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doi:10.15199/48.2020.05.15

Graphite-glass screen-printed film electron emitters

Abstract. *In this paper, we present the technology and principle performance of film electron emitters made of graphite-glass composite paste using screen printing. As a result, we got working emitters with emission current densities and the turn-on electric field voltage comparable to film electron emitters made of nano-scale carbon composites that were reported in the literature.*

Streszczenie. W tym artykule prezentujemy technologię i podstawowe charakterystyki pracy warstw emitujących elektrony i wykonanych techniką sitodruku z wykorzystaniem pasty kompozytowej grafitowo-szkłanej. Emitery te osiągnęły gęstości prądów emisji oraz napięcie progowe, przy którym rozpoczyna się emisja, porównywalne do tych, jakie zostały opisane w literaturze naukowej dla materiałów węglowych w nano-skali. ***(Graiftowo-szklane emitery elektronowe wykonane techniką sitodruku)****.*

Słowa kluczowe: grafit, szkło, kompozyt, emiter elektronów, sitodruk
Keywords: graphite, glass, composite, electron emitter, screen printing

Introduction

The electron emitters are used in electron guns [1] for high-resolution electron microscopy or X-ray inspections [2,3]. Usually, the electron emitter is a sharp tip of hundreds of nanometers in diameter [4]. Such a high-aspect-ratio structure ensures the electric field strength and prevents electrons from spreading in a wide-angle. Thanks to this approach, the formation of a focused electron beam can be facilitated for the next step i.e. the electron beam control by electro-optics included in the electron gun. For the fabrication of electron emitters, the commercial materials are tungsten (W), lanthanum hexaboride (LaB_6) or cerium hexaboride (CeB_6) [4]. Meanwhile, in the research, there has been noticed a growing popularity of nano-scale carbons or nanocarbons, such as graphene, carbon nanotubes [5,6]. Recently, these nanocarbons have been used as functional materials in a form of suspended nanoparticles in a solvent and next screen printed and dried to form an electron emitter [7,8]. Although the screen-printed technology is considered as a low cost and scalable technique to fabricate film structures [9], the nanocarbons reveal many application issues [10] compared to abundant and well-known graphite.

So far, for electron emitters, the graphite has been used as a building material for a rod alone offering robustness against ion bombardment with emission current exceeding 2 mA and anode current stability about 2.8% [11,12]. In other works, a graphite rod has played the role of a substrate for the nanocarbons (here: carbon nanotubes, CNTs) surrounding the rod's tip [13]. Such solutions have prolonged the lifetime of the CNTs, which were found to be deteriorated during emission due to the adherence issue.

In this paper, we present graphite-glass screen-printed film electron emitters as an alternative for the nanocarbons. The authors also discussed the potential and issues of graphite-glass screen printed electron emitters that were revealed during their testing.

Graphite based composites have been widely reported for electronics: transparent conductors [14], resistive layers [15, 16], and sensors for chromium [17], proteins [18], heavy metals [19]. Thick-film technology is especially required for high-temperature applications, where ceramic is a dominant substrate material due to its high-temperature stability exceeding 1000°C [20] It is especially crucial if we consider devices to be used in a harsh environment, which bring new functionality and where the electron emitter is a key component [21]. Graphite has shown its high reliability being applied in high energy fields e.g., in nuclear reactors [22] as control rods for fuels.

Graphite has been also used to make composites. However, the majority of these composites presented in the literature [15,16] has contained an organic matrix, which can withstand up to 150°C. Therefore, in our work, we decided to use glass for a matrix to fill with graphite. This approach enables to combine the benefit of high-temperature stability of glass with the good physical and chemical resistance of graphite. Moreover, the graphite's work function contributing to electron emission is close to the nanocarbon materials (4.62±0.02 eV vs. 5.1±0.1 eV for CNTs) [23, 24].

Experimental details

Three various composites were prepared and named as G-1, G-2, and G-3. These composites differed by a weight percentage content of graphite powder (Sigma-Aldrich, grains below 20 μm) being 1.5, 2.0 and 50 wt.-%, respectively (Table 1). For a matrix, we chose sealing glass SG-683K (Heraeus). It offers good adhesion to the various types of substrates (ceramic, silicon) and withstands high temperatures. In addition, this type of glass mixed with graphite powder provides good cohesion and viscosity of the final composite. The latest are important factors to make screen printing satisfactory. The graphite powder and glass were mixed manually for 10 min., next sonicated for 5 min. resulting in a high viscous paste, ready to use for screen printing.

Table 1. The summary of the films electron emitters.

Composite	Graphite [wt.-%]	Film dimensions [mm x mm]
G-1	1.5	3x3
G-2	2.0	3x3
G-3	50	5x5

The paste was screen-printed on a silicon substrate through the dedicated mask (screen 200 M), dried at 125°C, 20 min. on a hot plate. Next, the film was fired in an oven at 550°C for 100 min. This step was necessary to reorganize the matrix with graphite grains as it could be seen in figure 1, where the film is presented before (a) and after (b) firing.

Such prepared films were tested concerning their sheet resistance (Ossila Four Point Probe, UK) and then combined into the two-electrode set-up to confirm experimentally their ability to emit electrons. To build a two-electrode set-up, the substrate with the emitting film was covered by a glass frame acting as a dielectric spacer (0.7 mm thick) and a counter electrode. In both cases, the substrate was p-doped silicon with resistivity below 0.001 Ohm·cm). All these components were placed apart and formed a two-electrode set-up sample for measurements: a

substrate with an electron emitter acted as a cathode, while an opposite aligned substrate as an anode. The samples were placed in a high-vacuum chamber, where, at the pressure of about 1.0×10^{-5} mBar, we measured emission characteristics of the samples using high-voltage supply (High Voltage Power Supply Polon ZWN-41, PL) and a digital multimeter connected to a PC and handled by a software using data logging system (Bs25x Logging System, ver. 5.0.0.3, B.T.C. 2013). The voltage was applied to the anode (*V*) through a shunt resistor (100 kΩ) and the cathode was grounded. The emission current (*I*) was calculated from Ohm's law using the well-known resistance The schematic drawing of the two-electrode set-up sample is presented in figure 2.

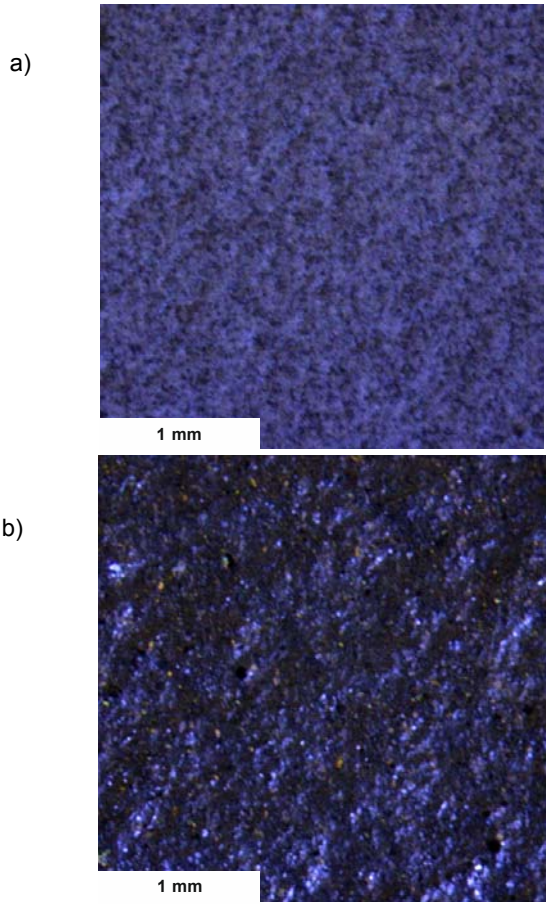

Fig.1. The optical microscope photography of the screen-printed film surface before (a) and after (b) firing

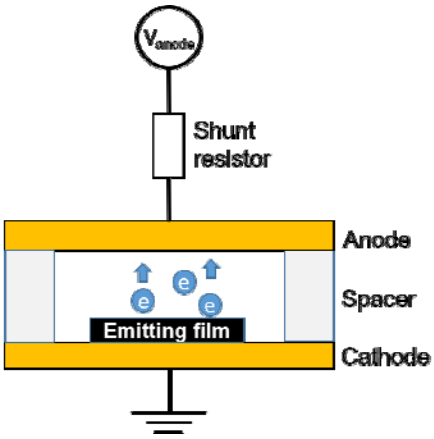

Fig.2. The schematic drawing: a two-electrode set-up of the measured samples including the electron-emitting film

First, twice one by one were confirmed the current-voltage (*I-V*) characteristics starting from 0 up to 3.5 kV with every 100 V step. Second, the current trend was presented on a time scale for at least 10 min. Third, the I-V was repeated for the third time.

Results

The measured sheet resistance of the prepared composites varied as follows: around 900 Ωmm^{-1} (G1), 800 Ωmm^{-1} (G2) and 550 Ωmm^{-1} (G3), respectively. We related the sheet resistance mostly to the distances between graphite grains, which could be observed on the film surfaces by scanning electron microscopy (SEM) images (fig. 3). There is a visible difference in the surface morphology: for the film made of G-1 (fig. 3a) - most of its surface was charged up due to the exposed dielectric glass content to the electron beam. Though the surface is smooth, there are many empty pores, which contribute indeed to the dead volume of the film. On the contrary, for G-3 (fig. 3b) there are multiple numbers of graphite flakes, densely packed between the glass and protruded vertically.

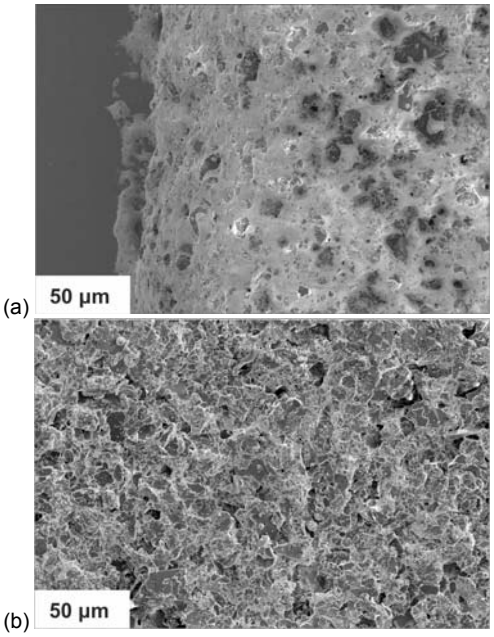

Fig.3. Scanning electron microscope images presenting the piece of graphite-glass film surface for the composite: (a) G-1, and (b) G-3

The instance of the obtained characteristic (provided according to the section "Experimental details") for an exemplary sample is presented in figure 4. As it is seen the first *I-V* curve does not have a non-linear and monotonic trend with the scattered points. The curves 2nd and 3rd became non-linear as it is expected for the electron emitter *I-V* graphs and are monotonic. Besides the turn-on field voltage, at which the emission current was detected, is slightly lower for the 1st curve compared to the 2nd or 3rd: 1.2 kV (0.17 Vcm^{-1}) vs. 1.4 kV (0.14 Vcm^{-1}), respectively. Hence, in figure 5 we present the data for the 3rd *I-V* curve.

In figure 5, there are presented the emission current dependences on the applied voltage for three types of composite films. The highest current level was achieved for paste G-1 with the lowest content of graphite. However, that curve was not as monotonic as in the case of G-3 composite. The film made of G-2 composite showed the shortest range of *I-V* curve: maximum current of 0.84 μAmm^{-2}, which was about 22 times lower than for G-1 film. For the film G1 and G3 it was 18.5 μAmm^{-2} and 5.6 μAmm^{-2}, respectively. Beside the G-1 film exhibited a less stable

emission than G-3: it has a peak at 1.2 kV, where the current dropped from 4.4 μAmm^{-2} down to 0.1 μAmm^{-2} and next started to increase.

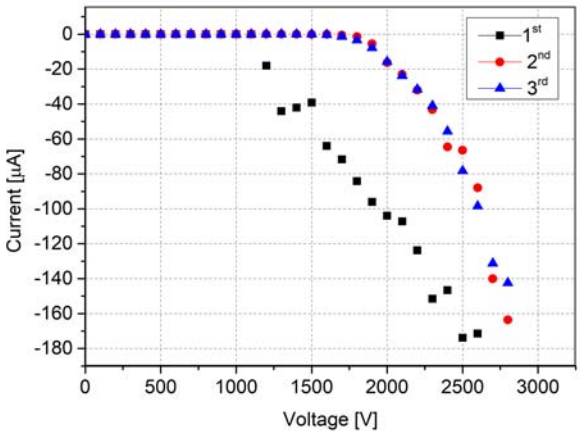

Fig. 4. The aging influence on an electron emitter - following I-V graphs for an exemplary sample using G-3 composite

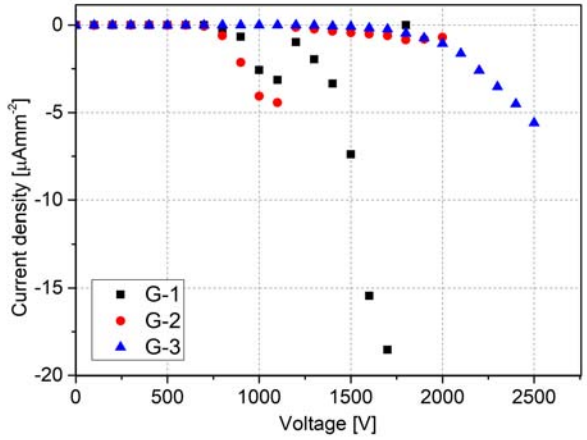

Fig.5. The *I-V* graph presenting the emission current dependence on applied voltage for film electron emitters made of various composites

Finally, figure 6 presents the current dependence on time. The sample was measured for about 10 min, at 2.2 kV. The current oscillated with the standard deviation of 1.5 μA, from the average current equaled to 30 μA what resulted in the coefficient of variation of 2.3%.

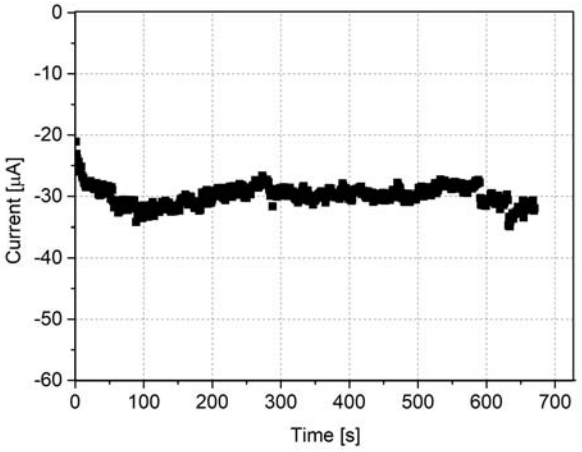

Fig.6. The graph presenting the current in time (G-3 sample) at 2.2 kV

Discussion

We presented the working emitting film based on abundant and well-known graphite mixed with glass to form a screen-printable paste composite.

Despite the graphite does not possess excellent mechanical and electrical properties as nanocarbon materials, it offers very good characteristics in terms of electron emission, achieving the emission current of hundreds of μA (fig. 4), which is comparable to those presented for the chemical vapor deposited CNT arrays or graphene-based composites [5-10]. It is especially here important when it is considered a low cost and accessibility of the technology, which for graphite is without doubt cost-effective, while processability is well known for the last 50 years.

We found the best electron-emitting properties possess the film made of the composite with the highest content of the graphite powder (non-linear and monotonic curve without peaks), albeit the highest current density was noticed for the lowest content composite (1.5 wt.-%) with 18.5 μAmm^{-2}. It is probably due to the so-called field screening effect which was noticed already for an emitter array [25]. We deduced it based on the SEM images, where we could observe, in case of the film made of the paste with the highest graphite content (fig. 3b), densely packed graphite grains protruded from the film surface and constructing indeed an array of point emitters. The current in time measurement resulted in the coefficient of variation was 2.3 % and does not vary from the number given in [12], i.e. 2.8%.

There are yet few issues that should be further developed: 1) stability of the current in time; and 2) the potential to increase the emission current density. Both of these issues need further research, especially in the field of composite film processing and post-processing. For example, we noticed the reorganization of the matrix, i.e. the graphite grains were pulled outwards the surface. In consequence, this increases the effective area of the usable point emitters, which is strongly related to the temperature and time of the process (fig. 1).

Acknowledgments

The work was financed by the National Science Centre Poland, project no. UMO-2016/21/B/ST7/02216 and statutory funds of the Wroclaw University of Science and Technology.

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T.M and K.L contribute equally to this work. T.M and K.L. defined the research topic, designed the experiments, SEM images, and wrote the paper. T.M designed and made graphite-glass composites, screen printing technology of electron-emitting films, did conductivity tests and related graphs. K.L. did measurements concerning electron emission of the composite films preparing the results in graphs.

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