Available online at www.sciencedirect.com

ScienceDirect

St. Petersburg Polytechnical University Journal: Physics and Mathematics 1 (2015) 47–55

www.elsevier.com/locate/spjpm

Field-induced electron emission from nanoporous carbon of various types

Alexander V. Arkhipov [a], Pavel G. Gabdullin [a], Nikolai M. Gnuchev [a,*], Sergei N. Davydov [a], Svyatoslav I. Krel [a], Boris A. Loginov [b]

[a] *St. Petersburg Polytechnic University, 29 Politekhnicheskaya St., St. Petersburg 195251, Russian Federation*

[b] *National Research University of Electronic Technology, 5 Pass. 4806, Zelenograd, Moscow 124498, Russian Federation*

Available online 12 March 2015

Abstract

The influence of fabrication technology on field electron emission properties of nanoporous carbon (NPC) has been investigated. Samples of NPC derived from different carbides via chlorination at different temperatures demonstrated similar low-field emission ability with the threshold electric field strength of 2–3 V/μm. This property correlated with the presence of nanopores with the characteristic size of 0.5–1.2 nm determining high values of specific surface area (more than 800 m^2/g) of the material. In most cases, voltage–current characteristics of emission were approximately linear in Fowler–Nordheim (FN) coordinates (excluding the low-current part near the emission threshold), but the plot slope angles were in notable disagreement with the known material morphology and electronic properties, and this could not be explained within the frames of FN emission theory. We suggest that the actual emission mechanism for NPC involves hot electrons generated at internal boundaries, and that emission centers may be associated with relatively large (20–100 nm) onion-like particles observed in many microscopy images.

Keywords: Nanoporous carbon; Field electron emission; Carbon nanomaterials; Graphite-like nanoparticles.

1. Introduction

During the recent decade, carbon-based field emitters developed into a promising option of cold cathodes for various devices [1,2]. Carbon nanotubes (CNTs) [3] were the first nanocarbon form that found practical applications in microwave [4,5], light [6] and X-ray [7,8] sources, plasma devices [9], space thrusters [10], microelectronic components [11,12] and gauges [13]. However, the fabrication processes of controlled CNT arrays remain relatively complex and expensive. Furthermore, the problem of their fast degradation under operational conditions has not yet been solved [3,7,14–16]. Due to the very high geometric aspect ratio, the CNTs provide substantial local amplification of the applied electric field which helps to achieve low-field emission. Yet the resulting concentration of the emission current, electric force, thermal load and ionic bombardment at atomic-scale areas eventually

* Corresponding author.
E-mail addresses: arkhipov@rphf.spbstu.ru (A.V. Arkhipov), pavel-gabdullin@yandex.ru (P.G. Gabdullin), gnuchev.nm@spbstu.ru, nmg@rphf.spbstu.ru (N.M. Gnuchev), phys-el@spbstu.ru (S.N. Davydov), 8svyatoslav8@mail.ru (S.I. Krel), logi@miee.ru (B.A. Loginov).

http://dx.doi.org/10.1016/j.spjpm.2015.03.011

(Peer review under responsibility of St. Petersburg Polytechnic University).

lead to accelerated destruction of the emission sites. This drawback of the CNT-based technologies stimulates involvement into emission investigations of alternative forms of nanocarbon, such as nanodiamond [17–27], nanographitic [2,26–28], amorphous [29–31] and composite [32–36] films. All these materials have common features of heterogeneous composition and (more or less) disordered structure. Their surface topography is relatively smooth, so that the estimated values of field enhancement factor β are insufficient to describe the observed low-field emission within the frame of the classical Fowler–Nordheim (FN) theory. A number of principally different models were developed to explain this phenomenon [24–26,31–33,37–40]. Most commonly, a proposed mechanism of emission facilitation involves a multistage tunnel transfer of electrons via nanosized domains with contrast electronic properties [2,18–20,41–47].

2. Samples: preparation, physical and chemical properties

In the present work, we investigated field-emission properties of nanoporous carbon (NPC) – one of all-carbon materials with disordered nano-scale structure. Similar materials were studied previously in Refs. [48,49], but in our work we used a particular form of NPC, produced from carbides through chlorination process [50–55] in which selective etching reaction had removed all non-carbon elements and formed a solid structure with high porosity. Due to developed pore/skeleton interface, homogeneity of pore size, strong adsorption ability, relatively high electric conductance and mechanical strength, the carbide-derived NPC materials give considerable promise for diverse applications, including fabrication of field electron emitters [56].

Detailed description of the process of NPC samples fabrication from the carbides of boron, zircon, titanium and molybdenum and typical parameters of the product structure were disclosed in [53–55]. The structural parameters substantially differed for the samples of different origin. Thus, the mean pore size for the products of B4C and Mo2C chlorination was approximately 5 times greater than that for ZrC and TiC derivatives. As a result, the apparent density in the latter case was almost two times greater, while the pycnometric density (i.e. the density of carbon skeleton, with pore volume excluded from consideration) was close to the density of graphite for all the samples.

Silicon carbide was also used for fabricating NPC samples for the described experiments. As it has been showed in [55], the pore size for these samples varied

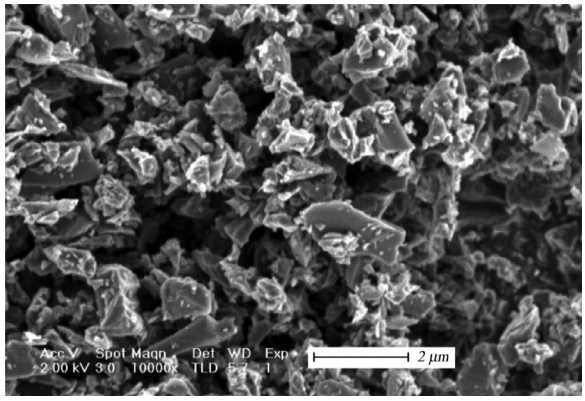

Fig. 1. A typical overview SEM image of an NPC sample (produced from SiC by chlorination at 1200 °C).

in wider range than for the derivatives of other carbides. Chlorination temperature had significant effect on the pore size distributions. In the samples prepared at low temperatures (700–900 °C), the pore size was close to 1 nm. If the chemical treatment temperature was higher (1200°), larger pores appeared and the sample densities (both apparent and pycnometric ones) decreased, presumably due to higher chlorine etching efficiency with respect to carbon atoms. After treatment at 2000 °C, only large pores (meso-pores) remained in the sample; the carbon skeleton lost more than a half of its mass and underwent a reconstruction with dramatic reduction of the specific surface area.

The morphology of the studied NPC samples may be overviewed from microscopic images. All overview images (with relatively low resolution and wide field of view) acquired with a scanning electron microscope were similar to the one presented in Fig. 1. The μm- and sub-μm-sized irregular NPC particles presented in the image inherit the shapes of the original carbide powder grains.

Atomic-scale images of small spots of NPC samples obtained by the transmission electron microscopy (HR TEM) are shown in Fig. 2a–c. They demonstrate that the studied materials included both amorphous (Fig. 2c) and ordered domains.

The latter were comprised of faceted (Fig. 2a) or curved (Fig. 2b) atomic layers. The distances between atomic planes (~0.35 nm) correspond to the graphite lattice period. Domain sizes between 20 and 100 nm were the most typical, though sometimes larger faceted crystallites were also observed (Fig. 2d). As much as it can be seen from microscopic data, the relative part of ordered domains in NPC samples derived from the same carbide usually grew with the increase of chlorination temperature [52,55].