

Photoemission characteristics of PLD grown Mg films under UV laser irradiation

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Received 15 June 2007, in final form 21 August 2007

Published 21 September 2007

Online at stacks.iop.org/JPhysD/40/5965

Abstract

In this paper we report a detailed description of the laser cleaning procedure and emission performance measurement on a pulsed laser deposited Mg film. During the tests performed after the end of each cleaning operation we have observed an increase in quantum efficiency (QE) in time. Then the QE apparently stabilizes at a remarkably higher value. The study of this phenomenon and its relation to chemical composition of the residual gases of vacuum environment is important because it determines both the achievable QE value and the lifetime of the Mg film based cathode. Moreover, the stability of the QE at remarkably high values has been revealed for a time scale of several days after each laser cleaning process, in our vacuum conditions. The adsorption of reactive chemical species leading to the lowering of the Mg work function is discussed.

1. Introduction

The electron injectors for the advanced projects of fourth generation x-ray sources, such as SASE-FELs [1], and for future linear colliders [2] are mostly based on laser excited photocathodes. The main requirements on the cathodes are high quantum efficiency (QE), promptness of response, emission uniformity over the irradiated surface and stability (lifetime). Metals have order of femto-second response and they are rugged in handling. Among them, Mg has premium QE, in the order of 10^{-3} at near UV wavelength (266 nm). However, bulk Mg cathodes have shown poor emission uniformity and failures in the high electric fields' environment of RF guns. Moreover, the QE value degrades in time even in the UHV vacuum of RF guns.

As an alternative, Mg films on copper substrates have been proposed and tested on the basis of their presumed better purity and uniformity [3]. Previous reports on Mg films grown by pulsed laser deposition (PLD) showed promising results

in particular with respect to uniformity of emission, quantum yield and adhesion to the substrate [4–6].

In order to reach the utmost QE value it is necessary to remove the inevitable oxide layer that forms on the film surface. Only two techniques were used to perform such an operation: laser cleaning and ionic etching [7]. The laser cleaning operation must be performed with particular care due to the limited thickness of the film and to avoid inducing surface roughness. It was evidenced that cleaning irradiation may determine a variation of the film surface morphology [8].

While several groups have studied magnesium in recent years as a potential candidate for the electron source in photoinjector devices, a complete study of the effects of laser cleaning that could explain the peculiarities in the emission performance of Mg films has not yet been done.

The aim of this paper is to describe the film deposition conditions, the laser cleaning procedure and to evidence the performance of Mg films from the photoemission point of view.

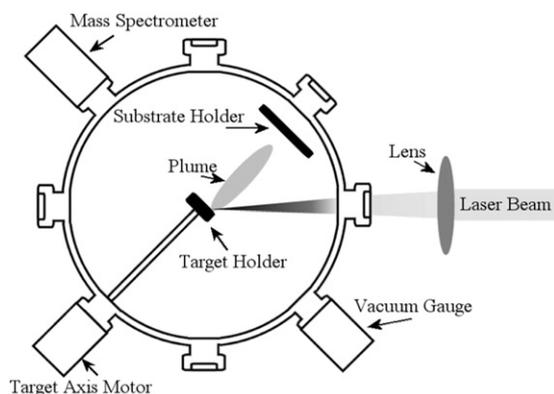


Figure 1. Schematic of PLD apparatus.

Table 1. Experimental parameters used for the deposition of Mg films on the Cu substrate.

Target	Mg
Substrate	Cu
Target–substrate distance	3.5 cm
Laser spot size	1.0 mm ²
Base pressure	5×10^{-6} Pa
Laser pulses	
• cleaning (5×10^{-6} Pa)	5000
• deposition (in He at 5 Pa)	50 000
Laser fluence	10 J cm ⁻²
Film thickness	2.5 μm
Film diameter	12 mm

2. Experimental

2.1. Cathode preparation

The PLD technique is a well-known method for thin films deposition of a variety of materials [9, 10]. The PLD apparatus used to deposit thin films is shown in figure 1. The deposition of magnesium films was achieved using a 308 nm wavelength pulsed laser beam produced by a XeCl* excimer laser ($\tau = 30$ ns). The laser was focused on a pure disc of magnesium (99.9%) rotating at a frequency of 1 Hz. The laser beam was incident on the target surface at an angle of 45° . The ablated material was collected on Cu polished substrates kept during the deposition process at room temperature. The target–substrate distance was 3.5 cm and the laser fluence was set at 10 J cm^{-2} . The PLD system was evacuated at a base pressure of about 5×10^{-6} Pa by a turbo molecular pump. During the deposition the vacuum chamber was filled with pure He at a pressure of 5 Pa to reach the plume confinement regime leading to an increase in the deposition rate [11].

With the aim of cleaning the target surface, a pre-irradiation treatment was applied with 5000 laser pulses. During this laser cleaning, the Cu substrate was shielded from the initial ablated material, which could contain impurities. Several films were prepared to optimize the deposition process. The deposition parameters of the tested sample are shown in table 1.

The cathodes were morphologically investigated by scanning electron microscopy (SEM) with the aid of a SEM JEOL 6480LV microscope.

2.2. Vacuum diode cell

The QE measurements were performed in a photodiode cell under UHV condition. The cathode and the anode separated at a distance of 3 mm were placed inside the photodiode cell (figure 2). The Mg film occupied the cathode position and was electrically grounded. The anode plate was biased with high dc voltages up to 5 kV thus allowing the generation of an intense electric field of about 1.7 MV m^{-1} inside the gap.

In order to illuminate the cathode and for precise alignment of UV laser beam on the cathode surface the anode plate was machined with two symmetric holes. They have a diameter of 4 mm and form an angle of 72° with respect to the normal of the cathode surface. This particular geometry was chosen for two main reasons.

- The first was to avoid the use of a metallic grid usually present in such experiments. Our previous experimental results clearly indicated that the light distribution on the cathode surface, in the presence of a metallic grid, was affected by diffraction structures and hampered uniform illumination of the cathode surface [6].
- Second, the angle of 72° was chosen in order to perform experiments with the same geometrical configuration used in the last generation of the BNL/SLAC/UCLA 1.6 cells S-Band RF gun [12].

The vacuum chamber in which the photodiode cell was inserted was evacuated at a base pressure of about 2×10^{-7} Pa by means of an ionic pump. The quality of the vacuum was controlled by a quadrupole mass spectrometer.

2.3. Laser cleaning and QE measurements

Laser cleaning and QE measurements of the Mg films were performed using the UV radiation of the 4th harmonic of a Q-switch, mode-locked Nd : YAG laser (QUANTEL YG-501) able to deliver up to $300 \mu\text{J}$ at 266 nm with a pulse duration of 30 ps.

The optical transfer line and signal acquisition scheme are reported in figure 2. The 4th harmonic of the laser beam was reflected by a mirror mounted on a gimbal for fine alignment; a variable aperture iris was used to select the central part of the beam and to align it. A beam splitter was used to sample the beam energy by means of a calibrated fast photodiode. When needed, a series of neutral density filters was used in order to decrease the laser energy down to a fraction of nanojoule. A couple of cylindrical lenses were allowed to transversely shape and collimate the beam in order to obtain on the cathode a circular laser spot; the laser beam was, when considered necessary, focused with a fused silica plano-convex lens (focal length 30 cm) mounted onto an xyz translational stage driven by stepper motors controlled by a computer (x and z movements were linked in order not to change, once fixed, the distance between the lens and the illuminated area of the cathode). Another beam splitter sampled out the laser beam in order to illuminate a Ce doped YAG screen used as a virtual cathode. Another variable aperture iris has been used to facilitate the alignment of the laser beam before its entry into the vacuum chamber through a quartz window in order to illuminate the cathode surface. A triggered CCD camera (Basler mod. 301)

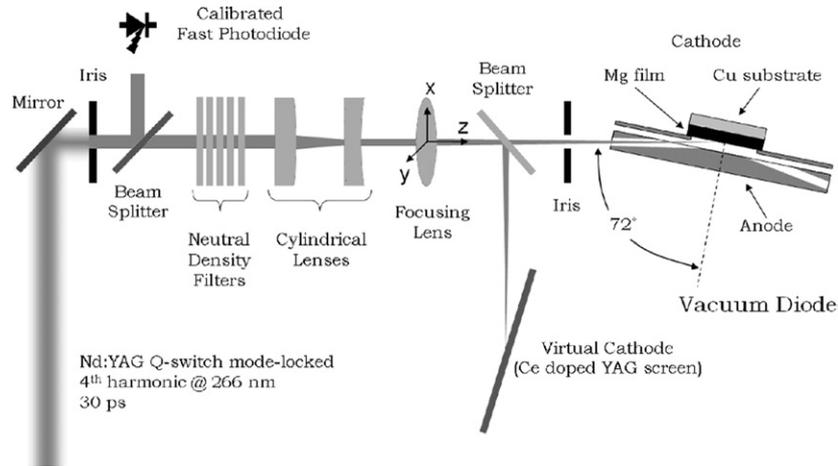


Figure 2. Detailed scheme of the apparatus for laser cleaning and QE measurements.

was used to observe the laser spatial distribution over the cathode surface.

The laser energy measurements were performed by integrating the signal of the calibrated fast photodiode, while the charge measurements were done using a charge integrator.

The laser cleaning procedure was performed by scanning the focused laser beam over an area of about $2.4 \times 2.4 \text{ mm}^2$. The laser beam had a diameter on the cathode surface of about $300 \mu\text{m}$ and energy of about $25 \mu\text{J}$ per pulse (power density and laser fluence were about 3 GW cm^{-2} and 35 mJ cm^{-2} per pulse, respectively). Such a value of the power density was experimentally determined during preliminary tests as being the threshold for the ablation of the oxidized layers. The power density threshold value for the ablation was deduced looking at the vacuum level of the UHV chamber: we observed that once such a value was reached, the vacuum level inside the chamber slightly worsened indicating that material ablation was occurring.

The scanning scheme was chosen in such a way that laser shots focused over consecutive horizontal path lines slightly overlap in order to make sure that all parts of the surface were exposed to the laser beam. Typically during the laser cleaning the laser repetition rate was set at 5 Hz and the scanning speed of the laser spot was on the order of 10^{-3} m s^{-1} .

After each laser cleaning procedure the focusing lens was removed and the laser beam was directed to the central part of the irradiated area of the cathode to measure the QE. In order to perform measurements far from space charge saturation, the laser energy was decreased by means of calibrated neutral density filters.

3. Results

The first emission measurement was performed before any laser cleaning treatment. It revealed a very poor QE of about 2×10^{-6} (figure 3). Just after the first laser cleaning procedure, performed as described above, the QE measured value rose by about 2 orders of magnitude reaching the noticeable value of 5×10^{-4} , very close to the value reported in the literature for bulk pure Mg [13].

During each laser cleaning procedure we recorded the mass spectra of the residual gases in the vacuum chamber. We

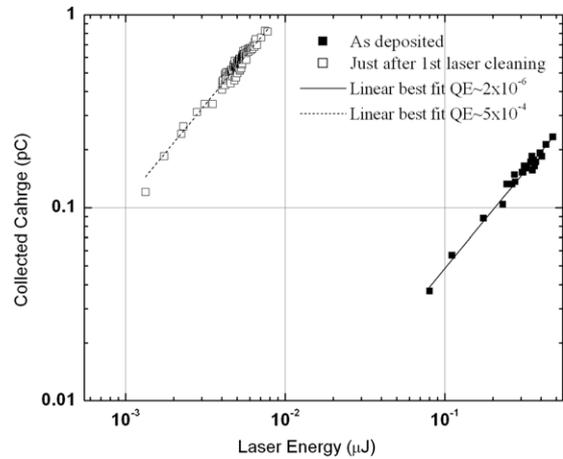


Figure 3. Emission curves as collected charge versus laser energy of the Mg film before and after the first laser cleaning.

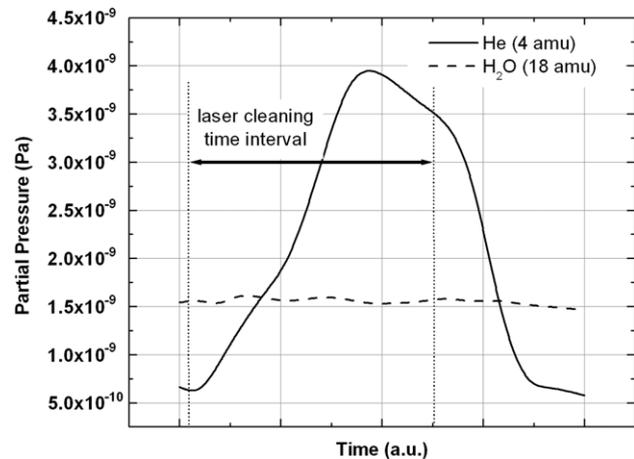


Figure 4. Partial pressure readings for masses 4 and 18 amu during laser cleaning of the Mg film.

observed that under the irradiation with laser power density suitable for laser cleaning the peak at 4 amu appeared in the mass spectra (figure 4). This should indicate that some atoms of He were trapped in the interstitial cavity during the growth of

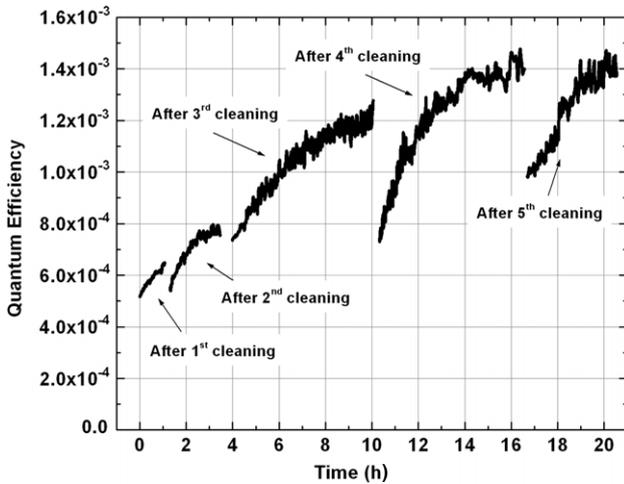


Figure 5. QE of the Mg films recorded as a function of time after each laser cleaning process.

the film and were released during the laser cleaning irradiation. We recall that the depositions were performed in a low pressure He atmosphere.

In order to study the stability of emission we performed QE measurements versus time for several hours (figure 5). The measurement after the first laser cleaning was performed for about 1.5 h. We detected a slight increase in the QE value during this time from the initial value (just after the cleaning) of about 5×10^{-4} up to 6.5×10^{-4} . After about 12 h, we carried out a new laser cleaning of the cathode surface. The QE value was monitored again for about 2.5 h. After the 2nd cleaning, the measured QE was slightly lower than the last measured value, but also in this case its value increased from 5.5×10^{-4} of up to about 8.0×10^{-4} . About 12 h later, we executed a 3rd cleaning and measured the QE continuously. We observed again that after an initial decrease just after the laser cleaning (from 8.0×10^{-4} to 7.5×10^{-4}), the QE value increased up to 1.2×10^{-3} during the next 6 h. The 4th cleaning procedure was accomplished about 12 h before the last QE measurements. In this case, the single raster scheme was performed 5 times. After the laser cleaning we detected a strong decrease in the QE that lowered to an initial value of 7.5×10^{-4} . During the next 6.5 h we continuously measured the QE value, observing a continuous increase up to a value of about 1.4×10^{-3} . The 5th and final laser cleaning, carried out using a single raster scheme, resulted in an initial QE value of 10^{-3} that rose up to 1.4×10^{-3} during the next 4 h. It is evident that there is a strong variation, up to a factor of 2, during each measurement.

The sample was kept under vacuum at a base pressure of 2×10^{-7} Pa during the next two days. After this time we performed new measurements without an additional laser cleaning procedure. We observed that the QE value was the same as that measured two days before, i.e. 1.4×10^{-3} .

This value was preserved also after the irradiation of the surface with about $5 \mu\text{J}$ for about 1 h with a repetition rate of 5 Hz (figure 6). The aim of the test was to verify the ability of such a cathode to maintain its emission performances also during irradiation with the laser energy slightly exceeding that required to extract electron bunches of 1 nC charge. During the irradiation with $5 \mu\text{J}$ energy pulses the QE measure was interrupted in order not to damage the charge amplifier.

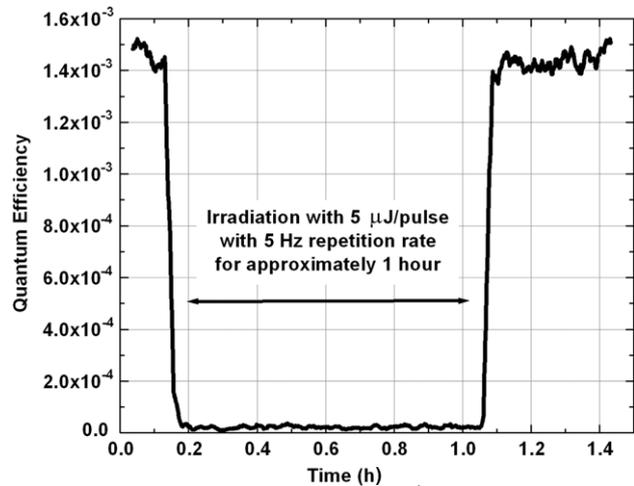


Figure 6. QE measurements before and after irradiation with high energy laser pulses.

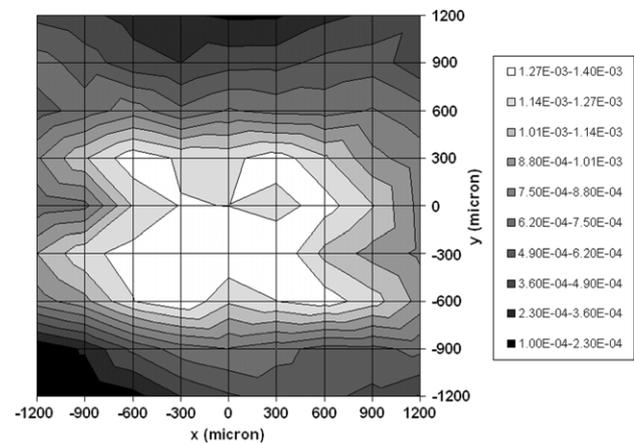


Figure 7. QE map of the laser-cleaned area.

Additionally the QE map of the irradiated area was drawn. In order to perform such a measurement the laser energy was lowered to few nanojoules by means of neutral density filters. The laser was focused on the cathode surface by a 30 cm focal length fused silica lens. The truncated Gaussian laser spot was then moved in succession over a grid of 9×9 points on the laser-cleaned area. The average QE on each irradiated area of about $300 \mu\text{m}$ diameter is evaluated from the slope of the emission curves, i.e. the collected charge versus laser energy, far from the space charge saturation regime. The $300 \mu\text{m}$ diameter is the minimum compatible with the sensitivity of our charge detector apparatus to remain below the extractable charge limit. Naturally this entails a limit on the spatial resolution which cannot be less than about twice the value of the laser spot diameter.

The QE map of the sample collected 72 h after the 5th and last laser cleaning process is reported in figure 7. With the limitations due to the size of the laser spot during such measurements the emission seems to be reasonably uniform inside a circle of about $500 \mu\text{m}$ of radius centred in the most intense emitting area.

Morphological investigations of the as-deposited and irradiated areas carried out by means of SEM are reported

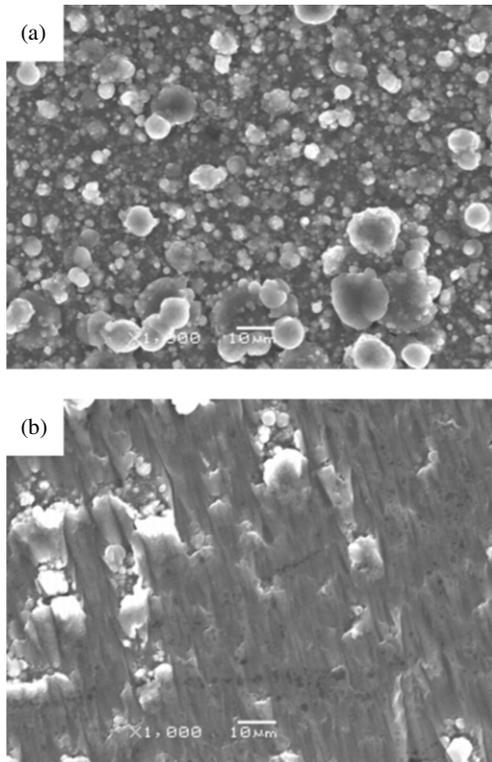


Figure 8. SEM micrographs of the sample surface before (a) and after (b) the laser cleaning processes.

in figures 8(a) and (b). Strong morphological changes induced by laser irradiation are evident. The observed surface modifications are interesting because the as-deposited rough structure of the Mg film may induce a field enhancement factor so high as to avoid the reaching of the high electric field gradient of an RF gun.

4. Discussion

QE values for Mg reported till now in the literature, either for bulk or film, are scattered in a range within 2.5×10^{-4} and 3×10^{-3} for an exciting wavelength of 266 nm. The reason for this spread can be the different experimental conditions, as e.g. vacuum base pressure and electric field intensities [14–16].

Theoretical prediction for the QE value for Mg at 266 nm indicates a value of about 5×10^{-4} . Higher values cannot be predicted assuming a work function of 3.66 eV. A decrease of such a value by means of the formation of some electric dipole on the surface due to the gas absorption may be the key to explaining such high photoemission performance from this material.

The very gradual laser cleaning procedure described before should remove only the uppermost deeply oxidized layer. It has the typical rock-salt structure of MgO and was formed by exposing the film surface to air during the time between the deposition procedure and emission characterization, both performed in the UHV environment. Reference [3] reports that successive laser cleaning procedures resulted in an increase in the QE. This is clearly observed also in our previous [4–6] and present experiments (see figure 3), demonstrating that a pure Mg metal

surface has been obtained with the removal of surface oxidized layers. Nevertheless, a continuous monitoring of the emission yield of the Mg film during a time interval of several hours after each laser cleaning clearly indicates that some other processes influenced the electron surface emission properties. A few years ago the effects of oxygen adsorption on the quantum yield of Mg films had been reported by Yuan *et al* [17]. They showed that a significant increase in QE is achieved by exposing the Mg film to controlled fluxes of pure O₂. After an initial increase, strongly dependent on the oxygen dose, the quantum yield deteriorates, pointing to the formation of a thick oxidized layer that delayed the emission of photoelectrons. Similar results were observed in 1935 by Cashman and Huxford [18]. They observed that the work function of pure Mg exposed to oxygen fluxes after an initial decrease, leading for a fixed wavelength of photons to an increase in QE, increased again after an excess of exposure to O₂, indicating also in this case the formation of a thick oxide on the sample surface. Their findings on the lowering of the work function during initial oxidation of the Mg surface were confirmed through numerical computation by Schröder *et al* [19].

Our experimental situation was quite different from those of the experiments reported in the literature. In our case no fluxes of oxygen have been introduced in the vacuum chamber. Our working base pressure was 2.5×10^{-7} Pa and the O₂ partial pressure was two orders of magnitude lower than that used in other experiments reported in the literature [17, 18]. Partial pressures of residual gases were measured by a quadrupole mass spectrometer. From the residual gas mass spectra we observed that the most abundant chemical species were H₂, H₂O, N₂ and O₂, with partial pressures of 1.9×10^{-7} Pa, 1.5×10^{-8} Pa, 3×10^{-8} Pa and 8×10^{-9} Pa, respectively. Yuan *et al* [17] observed that, after an initial increase in the QE of Mg films stimulated by admitting a slight oxygen quantity in the test chamber, the quantum yield of their samples was stable on the order of few 10^{-3} with a vacuum level of about 2.7×10^{-8} Pa.

According to our readings of partial pressure and the duration of the QE acquisitions, which, as reported in figure 5, were performed up to a maximum of about 6 h, we deduced that the Mg surface exposed to O₂, at a partial pressure level of 8×10^{-9} Pa, led to a surface coverage lower than 1 monolayer. In contrast, H₂ exposure during the same time, due to higher partial pressure of this chemical species with respect to molecular oxygen, may give rise to a surface coverage higher than 2–3 monolayers. According to Cashman and Huxford [18] who studied the emission properties of the Mg surface exposed to H₂ fluxes, we consider that the increase in the quantum yield of our sample is related to the chemisorption of hydrogen in the subsurface sites of the Mg film and to a lesser extent of oxygen. This should lead to a decrease in the work function because an electric dipole is formed under those conditions near the surface of the film with orientation that helps photoexcited electrons to escape in vacuum. Such an idea is partially confirmed by the findings of Sprunger and Plummer [20] who observed a decrease of 0.95 eV of the initial value of the work function after the complete hydrogenation of the Mg(0001) surface due to the formation of a metastable ‘hydride’ phase. They also reported that the activation energy for the chemisorption of H₂ on the Mg(0001) surface was

about 0.5 eV and thus at room temperature the formation of this phase should not be observed. This apparent contradiction is overcome looking at the SEM micrographs of the surface of our Mg film. Figure 8(a) shows the non-irradiated area revealing that the film consisted of agglomerated droplets with diameters ranging up to a few micrometres, while after the irradiation (figure 8(b)) the surface appeared in some way flattened, as a result of the annealing effect induced by the laser cleaning process. PLD films grown at room temperature usually do not present a well-defined crystalline structure. In particular, SEM pictures of the as-deposited surface (figure 8(a)) showed that the film is fully covered by droplets indicating most probably an amorphous structure. As a result of the laser cleaning processes, the irradiated surface of the Mg cathode presents a flattened surface (figure 8(b)). XRD spectra (not shown here) reveal that a polycrystalline Mg film was formed with a slight texture on (002) orientation. Under these conditions, we can expect that the activation energy for chemisorption of H₂ on Mg amorphous surfaces may be lower than that reported for Mg(0001), as also indicated by Nørskov *et al* [21].

Further experiments performed with controlled fluxes of molecular hydrogen are foreseen in order to have more insight into the kinetics of hydrogen chemisorption.

Tests performed by irradiating the cleaned area with laser pulses ($\lambda = 266$ nm, $\tau = 30$ ps) having $5 \mu\text{J}$ of energy show any influence on the QE. This result seems to indicate that the energy required to photo-dissociate the Mg–H bond should be higher than 4.67 eV.

The emission inside the central part of the laser-cleaned area within a radius of approximately $500 \mu\text{m}$ and considering the limitations of our experimental arrangements seems to be uniform within 20%. We found that the rapid decrease in the efficiency observed for vertical coordinate values close to the extreme of the measured area is just due to a non-perfect alignment of the laser beam inside the *bore* where it has to travel to illuminate the cathode surface. This misalignment does not influence the measurements in the central zone of the scanned area.

The soft laser cleaning performed as described before can be useful both in removing the oxidized layers to improve the emission properties of the Mg film and in smoothening the film surface removing the surface structures that can be at the origin of a localized electric field enhancement and possible source of electric discharge in the RF gun environment.

5. Conclusions

We presented the results of the laser cleaning effect in terms of QE, emission uniformity, surface morphology and structure of pulsed laser deposited pure Mg films on the copper substrate. Moreover, the influence of the chemisorption of hydrogen, always present as a residual gas in ultra-high vacuum operating conditions, has been discussed with particular attention with respect to the efficiency and stability of the emission performances of Mg surface. The results are promising for the attainment of a suitable cathode to be used in photoinjectors based on the radio frequency electron gun. These issues lead to new questions on aspects that should be clarified with new and dedicated experiments: the evolution of

the film crystal phase with laser cleaning and the role of low energy laser pulses in increasing the Mg surface reactivity.

Acknowledgments

CR acknowledges with thanks the CNR–NATO fellowship Pos. 216.2169, Prot. N. 0015503. LC acknowledges the collaboration of L Cacciotti, M Corrado and R Sorchetti in setting up the experiments. This work has been partially supported by the EU commission in the sixth framework program, contract no. 011935 EUROFEL and by MIUR, Progetti Strategici, DD 1834, December 4, 2002.

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