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The electric charge transport in titania–alumina composite cold cathodes made using atmospheric plasma spraying and laser engraving

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ABSTRACT

Titania composite layers made by atmospheric plasma spraying (APS) technique and laser engraving have been investigated as field electron emitters (Atmospheric Plasma Sprayed and Laser Engraved APSLE cathodes). Emission characteristics of the emitters made of pure TiO_2 and those made of Al_2O_3+13 wt.% TiO_2 appeared to be comparable with the conventional emitters made of nano-crystal diamond or diamond like materials. The paper presents the results of the mechanisms of the electrical charge transport through the bulk of the APSLE composite layers. The electrical properties of tested layers were determined by means of impedance spectroscopy (IS).

Two equivalent electrical models based on IS measurements have been proposed. Behavior of these models reflects the electrophysical phenomena in the APSLE composite layers. Analysis of these models indicates that the conducting paths in the APSLE layers are formed by defect rutile and titanium suboxides (Magneli phases). The dielectric bead consists of rutile (TiO_2), corundum (Al_2O_3) and spinel (Al_2TiO_5). Spinel and traces of organic impurities present in the $Al_2O_3+40\%$ TiO_2 composite may completely lock the charge carrier transport in the bulk of material. It is probable that the organic impurities could have been a catalyzer of the spinel formation. There is an interesting result of plasma spraying Al_2O_3—40 wt.% TiO_2 powders on sprayed coatings. The electric properties of the coating depend upon the powder manufacturing method.

1. Introduction

Composite field emission cathodes are the technological alternative for more sophisticated Spindt type emitters [1,2]. The most common composites used for the field electron cathode making are carbon based thin films such as the diamond-like coatings (DLC) or micro/nano-crystalline diamond ones. In both, the current conducting features are graphitic phases and/or some defects immersed in insulating, diamond matrix. The active part of the cathode, where the electric field penetrates, is the top layer tens of nanometers thick [3,4]. The conducting features play an important role in creating the electrical paths and influencing the local electric field enhancement phenomena [5–7]. In general: the composite emitters should be characterized by a high aspect ratio: $\beta \approx h/r$ of their height to the radius of their tip/edge. β is called the field enhancement factor. For the active layer 50 nm thick ($h=50$ nm), the field enhancement factor can reach values of the order ~$k \cdot 100$ ($k=1,2,3$), when the tip/edge radius r is of the order of ~$0.5/k$, that means a few nanometers or less. Such condition is typical for the carbon based thin layers where the crystallites are of nanometer size.

The studies on composite cold cathode layers made with an atmospheric plasma spraying technique (APS) have been carried in the past decade. The APS technique is a thick film deposition process. The powder particles are injected into high temperature and high velocity jet of plasma gasses (up to 14,000 K, 800 m/s, usually argon + hydrogen). The particles are accelerated and molten in the jet, then impact a substrate surface. On the impact the droplets are deformed, solidify and build up the coating [8].

Additionally, after APS process, resulting layers can be laser engraved. The unique microstructure of such prepared layers appeared to be profitable for the field emitters, ensuring high β factors. However, there are some difficulties concerning the explanation of electrical properties. For convenience we will call such prepared cathodes: Atmospheric Plasma Sprayed and Laser Engraved APSLE cathodes (coatings).

The APSLE layers are hundreds of micrometers thick. Their very complicated structure and microstructured composition may substantially influence the electric carrier transport mechanism. A commonly used tool for the investigation of these phenomena is the impedance spectroscopy (IS) [9–13]. In this paper, an attempt of explanation of the electric charge transport in the APSL cold cathodes has been carried out. The impedance spectroscopy was the tool chosen for this task.

The IS should take into account the particularity of sprayed coatings which are built up starting from flat forms, called splats. For

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the atmospheric plasma spraying these splats can reach diameters up to several tens of micrometers and their thickness does not exceed a few micrometers. Also the splats themselves are often cracked. The successive splats create coatings with characteristic lamellar structures. Because the splats do not perfectly adhere to each other, the coating is porous. Lamellar structure cracks and pores result in anisotropy of physical properties, such as thermal or electrical conductivity. Their mechanical properties are also different from the corresponding solid materials [8,14–17].

2. Manufacturing

The composite field emitters should contain at least two phases of different electrical properties, i.e. a conducting phase and a dielectric one. The conducting phase makes it possible to build-up current conducting paths and the dielectric phase allows for electric field penetration into the bulk of composite. The mutual electrophysical and geometrical relations of phases influence the electric field enhancement factor and the density of emitted current. Because the field penetration into such electrically non-uniform material reaches only several tens of nanometers, it is desirable to obtain nano-crystalline structure of the functionally active composite phases in order to get large electric field enhancement factor β. In the diamond-like layers the functional phases are nano-sized grains of diamond (dielectric) and graphite or defective nano-sized diamonds (conductors) [3–6].

The plasma sprayed coatings show all necessary properties for application as composite electron emitters. Due to the non-equilibrium thermal action of the plasma stream on powder introduced to it, such as rapid heating and very rapid cooling, the structure of deposited coatings differs considerably from the initial one. This may result in formation coatings being particularly suitable for field electron emitters. Plasma sprayed TiO_2 and alloys of TiO_2 with Al_2O_3 show such kind of properties. These coatings of these materials are widely used in printing industry to protect against wear. The coatings being additionally laser engraved are used for the anilox rolls to transport a desired quantity of ink [18].

These coatings for anilox roll coatings have been investigated for several years as the electron field emitters [19]. Their chemical compositions were as follows: TiO_2, $Al_2O_3 + 13$ wt.% TiO_2, and $Al_2O_3 + 40$ wt.% TiO_2. The initial powders were produced in different ways and had different crystal phases. The details of the investigations are described elsewhere [20]. It should be noted that the $Al_2O_3 + 40$ wt.% TiO_2 powder produced by spray-drying, contained organic binder and its spherical grains of alumina and titania were closely packed together. Consequently, the large contact surface between both oxides may have rendered a possible reaction during flight in plasma that was leading to the formation of spinel Al_2TiO_5 as reported elsewhere [21]. The formation of spinel may influence the electrical and emission properties of the field cathodes.

The coatings were plasma sprayed by Advanced-Coating (Liege, Belgium) and their surface grinding and laser engraving were made by Haldenwanger, Berlin, Germany.

3. Results

3.1. Microstructure and field emission measurements

An example of SEM micrographs of the APSLE TiO_2 laser engraved cathode surface with 100 cm^{-1} cell linear density (in direction of the densest cell engraved) is shown in Fig. 1. The tested cathodes were laser engraved to reach 60, 100 and 200 cm^{-1} cell linear density (cld). The microstructure of APSLE field emission cathodes was also characterized using XRD, Raman spectroscopy and XPS [19]. The XRD data are summarized in Table 1.

Prior to the field emission measurements, the samples were washed in isopropyl alcohol in ultrasonic bath. The field emission data were collected using diode configuration. The anode–cathode distance was about 15 μm and d. c. voltages ranged up to 2300 V [19]. The as-sprayed and polished samples, laser engraved ones with 200 cm^{-1} line density and all $Al_2O_3 + 40$ wt.% TiO_2 APSLE cathodes did not emit electrons in the electric field range. The TiO_2 and the $Al_2O_3 + 13$ wt.% TiO_2 coatings engraved with 60 and 100 cm^{-1} cld appeared to be good field emitters with emission characteristics comparable with carbon composite based cold cathodes [4,22]. Typical example of the *I*–*E* emission characteristics is presented in Fig. 2.

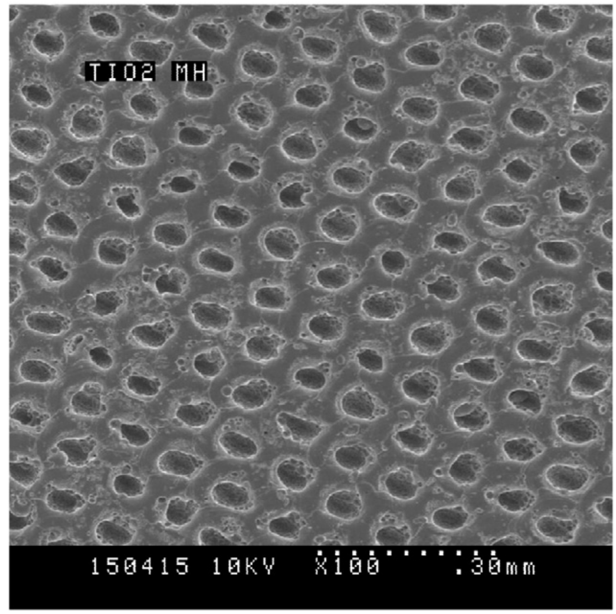

Fig. 1. SEM micrographs of the plasma sprayed TiO_2 field electron cathode laser engraved to reach the cell linear density of 100 cm^{-1}.

3.2. Impedance spectroscopy measurements

The impedance spectroscopy (IS) measurements were carried out with impedance analyzer Solartron 1260. The applied signal was 10 mV in the frequency range from 100 Hz to 1 MHz. The experimental data were analyzed with ZView program [23]. The electrical connection to the honeycomb-like surfaces was attained by the circular electrodes made of silver conductive lacquer. The contact diameter was about 2.5 mm. Examples of the experimental characteristics of the capacitance (C) and conductance (G) of the APSLE TiO_2–Al_2O_3 composites are presented in Fig. 3. An equivalent circuit model, shown in Table 2 with the frequency response identical with the measured IS data, have been developed using the ZView code. Components of the equivalent circuits reflect the physical phenomena induced by the electric field. In some cases the classic elements *R*, *L* and *C* are replaced by generalized element CPE (constant phase element) with admittance described by relationship $Y_{CPE} = Q(i\omega)^n$ where ω is frequency, *Q* and $0<n<1$ are parameters independent on

Table 1
The XRD microstructure data for the APSLE cathodes.

Cathode	TiO_2	$Al_2O_3 + 13$ wt.% TiO_2	$Al_2O_3 + 40$ wt.% TiO_2
Microstructure	TiO_2 (rutile)	TiO_2 (rutile)	↓TiO_2 (rutile)
		↓γ-Al_2O_3	↓γ-Al_2O_3
	↑*) Ti_xO_{2x-1}		↓Al_2O_3 (corundum)
		Al_2O_3 (corundum)	↑Al_2TiO_5
		Al_2TiO_5	
		Ti_xO_{2x-1}	

*) The arrows indicate the increase (↑) or decrease (↓) of the XRD spectra picks after laser engraving against the data for as sprayed coatings.