Measurement of the C12A7:e- thermionic emission enhancement due to photon exposure

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Abstract. In this work, a test set-up device is designed, developed and manufactured to perform a direct measurement of the current emission enhancement that the photon absorption can bring to the thermionic emission in a Photon-Enhanced Thermionic Emission Device (PETED) where the C12A7:e- electride is used as the semiconductor due to its low work function value of 2.4 eV. Even though the measured thermionic emission starts at low operational temperatures, obtaining for example a current density emission of 5 mA/cm^2 at 500 ºC, there is barely an increase of 1% in the current emission when the device is exposed to a source of photons. This effect is mainly due to the presence of a dielectric layer at the material surface, which acts as a barrier, reduces the current enhancement effect from photon excitation, and drives to a limited efficiency of 27 µA/cm^2/W.

1. Introduction

The essence of this work is based on the E.T.PACK project [1], which main objective is to develop a propellant-free device based on a low work function tether that operates under different principles. It produces a drag force by taking advantage of the natural space environment: the geomagnetic field, the ambient plasma, and the solar radiation. In this project, our own objective is to develop a Photon-Enhanced Thermionic Emission Device, hereinafter named as PETED, based on a C12A7:e- electride material due to its low work function value of 2.4 eV [2–4].
The thermionic emission is the release of electrons from an electrode by virtue of its temperature, when the thermal energy delivered to the charge carrier overcomes the work function of the material. This concept that has been previously published and studied [5,6]. Nevertheless, the photon-enhanced thermionic emission is a novel concept, firstly introduced by the Stanford University [7], consisting in combining the quantum effect of the large energy of solar radiation photons to excite electrons, as in photovoltaic cells, with the thermal mechanism of thermionic emission. In this way, our main objective is to perform a direct measurement of the emission enhancement in a PETE device where the electride is used as electron emitter, combining the effect of thermal and photonic energy sources. In Figure 1, a scheme of the PETED is provided together with an illustration of the produced electron emission, represented in red for electrons emitted as effect of the thermal source located under the electride (thermionic emission) and in blue for the electrons emitted due to the contribution in the emission of electrons due to the incidence of photons (photon enhanced emission).
The following sections describe the materials and the setup used for the tests, the different configurations employed, and the main results and conclusions.

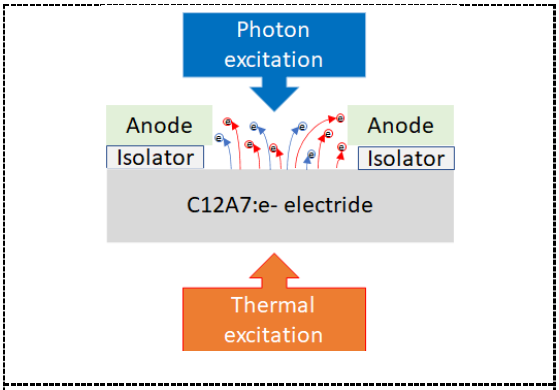


Figure 1. Scheme of the Photon-Enhanced Thermionic Emission Device (PETED)

2. Materials and setup

In the next section, a brief description of the electride material is introduced, along with the other required materials for the PETED. In addition, the setup used for the test measurements is also presented.

2.1. C12A7:e- electride material

The C12A7:e- electride, hereinafter named as electride, is a doped ceramic semiconductor which reaches electron concentration levels close to $2.3 \cdot 10^{21}$ cm^3, and with a work function of approximately 2.4 eV [2,8–11]. This material is synthetized from a wide-bandgap insulator with a reduction process at high temperature where the O_2^{2-} ions present at the crystal cells of the insulator are substituted by electrons. By means of this process, the electride behaves as a metallic conductor with high conductivity at room temperature. In this case, the injected electrons occupy the conduction band, and migrate through the electride crystal by tunnelling. In addition, this material can operate at low temperatures, it is chemically inert, and it is produced in Europe with unexpensive locally available materials and processes.

2.2. Oxide and metal layers

According to the scheme of the PETED presented in Figure 1, two layers on top of the electride material are required: the anode based on a metal layer, and the isolator based on an oxide layer. These oxide and metal layers were selected according to different criteria. The considered parameters for the selection of the oxide layer material were the TEC (Thermal Expansion Coefficient) matching, the evaporation rate in high vacuum, the reaction with electride at high temperatures, and the adherence of the oxide to metallic and to electride surfaces. In this case, the hafnium oxide (HfO_2) was the ideal candidate. It was deposited by means of reactive sputtering and PLD techniques. For the metal layer, molybdenum was selected due to its good adherence to the electride substrate, its good electrical conductivity and TEC matching, and its low oxidation enthalpy and low evaporation rate at high temperatures in vacuum.

2.3. PETED setup

In this section the PETED setup used for test and characterization is described (see Figure 2). The heater, located below the PETED, can reach up to 900 ºC and is based on an infrared lamp within a coated tube providing high confinement of thermal radiation. The photon source, such as an UV led or deuterium lamp, are positioned towards the emitter surface. The electride sample emitter is placed in the test setup on a graphite structure due to both a good thermal conductivity and an adequate TEC matching of both electride and graphite materials. This holder has also the mission to house the thermocouple to measure the temperature reached at the emitter. Regarding the electrical connection, several power supplies and meters are introduced to determine the operation conditions and to measure the current emission. This setup is placed into a vacuum chamber able to reach up to $1 \cdot 10^{-9}$ bar after a cleaning process with Argon.

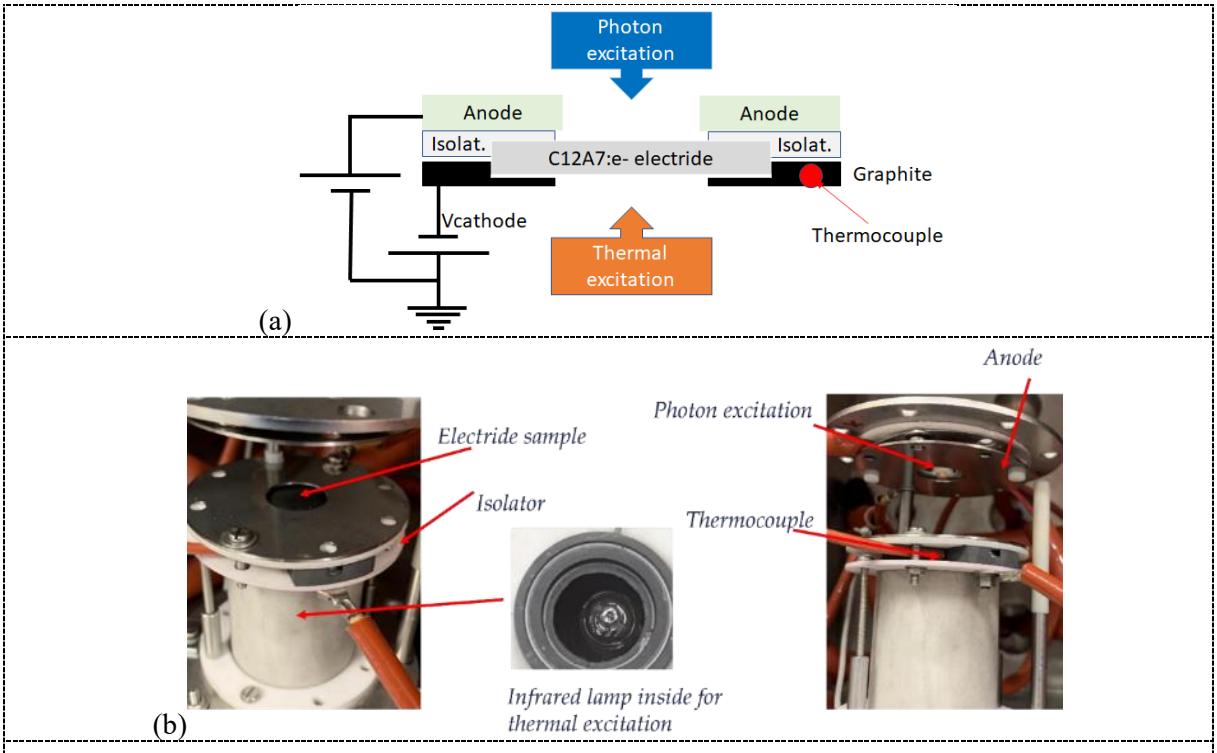


Figure 2. (a) General scheme of the PETED. (b) Photographs and description of the PETED setup.

3. PETED tests and results

In this section, the performance test of the PETED is evaluated through the combined effect of thermal excitation, for a temperature range between 300 and 500 ºC, and the contribution from the photon excitation provided by several UV LEDs with different wavelengths. Additionally, the device performance is also tested for the highest possible photon energy via a deep UV Deuterium lamp with a wavelength of 180 nm (6.89 eV). Regarding the electride layer, different configurations were tested using either thin-film depositions or bulk material. Table 1 presents a summary of the different combinations of configuration and excitation sources tested for the PETED.

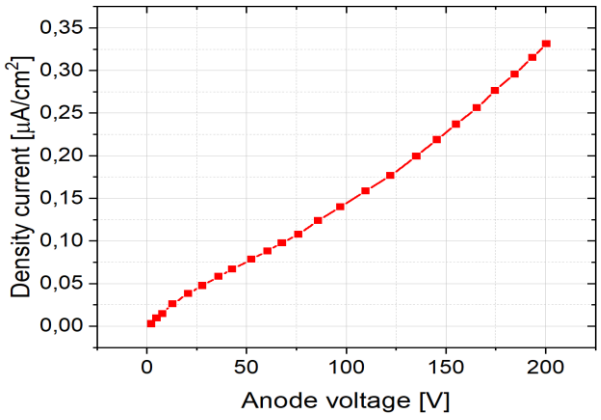
Table 1. Summary of the configurations used for the PETED performance tests

	Photon excitation	Thermal excitation	Photon + thermal excitation
Excitation source	UV LEDs Deuterium lamp	Infrared lamp	UV Led + Infrared lamp
Electride	Thin-film Bulk material	Thin-film Bulk material	Bulk material

3.1. Electride thin film with thermal excitation

In the first configuration, the PETED is based on an electride thin film while applying only thermal excitation with the heater. In this configuration, it is mandatory to guarantee that the deposited material keeps the thermionic emission properties. Pulsed laser deposition (PLD) and pulsed-DC magnetron sputtering techniques were employed to deposit the electride [12]. The highest quality and purity of the thin-film layer was obtained by means of the PLD. Nevertheless, the pulsed-DC magnetron technique was finally used due to the simplicity of the process, which enables to use any mask, but still obtaining an accurate composition of the material. Figure 3 shows the measured emission current at 700ºC of an

electride thin-film layer over a polished graphite disk used as substrate. In this case, the anode was located 2 cm above the PETE Device.



(b)

Figure 3. Emission current at 700ºC as function of the anode voltage

The results show a current emission in the order of pico-amps at 350 ºC. This current level is lower than what could be expected considering the low work function of the material. Nevertheless, as Figure 3 indicates, when the temperature and voltage extraction are increased, we were able to obtain a value of 0.32 μA at 700ºC with 200V in the anode.

3.2. Electride bulk and thin film with thermal excitation

Additionally, several other PETED configurations were designed based on a chip scheme to reduce the voltage and to increase the current emission when applying thermal excitation. In this case, different substrates were used while using the same configuration layer: metal/electride/oxide/metal (Figure 4).

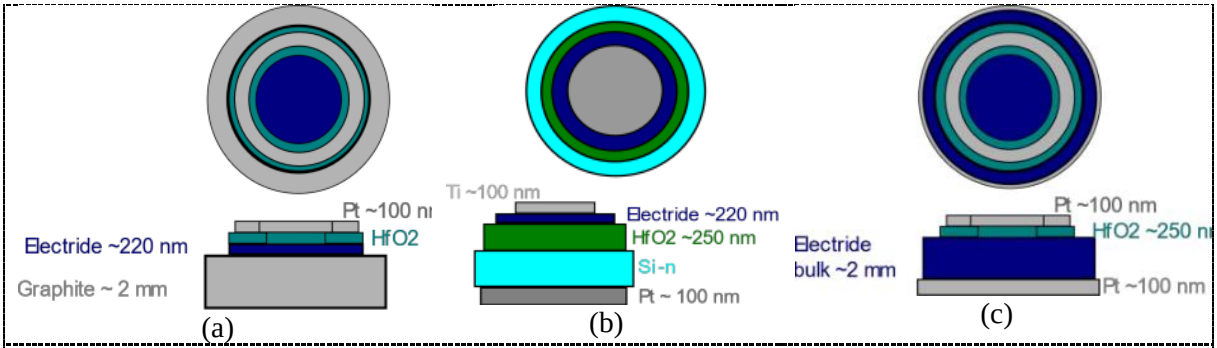


Figure 4. (a,b) PETED based on a thin-film layer of electride and (c) on bulk material

Nevertheless, for all cases, different short-circuits appeared between top and bottom metal layers indicating a non-effective isolation with the oxide layer. This was mainly due to the roughness of the surface. The alternative was to use a polish bulk electride sample in order to reduce surface roughness up to 20 nm (see Figure 5). With this idea no further short-circuits were observed, but still a low current emission in the order of micro-amps was measured at 500 ºC. This negative outcome, which is line with previous results [13,14] is, to our understanding, due to the presence of a non-conductive layer in the material surface which acts as a resistance, resulting in a low current emission under vacuum conditions.

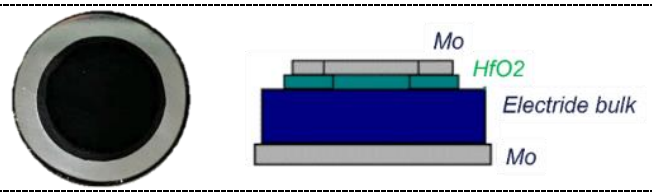


Figure 5. Picture and scheme of the PETED based on a polish electride sample

3.3. Electride bulk and thin film with photon excitation

In this section, a series of specific tests were performed using only photon excitation. In this case, a set of UV LEDs with different wavelengths, from 365 to 520 nm, were selected as photon sources. A spectrometer Anon Lasertrack LR2 Spectrometer 200-1200nm was used for the calibration process of the LEDs. As Figure 6 shows, a maximum current emission of 100 nA/cm^2 was obtained with an UV LED of 365nm. Similar results were also obtained with other wavelengths of 445 and 520 nm. This current emission is not relevant compared with the previous response to thermal excitation, since it only represents an enhancement of approximately 1% to the total current emission previously measured.

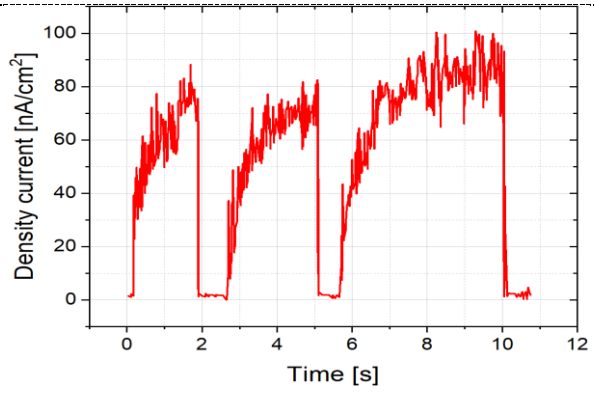


Figure 6. Current emission measured during different on/off cycles with an UV LED of 365nm.

Finally, the PETED was also tested with the highest possible photon energy via a deep UV Deuterium lamp with a wavelength of 180 nm, which corresponds to an energy of 6.89 eV (see Figure 7). The objective of this test is to verify if the low contribution of the photon excitation is due to a low energy level of the photons.

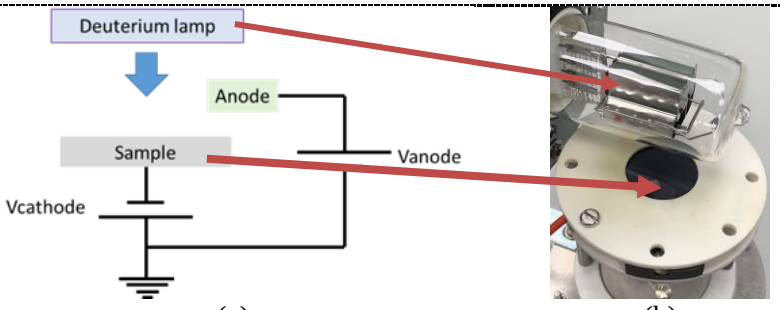


Figure 7. (a) Scheme and (b) picture of the PETED test set-up with the deuterium lamp as photon source

Still, this UV source continues showing a minor effect in the emission current since only a density current emission of approximately 28 nA/cm^2 was observed with an anode voltage of 400V. This negative outcome, as previously commented, is due to the dielectric layer at electride surface.

3.4. Alternative solution of the PETED based on PEDOT:PSS with photon excitation

Based on the previous results, the photon excitation has shown a neglectable effect on the current emission. Nevertheless, an additional test was performed with the objective is to determine if the photon excitation has some effect on the electron emission of the device due to the p-n union, and to validate the scheme of the PETED. In this alternative configuration, the PETED is based on PEDOT:PSS which is a polymer mixture of two ionomers (one component carries a negative charge and the other a positive charge) [15,16]. Thin-films of PEDOT were used as an interface layer between top metal layer and Si-n substrate. In addition, the same configuration was used with an electride bulk sample as substrate.

The PETED was exposed to three photon excitation levels: darkness, lab lighting and a UV LED of 392 nm. Additionally, two different anode metals were used: Au and Pt. As Figure 8 indicates, there is an emission enhancement due to photon excitation which validates the designed PETED architecture. The response with the Au metal is superior due to its lower work function. Nevertheless, this result was not reproducible when using the electride as substrate. This means that the Si-n is sensitive to photon excitation, while the electride is not. This is in line to the previous results obtained with photon excitation, due to the non-conductive surface layer of the electride.

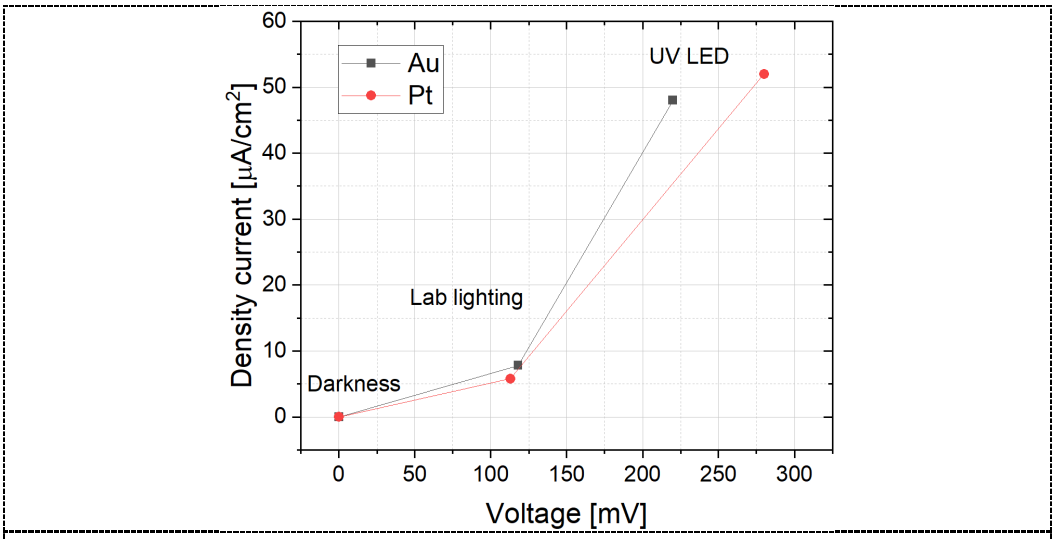


Figure 8. I-V curve of the PETED based on PEDOT:PSS with Si-n as substrate

3.5. Electride bulk with photon and thermal excitation

After all experiences learned during the previous configurations, a final prototype was manufactured for measuring PETED performance with the combination of photon excitation, with an UV LED of 380 nm, and thermal excitation in the temperature range of 300 to 500ºC. In this case, new materials, such as Mica or Macor, are used since these are thermal resistant and support temperatures up to 800 ºC with no degradation. Figure 9 shows a scheme of the PETED engineering prototype together with a picture of the device under operation inside the vacuum chamber. In this configuration, during the continuous thermal excitation, the UV LED was switched on/off obtaining only an enhancement of approximately 1% to the total current emission, which is the same behaviour as described in the previous experiments. Nevertheless, as Figure 10 indicates, we could observe that the extracted current emission is proportional to the applied anode voltage being able to obtain 5 mA/cm^2 at 500ºC with 150V. It is important to identify that to achieve that temperature almost 180W are required in the heater element. Therefore, the relationship density current/power is 27 μA/cm^2/W with 150V, or 1.86 μA/cm^2/W with 0V (open loop).

With a power input of 180 W and a 0.75 W of generated output, an efficiency of 0.42% has been achieved with this PETED configuration.

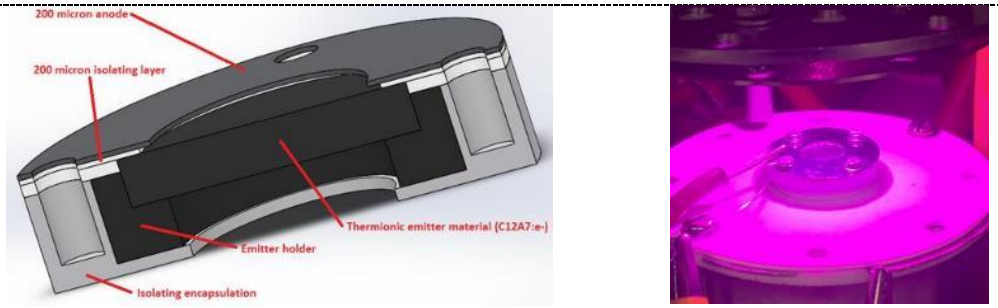


Figure 9. (a) Scheme of the PETED. (b) PETED with photon/thermal excitation

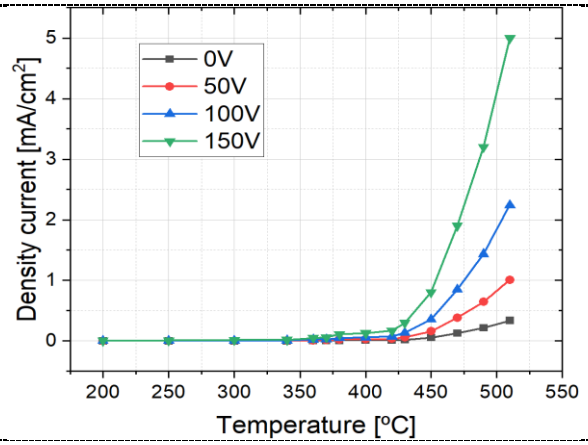


Figure 10. Current emission as a function of the temperature and voltage

4. Conclusions

The stability of the electride at room temperature, is a unique case for a material with such a low work function (2.4 eV) that should immediately deteriorate in any oxidizing environment. This protection is due to the formation of a dielectric layer on the surface due to the physical impossibility of finishing the crystalline cells at the edge of the material keeping the electrons confined. This layer reduces the current emission and can also produce instabilities if it is not properly operated. Additionally, the thermal radiation emissivity coefficient of the electride (0.9) is also a drawback since the heat radiation energy will be spent in thermal radiation emission of the electride emitter rather than contributing to electron emission.

Therefore, only with the appropriate design criteria of the PETED, it is possible to obtain a satisfactory current emission of 5 mA/cm^2 (500ºC) when using thermal excitation. Nevertheless, with photon excitation only an enhancement of 1% to the total current is measured. In conclusion, although a low current of 27 µA/cm^2/W with 150V is obtained, the PETED have a broad range of applications where typical photovoltaic panels are not viable when required to operate under high temperatures.

Acknowledgements

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