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Lighting sources with a cold cathode electron tube

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Abstract. Lighting sources with a cold cathode are widely used in electronics. The lamps with a cold cathode are used primarily as sources of white light in optical scanners, digital indicators, display panels and signalling devices. In the paper the advantages of carbonaceous materials as emitters of cold electrons and the possibilities of using them to create a cathode in an electron lamp are discussed.

Key words: carbonaceous cold electron cathodes, electron lamp, cold electron emission, lighting elements.

1. Introduction

Nano-materials are characterised by grains sized from 1 nm (several atoms, depending on the atomic diameter) to 100 nm (1 nm $= 10^{-9}$ m). Basic mechanical, physical and chemical properties of these materials, so different from properties of traditional polycrystalline materials, are related to their small size. Since they display limited possibilities of generating and transferring e.g. structural defects, responsible for plastic deformations, their resistance properties are much better. Decreasing the grain size can lead to changing properties of materials. Materials' modified performance of on a nanometric scale is also related to such phenomena as e.g. Coulomb blockade, quantum mechanisms or the predominance of border phenomena over the volumetric ones. Thanks to their exceptional qualities, the nano-materials are not only likely to improve our existence in the future, but also be intelligent enough to take over some tasks at present available only to humans. In order to produce these materials it is necessary, apart from having profound knowledge of physics, chemistry, biology and mathematics, to have access to research equipment enabling observation of nanometric phenomena. Because of the development of technology and introduction of modern research methods such as a scanning tunneling microscope, atomic force microscope, electron microscope or laser spectroscopy it is possible to observe and interpret the effects in new nano-materials.

For many years scientists have been interested in new materials using the cold electron emission effect. Special attention is paid to developing new nano-materials. Carbon is a particularly interesting material due to its ability to create various chemical bondings by means of variable participation of π and σ electrons in such bondings. For this reason carbon can create structures with any electric conductivity properties, starting from insulation (for diamonds) and ending with a metallic one for nanotubes. The fullerene addition helps obtain materials with different conductivity properties such as semiconductive, superconductive or semimetallic. Metallic nanostructures introduced into carbonaceous matrix can not only modify the electron structure of the system, but also generate quantum size effects and change certain properties not observed on a macro scale (e.g. light or electron emission).

The phenomenon of a cold electron emission has been known for decades. Its first quantification was published by Fowler and Nordheim [1–4], who studied cold emission of metal electrons. They initiated a series of studies on the cold emission of electrons from various materials such as metals, semiconductors and dielectrics. Among these studies there is a group of works connected with cold emission from carbonaceous materials, such as layers of diamond-like carbon (DLC) [5, 6], amorphous carbon [7, 8] or carbon nanotubes [9, 10]. Cold electron emission from the first two materials is observed for low values of threshold electric field, but its efficiency is not significant, the electron emission current obtained is unstable and tends to disappear quickly. For cold emission from carbon nanotubes, the current density is high, but there are problems with stability related to damaging the nanotube layer by the electric field.

2. Cold electron emission

Fowler-Nordheim (F-N) theory [1] describes the cold electron emission from metals to the vacuum taking into consideration tunneling effect of the electron wave function by the triangular potential barrier (Fig. 1). This theory is based on several assumptions, without providing for such effects as creating Schottky's barrier, the existence of ballistic or surface electrons or creating dipoles on the emitter's surface. All these effects cause decreased of effective work function by lowering of the value of the external electric field.

This theory is based on the following assumptions [1, 2]: 1) the electron structure of metal is typical for unbounded electrons; 2) the electrons are in a thermodynamic equilibrium; 3) metal is in 0K temperature and has flat surface; 4) local work function is identical for the entire metal surface and does not depend on the external electric field, which is homogeneous over its surface; 5) interactions between emitted electrons and the metal surface can be depicted in the

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form of a classical potential; 6) transmition coefficients for the potential barrier can be calculated on the basis of JWKB theory [11].

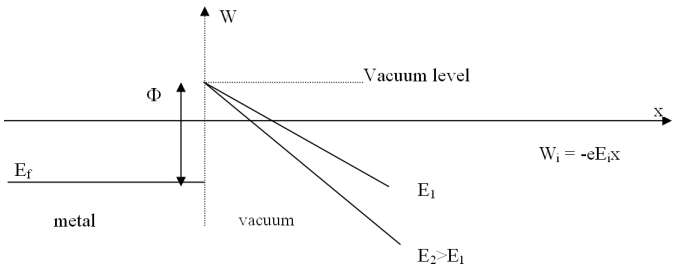

Fig. 1. Schematic presentation of the potential barrier used in the F-N theory for electric fields $E_2 > E_1$, E_f – Fermi level, W – potential energy, Φ – work function

The elementary formulation of F-N theory in its first approximation neglects also the interaction of electrons with the surface. As results of these assumptions can be obtained the following relation of the electron emission current intensity I, the electric field E and the work function from the metal Φ:

$$I = RE^2 \exp(S/E) \tag{1}$$

where:

$$R = Aa\Phi^{-1} \tag{2}$$

$$S = -b\Phi^{3/2} \tag{3}$$

A – emission area, a, b – universal constants:

$$a = e^3/8\pi h = 1.541434 \times 10^{-6} AeV/V^2 \tag{4}$$

$$b = 8\pi/3(2m_e)^{0.5}/eh = 6.830888 \times 10^9 eV^{-3/2}V/m. \tag{5}$$

The equation describes an ideal situation in physical conditions which are difficult to obtain. In practical case the following effects must also be taken into consideration: 1) the studied object has local electronic structure; 2) electrons come from the object with the temperature exceeding 0K; 3) the surface is inhomogeneous and the electric field above it is also not homogeneous (which means that the work function depends on the local surface topography); 4) there can be electric charges on the surface; 5) the transmition coefficients for the potential barrier can vary (they depend on the type of theory applied).

The simplest coefficient to take into consideration is the field enhancement coefficient γ related to emitter geometry. This coefficient makes adjustment for value of the electric field changes generated by the emitting object with an established shape. Then:

$$E' = \gamma E \tag{6}$$

and the γ depends on emitter shape.

It is almost impossible to solve the problem taking into consideration all effects mentioned above. For this reason there is still no adequate theory explaining the electron emission phenomenon from the structurally complicated layers such as carbonaceous layers (e.g. DLC or amorphous carbon).

2.1. The basic assumptions of Fowler's theory concerning electron photoemission. The elementary theory presented by Fowler concerning the electron emission as a result of illuminating the clean metal surface assumes that [12]:

- the number of electrons emitted as a result of light quantum absorption is proportional to the number of electrons existing in a metal volume unit and to the radiation intensity;
- kinetic energy connected to normal direction to the metal surface of these electrons increased by $h\nu$ suffices to cross or tunnel the metal-vacuum potential barrier;
- the electrons are fermions and therefore their n number in a volume unit is expressed by:

$$n(u,v,w)dudvdw = 2\left(\frac{m}{h}\right)^3 \frac{dudvdw}{\left[\exp\left(\frac{(m_e(u^2+v^2+w^2)-\varepsilon^*)}{2kT}\right)+1\right]} \tag{7}$$

  u,v,w – velocity components, ε^* – Fermi energy
- only electrons with energy higher than the potential barrier height (long-wave photoemission threshold) are counted among the electrons taking part in photoemission (for $T = 0$).

Such assumptions give the number of electrons capable of photoemission (N – proportional to the measured intensity of electron emission current I):

$$N = A[\pi^2/6 + \phi^2/2 - \{\exp(-\phi) - \exp(-2\phi)/2^2 + \exp(-3\phi)/3^2 - ...\}] \tag{8}$$

with A is a constant depending on temperature (T), light quantum energy $h\nu$ and the height of the potential barrier χ_o:

$$A = \frac{2(2\pi m_e^{3/2})^{1/2}(kT)^2}{h^3}(\chi_0 - h\nu\}^{1/2}. \tag{9}$$

This leads to the conclusion that:

$$I \infty \Phi^2. \tag{10}$$

An example of Fowler's theory application has been discussed in the paper [13]. This theory, unlike F-N theory, does not introduce many restrictions and can be with an appropriate approximation used for many systems, taking into consideration the fact that the photons in metals absorb electrons from the conduction band, and in dielectrics and semiconductors the valence electrons related to surface state and defects. Practically, the information concerning the energy necessary for the electron tunnelling cross the potential barrier are provided to a lesser extent by surface states than in case of field emission due to the character of radiation absorption. The factor influencing the work function value is the effect of ionisating atoms being on the way of the high energetic electrons. The

formation of ionised layer near the surface has significant influence on the potential barrier height and then on the work function value.

3. Cathodes emitting cold electrons

Table 1 presents data concerning the field emission for various materials suggested as carbonaceous cold electron cathodes: carbon nanotubes, DLC layers, layers of modified carbonaceous structures and composite carbonaceous layers. There have been many studies written on the subject and they cannot be discussed in such a short study.

According to Table 1 the cathodes made of composite material generate the electron emission current with the density higher than the one obtained by many other authors using DLC cathodes or a system of carbon nanotubes. The majority of authors do not indicate the work function value for the studied materials.

Field emission has many advantages when compared with thermoemission: high current density, narrow energy spectrum of the emitted electrons, coherence of the corresponding wave, fast switch-on of the emitter without pre-heating the cathode, possibility of miniaturising the devices and of stable work of devices with a high vacuum (10^{-4} Pa) while the metallic emitters need ultra-high vacuum of $\sim 10^{-8}$ Pa.

3.1. Carbonaceous cold electron cathodes. Recently many research teams have been working on the field emission from silicone tips, the so-called Spindt emitters. Spindt field emitters are obtained with micro technology, and the processes are expensive and ineffective. While the cold electron emitters made of Spindt silicone structures [20–23] need to be obtained in a highly complicated way, carbonaceous emitters are easy, cheap and ecological to obtain. In this article we shall concentrate on carbonaceous emitters made of such materials as layers of carbon fibres, oxidized carbon fibres, carbon nanotubes layers and in particular on the heterostructural carbon layers.

3.2. Carbon fibre cathodes. Carbon fibres are obtained by means of heating another carbon polymer (e.g. polyacrylonitrile) in high temperatures. They are characterised with high flexibility ration and are both chemically and thermally resistant. Carbon fibres are used primarily for composite materials. In 90s there were attempts to used them in flat displays [24], but the electron emission from surfaces covered with fibres was not homogeneous enough.

3.3. Carbon nanotube cathodes. Nowadays much research is done in the field of nanotubes of various kinds. For example, the nanotubes with a bamboo-like structure are obtained by means of chemical vacuum evaporation method with plasma assistance. In this method the nanotubes are obtained by a decomposition of methane and nitrogen mixture passed through a chamber, in which plates of porous silicone with Ni or Fe particles are placed in the temperature of 500°C [25]. Individual short closed nanotubes are inserted one into another just like elements in a bamboo stick. A layer composed of such nanotubes exhibits a stable and efficient field emission (j$\sim$200 mA/cm^2) appearing at 1 V/μm [26]. Among the published studies results there are many devoted to obtaining nanotubes and removing the reaction products [27–37], and also to investigating their qualities as electron emitters. One of the most popular methods of obtaining nanotubes is a high-temperature pyrolytic method where the nanotubes are obtained as a result of hydrocarbons' decomposition on the matrix with catalytic grains, e.g. Ni or Fe.

3.4. Cold electron cathodes made of other composite-type carbonaceous materials. Another type of carbonaceous materials exhibiting cold electron emission are heterostructural carbonaceous materials with an admixture of metallic nanocrystallites. In our team (Tele&Radio Research Institute) such materials are obtained with a physical vacuum deposition (PVD) method in which we used two separated sources: one with a composition of C_{60}/C_{70} fullerenes, and the other with an organic metal compound. The results of the research into the synthesis and properties of these materials were published in the past [38–48]. The film can be deposited on any substrate; it has a composite complex structure (composed of carbon nanograins in different allotropes and metal nanocrystallites) and display cold electron emission, which depends on the quantity and type of metal.

Using these materials as a large-size displays, flat display or lighting elements have been a subject to frequent research. All these lamps belong to the group of electron tubes.

Table 1
Comparison of electron emission current density depending on the extracting field for various electron emitters

Emitter type	Emission current density [A/cm^2]	Extracting field [V/μm]	Cathode – anode distance [μm]	Reference
Spindt's carbonaceous cathodes	3×10^{-8} (form the cantilever)	8	160	[14]
Admixtured layer of amorphous carbon N – g-C:N_2	10^{-4} for 15% N w warstwie 10^{-8} for 7% N w warstwie	10	50	[15]
DLC layer on Si	10^{-7}	10	100	[16]
Carbon nanotubes layer	0.1–0.2	50	10–40	[17]
BN	10^{-7}	25	75	[18]
Nanocomposite layers nanotubes+nanocarbon +nanocrystallites Ni	1.2×10^{-3}	4	300	[19]

4. Cold cathode lighting element

A typical electron lighting element is a glass bulb (sometimes in a steel casing) with a set of electrodes. The element is usually filled with gas under specific pressure; there are also vacuum elements. A cathode is the source of electrons. If the cathode is heated (directly or indirectly), the electrons are emitted as a result of thermoemission. The elements with a cold cathode emit electrons due to the phenomenon of field emission, characteristic for materials with a low work function value. These materials emit electrons because of extracting electric field.

4.1. Cold cathode lighting element made of carbonaceous composite materials. Under the framework of cooperation of the Kielce University of Technology and Tele&Radio Research Institute there is research carried on [49, 50] the application of the heterostructural carbon materials with an admixture of metal nanocrystallites (Ni or Pd) for constructing cold cathode lighting elements which emit electrons due to the field emission phenomenon.

4.2. Technology. Heterostructural carbon films are obtained with PVD method from two separated sources containing fullerenes (fullerene composition C_{60}/C_{70} in the weight ratio 85:15) and organic metal compound (usually an acetate). Films were deposited on Mo band. Details of technological process are presented in papers [51, 52]. These films are composed of carbon nanograins (various carbon allotropes) and metal nanocrystallites placed in the carbonaceous matrix [6]. Heterostructural carbon films show high electron emission efficiency depending on the structure type, although the field electron emission in these films is less efficient than for the nanotube or for layers of carbon nanofibre emitters. An indisputable advantage is that the field emission is stable and it starts at low electric field threshold values.

4.3. Films' structure and properties. Heterostructural carbon films with metal nanocrystallites are composed of grains built of carbon and metal nanocrystallites. This means that they contain metal, fulleren, graphite or amorphous carbon nanograines. The structure and size of these crystallites are different for films containing different metal concentration. Depending on the metal concentration, the observed metal nanograins sizes vary from 1.5 to 8 nm. Carbon grains, with sizes differing 10-10^2 nm, are a matrix for metal nanograins. Depending on the type of metal, the observed growth can be columnar (e.g. for palladium) or insular one (e.g. for nickel).

In the case of carbon-palladium films, palladium is dispersed in carbonaceous lattice and has probably the form of clusters with a diameter not exceeding 1 nm. In this case the carbon matrix is of fullerene *fcc* type. Changing the technological process parameters (deposition time, substrate temperature) helps obtain palladium nanograins of various sizes.

Films containing nickel have a multi-phase structure and include Ni grains sized 2–6 nm and carbonaceous grains in various carbon allotropes (amorphous carbon, graphite, fullerene).

A detailed description of both structures can be found in studies [38–50].

4.4. Lighting element structure. Lighting element based on the different types of cold cathodes were described in literature previously [53, 54]. The applied cathodes were prepared from various carbonaceous materials (carbon fibers and carbon nanotubes) as well as their working parameters depended on the material type and lamp construction.

The Tele&Radio Research Institute in Warsaw in cooperation with Kielce University of Technology prototype a cold cathode lighting element (Fig. 2a). The design was based on the assumption that particular components should be easily replaceable. For this reason no chemical compound which would absorb gases (getter) was used and the prototype is connected with a turbomolecular pump. Cathode and anode were placed in a cylinder glass within a distance of 35 mm. The cathode was the heterostructural carbon film containing nickel nanocrystallites placed on metal substrate. This type of material for cathode was chosen because of its higher emissive efficiency then emission efficiency for carbonaceous-palladium films. A steering electrode is located about 1 mm higher over the cathode. The anode is a luminescent screen prepared in Kielce University of Technology. The screen of a glass plate (sized 15 mm $\times$ 25 mm) covered with indium tin oxide was prepared at Tele&Radio Research Institute. A three-band phosphor with the colour rendering index $R_a \geq 80$ (Class 1b) has been used. This class of phosphors is composed of three different fluorescent powders emitting waves 440, 540, 610 nm long [55] in narrow bands.

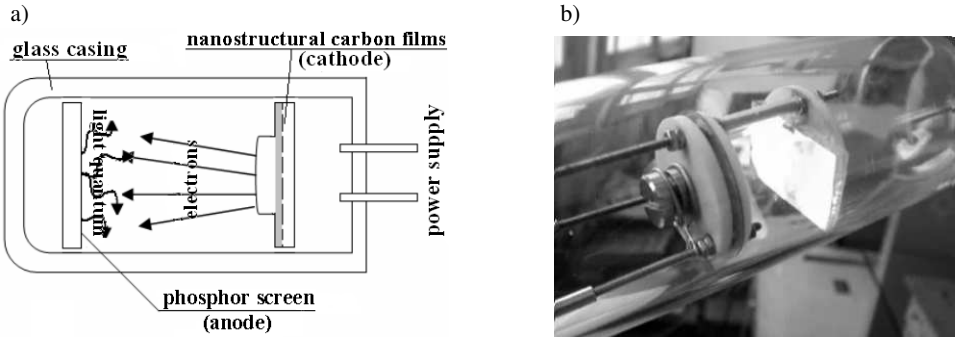

Fig. 2. (a) Diagram presenting the structure of the cold cathode lighting element, (b) light emission observed

The experiments revealed strong light emission in visible spectrum. Figure 2b presents emission of the lighting element described. This emission is durable and stays for many hours with the supporting voltage of 0.8 kV, with the distance between anode and cathode about 3 cm. The extracting field for this type of cathode in the mentioned experimental condition was higher than supporting voltage and achieved 7 V/μm. After few minutes this voltage could be lowered to the supporting voltage value.

Further research into increasing the lighting capacity of the lighting element by means of anode optimalisation, related to choosing appropriate phosphor and method of its placement is being conducted. The thickness of phosphor layer and its granulation shall be the most important factors.

4.5. Possible applications. Cold electron cathodes made of carbonaceous materials are used in various electron devices. Carbon fibres are widely used as emitters in electron tubes (traveling wave tube) [56–58]. Cathodes of such a type are also used in portable x-ray machines, electroluminescent light sources and displays [59–62].

The application of cold electron cathodes made of carbon materials usually means decreased energy consumption. Such cathodes do not require high activation temperature.

Cold cathode made of carbon nanotubes can also be used for constructing microwave transmitters. The experiments conducted confirm that these cathodes are able to emit microwaves with the frequency of 1.5 GHz for 40 hours. An important advantage of microwave transmitters with carbon nanotubes is minimising the period necessary for activating the transmitter. It is possible to obtain instant contact between the transmitters. The tests confirm that a carbon nanotube cathode has parameters identical with those of the microwave transmitters used in the space industry [63].

5. Conclusions

Carbonaceous composite materials may have only recently caught the attention of the world but many advances have been made since their discovery about decade ago. They are unique nanostructural materials that show the properties of any other known materials. Due to these qualities the field of applications is almost endless.

Our preliminary results imply the prototype element is suitable for commercialisation.

The modification of traditional electronic devices and their application while developing carbon materials being emitters is supported not only by economic reasons but also environmental issues. For example no heavy metals are used while building cold cathode lighting elements and for this reason they are environmentally-friendly. Moreover, the tests prove that such elements are characterised with lower energy consumption and long life (of several thousand hours). Therefore it can be expected that further modifications of carbon structures will lead to increasing field emission efficiency. As a result the new materials will be used in a growing number of devices.

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