Copper Surface Treatment with deep UV Ultrafast Laser for Improved Photocathode Photoemissive Properties

B Groussin, M Martinez Calderon, B Marsh, R Rossel and E Granados

CERN, European Organization for Nuclear Research, 1211 Geneva 23, Switzerland

E-mail: eduardo.granados@cern.ch

Abstract. Cesium Telluride (Cs_2Te) constitutes today the photoemissive semiconductor material of choice for electron accelerators due to its high quantum efficiency (QE) in the deep ultraviolet (DUV) spectral range, and capability to produce high charge over a long operation lifetime. Unfortunately, its chemical instability requires ultra-high vacuum (in the 10^{-10} mbar range). This inevitably complicates Cs_2Te photocathode handling, and increases the overall cost compared to metallic counterparts. Copper photocathodes are alternative candidates, and although they are much more tolerant in terms of vacuum requirements, their use in high average current photo-injectors is limited due to their orders of magnitude lower QE (around 10^{-5} per unit). With the development of nanophotonics, plasmonic phenomena can now be exploited to tailor a new range of effects in the photoemission process. In this work, we focus on direct laser fabrication of nanostructures for plasmonic electric-field enhancement on copper, and study their potential for enhancing the quantum yield. We develop a methodology to fabricate the nanostructures by irradiating the Cu surface with 257 nm femtosecond pulses, well above copper's work function. We directly obtained nanostructures 100-200 nm, matching the plasmonic resonance for photoinjector wavelengths. The study is accompanied by a parametric scan allowing to obtain the optimal laser machining parameters, and the analysis of the nanostructure morphologies obtained.

1. Introduction

High energy and charge electron beams are becoming increasingly popular in accelerator technologies. In that matter, Radiofrequency (RF) photoinjectors have become the workhorse when low emittance and high peak current are required. Some of these applications at CERN include the production of witness electron bunches for plasma wake field acceleration in 10 m plasma columns [1, 2, 3], or irradiation experiments at GHz repetition rates in the CLEAR facility [4, 5]. Beyond CERN, free electron lasers (FEL), electron diffraction microscopy, or high photon energy sources in the X-ray and γ-ray regimes [6], are examples of machines that require ultrafast and well synchronized high peak current electron bunches. The existing technologies are suitable for accelerator facilities, but they require drastic modifications in order to be considered for industrialization and adaptation to different work environments. One such modification is related to the cathode technology. For instance, replacing Cesium Telluride by copper as a photoemissive medium would be beneficial : its much lower requirements for vacuum, and better lifetime (normally years of continuous operation) would prevent numerous
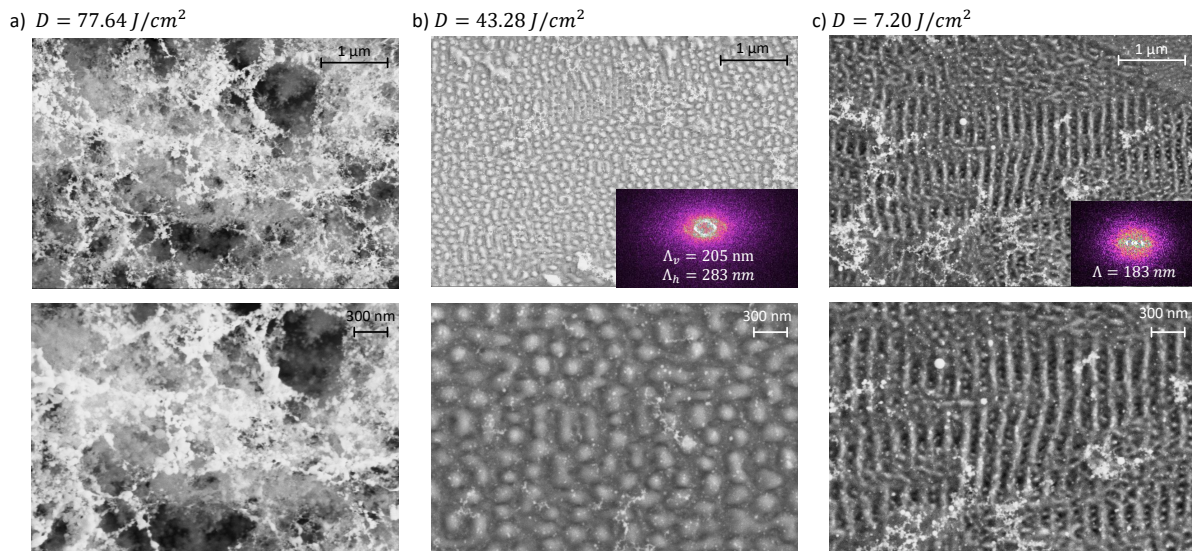
Figure 1. SEM micrographs of laser processed copper surfaces showing three different machining regimes : (a) intense ablation at $D = 77.64$ J/cm^2 with no discernible structures; (b) "nanohills" structures in the shape of hatched LIPSS at a dose $D = 43.28$ J/cm^2 with vertical and horizontal periodicities Λ_v and Λ_h given by the 2D FFT; (c) LIPSS structure of low spatial frequency at $D = 7.2$ J/cm^2 with a main periodicity Λ given by the 2D FFT.

manipulations including photocathode exchanges or rejuvenation, allowing for true continuous operation without interruption.

To make a metal comparable to their rival semiconductor photoemitters, the main challenge is to improve its QE performance in a way that is simple to fabricate, in-situ, and durable. We aim at optimizing the plasmonic photocathode approach [7, 8] for DUV-irradiated copper, thanks to tailored nanostructures being the result of a surface treatment done directly in the RF gun with the same laser used for producing the electrons. Such strategy then does not require an intervention in vacuum systems, shipment of cathodes, or utilizing equipment that is not already present in the photoinjector. The study of the interaction of light with nanostructures is a very active and fast-paced area of research [9, 10] . Achieving sufficient field enhancement using nanostructures is challenging, in particular producing them accurately over large areas. In fact, the highly local nature of the phenomenon in the nanometer range demands extreme precision and hence induces very long production times over large areas (with Electron Beam Lithography, for instance). For electron emission, the enhancement of laser fields in nanostructures has been shown to be an efficient manner of extracting electrons with enormous spatio-temporal precision [11, 12]. Such schemes normally enhance the emission due to multi-photon or tunneling processes occurring at the tips of the nanostructures or needles. Comparatively, less attention has been given to the enhancement of both the electron emission probability and electron supply function of materials, when irradiated under intense laser fields but operating photoelectrically above the work function. Such regimes of higher intensity would indeed increase the maximal charge producible, but at the same time inevitably increase the emittance. Yet many applications do not require such low emittance to operate, but they require rather high average or peak currents. In such a scenario, it is then logical to consider the benefits of exploiting laser produced strong-fields at metallic nanostructures. Moreover, the requirements for spatial regularity and morphological precision of the nanopatterns is further alleviated.

In this paper, we study the generation of such nanostructures in copper using exclusively

DUV ultrafast pulses produced by our photoinjector laser. We demonstrate the possibility to produce Laser Induced Periodic Surface Structures (LIPSS) as well as other types of periodic nanometric morphologies at high repetition rate, very low laser fluence, and with very finely tuned machining parameters.

2. Ultrafast DUV Laser Nanopattering in copper

Of all the possible means to nanopattern a copper surface, we have chosen Laser Induced Periodic Surface Structuring (LIPSS), for it is a fast and efficient method to easily produce quasi-periodic nanostructures of tunable size using an ultrafast laser beam [13, 14, 15]. The electric field of the incident pulses excites resonantly Surface Plasmon Polaritons (SPP) which induces a periodic modulation of the electromagnetic energy at the surface. This organized spatial variation of energy density ultimately ablates and reorganizes matter into quasi-periodic ripples. The subsequent pulses reinforce the pattern thanks to the seeding of the previously produced surface ripples, allowing high regularity over large surfaces. The spatial periodicity Λ of such structures is directly linked to the wavelength of the incident pulse λ through the relation:

$$\Lambda = \lambda \times \Re \left\{ \sqrt{\frac{\varepsilon_m + \varepsilon_d}{\varepsilon_m \varepsilon_d}} \right\} \tag{1}$$

where $\Re$ signifies the real part of the complex dielectric constants ε_m and ε_d of the metal and dielectric media, respectively. This equation tells us that a given incident wavelength λ will produce LIPSS of periodicity $\Lambda < \lambda$ in most cases, although it ultimately depends on the detailed irradiation conditions.

In order to obtain the maximal field enhancement possible during the photoemission process, the peak of the plasmonic resonance must match the photoinjector laser wavelength. This suggests that the structures should be fabricated with the same wavelength that will later irradiate the surface to extract electrons, although it is not strictly required in general due to the flexibility of the process to adjust the ripples' periodicity. Nevertheless, the use of DUV ultrafast pulses to process Cu substrates remains largely unexplored beyond the picosecond regime at high repetition rates [16]. A possible reason is linked to the work function of Cu being $\phi = 4.46$ eV which corresponds to a wavelength of 278 nm, and so the absorption-emission regime beneath this value will consist mostly of single-photon processes. It is expected that electron temperature and density at the surface will experience significantly different dynamics when compared to longer wavelength multi-photon excitation.

To fabricate nanostructures on a copper surface with a DUV beam, we developed a nanomachining setup based on a PHAROS femtosecond ultrafast laser source. This laser is a Yb:KGW diode-pumped type, delivering an output beam in the infrared at 1030 nm up to 2 mJ, with a pulse duration between 190 fs and 10 ps. The beam is then converted to DUV using efficient second and fourth harmonic generation stages using thin BBO crystals, to reach a working wavelength of 257 nm. For our experiments, the output in the infrared was set at 15 µJ and a repetition rate of 10 kHz, giving an energy per pulse of 300 nJ and a pulse duration of approximately 170 fs. The pulse energy impinging the sample was adjusted using a combination of a Brewster Thin Film Polarizer (TFP) plate and a motorized zero-order half-waveplate at 260 nm to control precisely the amount of light delivered to the cathode surface. Finally, the beam was focused with a 100 mm focal length lens onto the sample, which was placed on a 3-axis nano-positioning stage to allow displacements down to 200 nm with repeatability and accuracy. The cumulative energy deposited on the sample surface, which is the key quantity to tune the morphology and periodicity of the plasmonic structures, is expressed as the integrated dose parameter D, in J/cm^2, defined as :

$$D = F_0 \times N = \frac{E_0}{\pi \omega_0^2} \times \frac{2\omega_0 f_{\text{rep}}}{v} \tag{2}$$

where $F_0 = E_0/\pi\omega_0^2$ is the single-pulse fluence as a function of the single pulse energy E_0 and the Gaussian beam waist at focus ω_0, and $N = 2\omega_0 f_{\text{rep}}/v$ is the cumulative number of pulses deposited on the surface as a function of the repetition rate f_{rep} and the machining speed of the stage v. Note that the dose is not constant along the axis of the stage's movement, and so D here is an average exposure of the sample to the DUV radiation.

The parametric study was conducted by producing so-called "matrices" of surface nanomachining, consisting of a series of consecutive parallel laser scans, and each matrix has a different set of parameters to parametrically cover a wide range of integrated doses D. The machining speed v, the spatial separation between consecutive and adjacent laser scans, and the single pulse energy E_0 were the main parameters investigated. We found that these are the ones giving the widest tunability range for nanostructure morphology and periodicity. The speed was adjusted between 50 and 2000 µm/s and the pulse energy was set to three different values: 61, 43 and 34 nJ. Taking a spot size $\omega_0 =10$ µm (experimentally measured value), we obtain a dose D in the range between 2.58 and 77.64 J/cm^2.
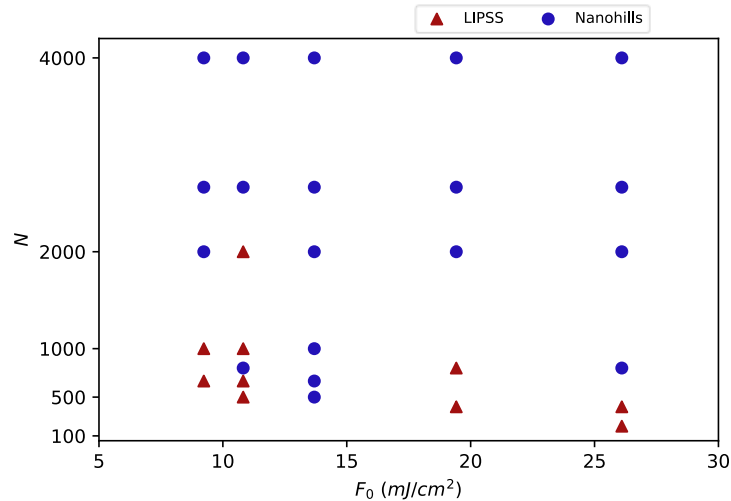

Figure 2. Distribution of different nanostructure types depending on the single-pulse fluence F_0 and the cumulated number of pulses N.

2.1. SEM analysis

Indicative results of the different processing regimes are depicted in Fig. 1. The maximal dose delivery induces an "intense ablation" regime where the Cu surface is melted and highly oxidized with no perceptible regularity or ordered structure formation. At a very low dose level beneath 8 J/cm^2, LIPSS formation is achieved, as it is apparent in Fig. 1.c. Their periodicity Λ was in the range of 175 nm to 190 nm, as given by the 2D FFT analysis of the pattern shown inset. To our knowledge, this constitutes the first demonstration of LIPSS patterns obtained under femtosecond DUV irradiation at such a low fluence, showing a periodicity that goes well below the previous results obtained under green and infrared illumination. This is an expected result given by Eq. (1) with an incident wavelength in the DUV like ours. We have also generated an unusual nanopatterning regime in an intermediate range of doses between 50 J/cm^2 and 5 J/cm^2, shown in Fig. 1.b. These structures resemble LIPSS in the overall

morphology, but have periodic grooves in both vertical and horizontal directions, turning the ripples into nanometric blobs of "hills" with variable shape from a perfect hemisphere, to an ellipsoid. They also present slightly larger spatial periodicity in both the vertical and horizontal direction, as given by the 2D FFT in Fig. 1.b. This larger periodicity most likely corresponds to the linear combination of the superposition of two perpendicular regimes, modulating the SPP amplitudes, resulting in shallower grooves and thus, larger periodicities. These results, although similar to previous work conducted regarding DUV LIPSS in copper [16], suggest that there is an importance in the choice of laser and machining parameters beyond irradiation fluence and wavelength. In fact, with a pulse duration two orders of magnitude below and a higher repetition rate, we obtained structures similar in morphology but significantly scaled down in periodicity, and at lower cumulative fluence. Figure 2 shows a summary of parameter space where the two main nanoprocessing regimes occur, namely "nanohills", corresponding to structures with morphologies resembling the ones depicted in Fig. 1.b, and LIPSS patterns as seen in Fig. 1.c.

3. Conclusion

The direct laser fabrication of DUV resonant plasmonic nanostructures was demonstrated in copper employing 10 kHz DUV femtosecond pulses. A wide range of nanostructures were produced overcoming the challenges arising in this above-work-function plasmonic DUV regime, showing the flexibility of our fabrication technique. Different ranges of cumulative laser fluence showed the production of different type of nanostructures, due to the variable morphology of the SPP generated and its complex spatially distributed interferences. LIPSS nanostructures as well as a new regime of nanometric "hills" (hemispherical) were obtained, both with spatial periodicity below 200 nm as expected. It should be noted, however, that the range of parameters where the nanostructures are formed requires fine-tuning in terms of integrated fluence parameters such as beam energy, machining speed and laser spot size. The next steps of the study will include the production of an operational DUV-nanostructured photocathode to be installed in RF guns at CERN, and to compare its performance with the currently existing green photocathodes. The results showcase the possibility of accessing plasmon-assisted photoemission in a simple and in-situ manner.

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