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Comparison of the properties of Pb thin films deposited on Nb substrate using thermal evaporation and pulsed laser deposition techniques

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Abstract

Pb thin films were prepared at room temperature and in high vacuum by thermal evaporation and pulsed laser deposition techniques. Films deposited by both the techniques were investigated by scanning electron microscopy to determine their surface topology. The structure of the films was studied by X-ray diffraction in θ -2 θ geometry. The photoelectron performances in terms of quantum efficiency were deduced by a high vacuum photodiode cell before and after laser cleaning procedures. Relatively high quantum efficiency ($>10^{-5}$) was obtained for all the deposited films, comparable to that of corresponding bulk. Finally, film to substrate adhesion was also evaluated using the Daimler-Benz Rockwell-C adhesion test method. Weak and strong points of these two competitive techniques are illustrated and discussed.

Keywords: Thin films; Photocathodes; Pulsed laser deposition; Thermal evaporation; Quantum efficiency; Adhesion strength.

1. Introduction

Superconducting radio frequency guns (SRF-guns) are a new and competitive generation of RF guns able to operate with continuous wave at accelerating gradients >20 MV/m and with lower dissipated power [1,2] than conventional photoinjector guns. The main weak point of SRF-guns is the low quantum efficiency (QE) of Nb, which is the most commonly superconductor material used for such devices [3,4]. To overcome this problem, the use of a photocathode based on Pb thin film deposited on Nb substrate has been suggested [5]. The QE of Pb bulk (around 7×10^{-5} @ 250 nm) [6] is higher than that of Nb bulk (around 1×10^{-5} @ 250 nm) [6]; in addition, Pb presents high chemical stability and the possibility of preserving the superconducting properties of Nb cavities.

An array of different deposition techniques has been used for the deposition of Pb thin films [6] but very little work has been done with pulsed laser deposition (PLD) and even less with the thermal evaporation (TE) technique [2].

The deposition of metallic thin films by PLD to be used as photocathode in SRF-guns has shown interesting photoemission properties [7,8]. The basic principles of the PLD technique have been reported many times in the literature [9-11]. Its main advantages are: growth of multi-layer structures, deposition of high purity films, deposition at room temperature of highly adherent films. However, the presence of droplets and particulates of different sizes on the film surface could affect the photoemission quality of the cathode based on metallic thin film in terms of dark current and thermal emittance. Moreover, the angular distribution inhomogeneities of ablated material are transferred onto the substrate, resulting in low uniformity of the film thickness. On the contrary, the TE technique allows

us to prepare more uniform films and without droplets on their surface. Moreover, TE is a non-directional deposition technique. This implies that a very large target-substrate distance can be chosen, resulting in highly uniform films. The main weak point of this technique is the low adherence of the films on the substrate, as shown by adhesion testing of coating on the substrate carried out in the present study.

In this context, we studied the photoemission performance of Pb thin films deposited on Nb substrate using both techniques.

2. Experimental procedures

Both deposition techniques were carried out in a high vacuum system and at room temperature. For the thermal evaporation, a W crucible was charged with Pb pieces obtained from a disk of 99.99 % purity while the substrates were held about 15 cm above the source. The system was evacuated at pressure of about 2×10^{-4} Pa. The deposition rate was continuously monitored by a Maxtek quartz microbalance in the range 0.45-0.75 nm/s. In order to obtain a film of relevant thickness of about 500 nm with low internal stress or strain, the deposition process was suspended for 120 s every 150 nm of accumulated thickness, allowing time for thermal dissipation. The final thickness was subsequently measured by an Alphastep thickness profilometer on various positions of the sample and was found to be about 470 nm with uniformity better than 10%. The mean deposition rate was 0.62 nm/s.

The details of the PLD vacuum system for the deposition of Pb thin films on Nb have been illustrated elsewhere [12]. The output of a frequency-quadrupled Q-switched Nd:YAG laser ($\lambda = 266$ nm, $\tau = 7$ ns, $f = 10$ Hz) was focused onto a Pb target having the

1 same purity used in TE experiments. As usual in PLD experiments, the target rotated
2 around its horizontal axis with a frequency of 3 Hz. The laser beam was incident with an
3 angle of 45° with respect to the target normal. The operating laser fluence was fixed at 0.5
4 J/cm^2 by using an energy attenuator and iris; this value was chosen very close to the laser
5 ablation threshold, about $0.4 \text{ J}/\text{cm}^2$, which was theoretically calculated according to the
6 thermal model of Singh and Narayan [13]. Before the film deposition, a retractable shield
7 covered the substrate during the laser cleaning process of the target surface. The Nb
8 substrate was placed in front and parallel to the target surface and was ultrasonically
9 cleaned in acetone for 30 minutes and dried by nitrogen.

10 The remaining experimental conditions are displayed in Table 1.

11 Scanning electron microscopy (SEM, model JEOL-JSM-6480LV) was used for the analysis
12 of the films' morphology, while X-ray diffraction, in Bragg–Brentano geometry using a
13 Rigaku D/MAX-Ultima diffractometer equipped with a MPA2000 thin film attachment
14 stage and a Cu anode, was utilised for the characterisation of the structure and crystal
15 orientation of the deposited films.

16 Adhesion of the films to the substrate has been evaluated by the Daimler-Benz
17 Rockwell-C adhesion test method [14]. Indentation were done with a standard Rockwell
18 hardness tester fitted with a Rockwell C-type diamond cone indenter with an applied load
19 of 150 kg. The adhesion result is obtained by using an optical microscope and classifying
20 the adhesion failures as *HF1* to *HF6* according to the level of cracking and coating
21 delamination around the indent [14].

22 Finally, the *QE* of the films was measured by a home-made photodiode cell as shown in
23 Fig. 1. The vacuum chamber, in which the photodiode cell was inserted, was evacuated at a

base pressure of about 2×10^{-6} Pa by means of ionic and turbomolecular pumps. The quality of the vacuum was controlled by a quadrupole mass spectrometer.

The anode consisted of a copper ring of 25 mm in diameter separated from the cathode at a distance of 3 mm. The anode was biased at DC voltages up to 5 kV thus allowing the generation inside the gap of a maximum electric field of about 1.7 MV/m, while the cathode was connected to an oscilloscope (Tektronics, TDS 5104, 1 GHz, 5 GS/s) to catch the positive signal originating from the photoemitted electrons.

3. Results and discussion

Both deposition techniques were applied to grow Pb thin films on Nb substrate at room temperature and at high vacuum. Several films were prepared to optimize the deposition process of both techniques. However, only one specimen for each deposition technique was sampled out for the present investigation.

Figure 2a shows a representative SEM image of PLD Pb film deposited onto Nb substrate. A grainy surface structure with well-defined individual grains and some voids between them are observed. This fact could be attributed to a large surface tension, which leads to the growth of the film on the substrate surface as an agglomeration of grains in the micrometric range. The granular structure seems to be an intrinsic characteristic of Pb thin films. In the case of TE Pb film, a porous framework of melted material is visible (Fig. 2b). The morphology is much more irregular than that observed in PLD films; on the contrary, the density of voids is lower and the coverage of Nb substrate seems to be better.

Figure 3a shows the XRD pattern of a PLD Pb film deposited on Nb. In addition to the (110), (200) and (211) peaks of the Nb polycrystalline substrate, the figure shows a

1 relatively intense peak at an angle of 31.30° , along with weaker peaks at 36.26° , 52.24° ,
2 62.14° , 65.24° and 76.95° ascribed to the Pb deposit in the cubic crystalline form. The
3 peaks can be ascribed to the (111), (200), (220), (311), (222) and (400) planes of cubic Pb
4 respectively [15,16].

5 A similar polycrystalline structure is observed for TE Pb film deposited on Nb (Figure
6 3b). However, the peak intensities related to Pb are higher than those associated with the
7 Nb peaks. The lower Nb peak intensity may be due to the better coverage of the Nb surface
8 during the TE deposition process, as shown in SEM images given in Figure 2.

9 The values of the collected charge versus the laser energy for the PLD films are
10 reported in Figure 4. The photocathode drive laser ($\lambda = 266$ nm) was the same as that used
11 in the PLD experiments. The energy density on the cathode was controlled by adjustment of
12 both mask size and the telescopic focusing lens. Firstly, the measurements were carried out
13 on an as-deposited Pb sample. Figure 4 shows a linear relationship between the collected
14 charge and laser energy, indicating that the photoelectron emission process occurs mainly
15 via a one-photon absorption mechanism, as predicted by the Fowler-DuBridge theory [17].
16 A QE value of 1.3×10^{-5} was deduced from the linear fit. This value is lower than the QE
17 found for the Pb bulk because the surface of the Pb film was covered by some layers of
18 PbO formed during the exposure (for some days) in the open air. If the exposure is very
19 long (many months), a thick PbO is formed on the surface with a work function higher of
20 Pb which requires the absorption of two photons for one electron photoemission [17]. In
21 this last case, the collected charge vs. the laser energy shows a parabolic behaviour. In order
22 to eliminate the oxide layers formed on the Pb surface, *in-situ* laser cleaning treatments
23 were applied with laser power densities lower than the Pb ablation threshold. The laser

cleaning was performed with the full beam area, resulting in a cleaned area of 0.2 cm² on the cathode surface and laser energy density of about 60 mJ/cm². After 600 pulses of laser cleaning, the charge of the electrons emitted as a function of laser energy was as depicted in Fig. 4. From these last measurements it is evident that a light space charge effect occurs at laser energies higher than 35 μJ. The value of QE was calculated in the low charge limit. The increase of QE up to 3.7×10^{-5} after the laser treatment is about a factor of 3, lower than the typical QE increase observed before and after cathode cleaning for Mg cathode [18]. This last achievement is related to the good chemical stability of Pb.

Identical plots are found for TE thin films. Figure 5 shows the charge of the electrons emitted from Pb cathode prepared by TE as a function of laser energy before and after laser cleaning. The QE values measured are close to those deduced with PLD Pb film.

In order to study the effect of the electric field on the electron emitted charge, well known as Schottky effect, we changed the electric field value, E , applied to the photodiode. Fig. 6 reports the $QE^{1/2}$ values as a function of $E^{1/2}$ after the laser cleaning of films. For electric field values lower than 0.36 MV/m the space charge effect is evident, while for values higher than 0.36 MV/m, the data follow a straight line according to the relation:

$$QE^{1/2} = A[h\nu - \varphi_0 + (\alpha \beta E)^{1/2}] \quad 1)$$

where A is a material-properties dependent constant, ν is the frequency of the drive laser, φ_0 is the work function at zero field (4.0 eV for Pb), β is the field enhancement factor and $\alpha = \sqrt{e/4\pi\epsilon_0}$ (e is the electron charge and ϵ_0 is the dielectric constant) is about 3.8×10^{-5} in MKS. The term $(\alpha \beta E)^{1/2}$ is the lowering of work function due to the applied electric field according to the following relation:

$$\varphi_{eff} = \varphi_0 - (\alpha \beta E)^{1/2} \quad 2)$$

From the slope of the fit lines depicted in Fig. 6, the values of field enhancement factor β have been deduced. In the case of PLD film, the slope is found to be 2.63×10^{-6} , corresponding to a β value of about 169 and the intercept gives an A value of about $4.9 \times 10^{-3} \text{ eV}^{-1}$, while for the TE film the graph gives a β value of about 576 and an A value of $2.6 \times 10^{-3} \text{ eV}^{-1}$. The high value of β for TE film is strongly related to its irregular surface morphology, which influences the ability of the cathode to increase the local electric field and, hence, the field enhancement factor.

The adhesion test revealed for the TE sample small delaminations around the crater caused by the piling up of the substrate, which can be related to the poor adhesion of the film to the substrate, and classified as adhesion strength quality *HF3*. On the other hand, the adhesion test in the PLD sample shows no visible delaminations around the indentation crater, and the presence of very few fine cracks, typical of good adhesion strength quality *HF1*.

4. Conclusions

In this paper, we have demonstrated that PLD and TE films present similar polycrystalline structure and photoemission properties. The coverage of the Nb substrate seems to be better with TE films, but the adhesion on the substrate is better on films deposited by PLD, as shown by adhesion measurements. The utility of TE films as an efficient and reliable photocathode in the harsh environments experienced in the SRF-guns is strongly compromised by its poor adhesion to the Nb substrate.

The present results suggest that metallic photocathodes based on thin films deposited by a

1 PLD technique are better suited for use in RF photoinjector electron guns. However, even
2 in high vacuum ($<10^{-6}$ Pa), the Pb surface suffers contamination from the background
3 gases, partially weakening its performance as a photoelectron emitter. For this reason for a
4 better use of metallic photocathodes, *in-situ* laser cleaning treatments should be taken into
5 account.

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Figure and Table Captions.

Table 1. Experimental conditions for PLD thin film deposition.

Figure 1. Scheme of the photodiode cell used for the measurement of the QE of the deposited films. M: Mirror; A: Attenuator; I: Iris; L: Lens; MS: Mass Spectrometer.

Figure 2. SEM images at two magnifications of Pb films: a) deposited by PLD; b) deposited by TE.

Figure 3. XRD pattern recorded for Pb film as-deposited onto Nb: a) by PLD technique; b) by TE technique.

Figure 4. Charge of the electrons emitted from Pb cathode prepared by PLD as a function of laser energy before ($\square$) and after ($\bullet$) laser cleaning.

Figure 5. Charge of the electrons emitted from Pb cathode prepared by TE as a function of laser energy before ($\square$) and after ($\bullet$) laser cleaning.

Figure 6. Experimental results and theoretical best fit by Eq.1) of the Schottky effect observed in our photodiode cell.

Table 1

Target	Lead
Substrate	Niobium
Target-substrate distance	4 cm
Deposition temperature	300 K
Laser spot area	1.1 mm ²
Laser fluence	0.5 J/cm ²
Number of pulses for the target cleaning before deposition	3,000
Number of pulses during the deposition	15,000
Pulses/site	700
Film diameter	13 mm
Background pressure	6×10 ⁻⁶ Pa

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FIG. 1

FIG. 2

a) PLD

b) TE

FIG. 3

FIG. 4

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FIG. 5

FIG. 6