for the cathode in SRF guns. However, the laser cleaning process becomes crucial for improvement of the QE when the films are exposed to air for long periods.

These results suggest that ultrashort PLD of Pb on Nb provides an excellent alternative for the fabrication of Pb photocathodes based on thin films, which are compatible with superconductive cavity technology.

ACKNOWLEDGMENTS

This work was supported by the Integrative Initiative of European Laser Research Infrastructures LASERLAB (Grant Agreement No. 001830) and by the Istituto Nazionale di Fisica Nucleare (INFN). The authors gratefully acknowledge Professor N. Lovergine for XRD analysis of samples.

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