Fabrication and complex investigation of LAFE based on CNT by PECVD with island catalyst

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Abstract. This paper presents a study of large area field emitter based on carbon nanotubes grown by PECVD method on Si/SiO2 substrate with Fe catalyst. The catalyst was deposited by CVD on the substrate from ferrocene in the form of islands. The sample creation technology was described and results of the emission properties study were presented. Current-voltage characteristics were registered and tested for compliance with the cold field emission regime. The fluctuation statistic of effective microscopic parameters was constructed. Using data from a computerized field projector, the emission profile of the sample was calculated.

1. Introduction

Aligned to the substrate surface carbon nanotubes (CNT) are promising candidates for production of various micro-sized devices: electrodes of electrochemical devices such as photovoltaic and lithium-ion cells, supercapacitors, chemical and biological sensors etc. [1]. A special place is given to the development of sources of free electrons based on the field emission effect. The sources can be used to create electron nanolithography systems, photoelectric converters, amplifiers of electrical signals (traveling wave tubes), and devices for household and scientific research purposes: monitors, lamps, X-ray machines, gas sensors, microscopes, space telescopes, etc. [2-3]. Large area field emitters (LAFE) based on CNTs have a low threshold field [4] and allow obtaining high emission currents (~ 2 µA for one single-wall CNT [5]). This is due to the large aspect ratio, high conductivity and thermal stability of CNT [6]. In a vacuum electrical system with flat electrodes, CNT provides intensification of the electric field at its apex up to 2000 times [7], that is significantly higher than intensification of other microtip emitters. For example, silicon pyramids demonstrate intensification up to 500 [8], Si nanocrystals - up to 1200 [9], ZnO nanocrystals - up to 800 [10], graphene - up to 100 [11]. The technologies of CNT growth and ordering are very diverse. The electronic, optical and emission properties of CNT based materials strongly depend on the CNT structure and morphology. The best emission characteristics are possessed by emitters with vertically aligned CNT (VACNT). In such systems, an increased density of emission sites and the best degree of current uniformity over the area are achievable [12]. Today, there are many ways to grow CNTs on various substrates. Among them are the electric arc method [13-14], laser ablation [15], chemical vapor deposition (CVD) [16]. The CVD method has a significant advantage among these three methods, in particular, due to the relatively low growth temperature (600–950 °C) [17].
The addition of a catalyst in the CVD method increases the mass percentage of CNTs and also makes it possible to control their position [18]. Typically, the catalytic structure is formed on a substrate from a layer of a metal (Ni, Fe, Co, etc.) suitable for catalysis, prepared by vacuum thermal or magnetron sputtering. To further reduce the temperature in the CVD, the carbonation of the precursor gas is carried out in plasma (PECVD). This low-temperature deposition becomes important when metals are used as a catalyst, which quickly diffuse into the substrate and form silicides there [19]. In some cases, it is possible to reduce the temperature to 150 °C [20].

To create a VACNT array, an external factor that sets the CNT growth vector, such as an external electric or magnetic field, is required. It is known that the DC-PECVD (Direct current plasma-enhanced CVD) method, where electric field of the plasma is the guiding factor, is the most reliable for growing VACNT arrays [21]. The method gives the best indicators for the verticality and correctness of the CNT shape, independent of the density of their nucleation, as well as the perfection of the structure of the CNT walls and the level of their contamination by foreign phases. The introduction of additional electrodes can improve the orientation of CNTs [22].

The regularity and isolation of small VACNT arrays can reduce the screening effect and increase the overall emission current. For this, a catalyst is used in the form of separate islands. The use of electron-beam lithography methods makes it possible to produce a regular and rather rarefied structure of catalyst islands [23-24]. Lithography methods are the most reliable in terms of reproducibility, but at the same time, the most expensive and ineffective for processing large-area substrates (emitters with a large area are needed to increase the total current). Another, cheaper method is the coating of the substrate with a continuous layer of catalyst, which is then subjected to heat treatment, as a result of which the integrity of the layer is violated under the action of surface forces, and it turns into an island one [25-26]. Moreover, the size and density of the arrangement of the islands strictly depend on the initial thickness of the metal layer. This method has a significant drawback: the density of islands is often too high, so that the distance between them does not allow removing the screening effect of growing VACNTs.

Of particular relevance are VACNT structures grown on silicon, which makes it possible to combine the technology of manufacturing electron sources with modern technological processes in silicon microelectronics. In [19], the interaction of silicon wafers and Fe as a catalyst deposited by the CVD method was studied. It was shown that Fe reacts and forms iron silicide (FeSi2) and iron silicate (Fe2SiO4) with silicon at high temperatures, losing its catalytic ability for CNT growth. The introduction of an additional buffer layer helps to solve this problem. The SiO2 oxide layer has proved to be an ideal catalyst support for growing VACNT, since the sublayer formed by it isolates the interaction of the catalyst with the silicon substrate. Such a buffer layer has a high surface roughness, which improves the adhesion of nanoparticles and prevents their agglomeration [27]. On the other hand, the SiO2 layer is created so thin that it is tunnel-transparent for electrons. It is possible to use other promising buffer layers. For example, a TiN layer [28-29].

Let us consider several works where the field emission properties of VACNT arrays grown by the PECVD method were investigated. The main characteristics that are recorded and used to determine the emission properties of LAFE are: current-voltage characteristics (IVC), estimation of the effective field enhancement factor and emission area, time dependence of the current level (temporal stability test), uniformity of emission sites in the field emission luminescence pattern. In [22], a uniform VACNT array was created using DC-PECVD method in a triode configuration of electrodes (without a catalyst), where CNTs are grouped into separate cone-like structures. Using a phosphor screen, an increase in the density and uniformity of emission sites was shown as a result of the use of a third electrode in the process of CNT growth. The optimal voltage at this electrode, which is required to obtain a structure with the maximum emissivity, has been determined. The best threshold field for emission switching on was 0.6 V/µm, and the maximum recorded macroscopic current density was 1.5 mA/cm² at a macroscopic field strength of 2.7 V/µm. In [29], LAFE was investigated from vertical beams of MWCNTs on a smooth silicon substrate with the (100) orientation of n-type conductivity, as well as arrays of several discrete and separated CNTs (the catalyst was deposited by electron beam lithography). IVCs were measured for samples fabricated under different conditions; the values of the threshold electric field (8 V/m) and
the maximum macroscopic emission current density (0.4 A/cm² for a field of 20 V/m) were obtained. The trend line for IVC plotted in Fowler-Nordheim coordinates was used to estimate the field enhancement factor (from 240 to 430). The field enhancement factor was also estimated in [30], where the catalyst was deposited by magnetron sputtering. In [31], an emitter in the form of a CNT array was created using the three-electrode DC-PECVD method. The temporal stability test showed that the emission current with macroscopic density of 1.6 mA/cm² remained stable for 60 min.

In this work, we propose a new concept of the technology for creating LAFE from nanotubes, using the CVD method for the deposition of the catalyst metal immediately in the form of islands without subsequent thermal annealing. Due to the peculiarities of physical-chemical growing of the catalyst layer, there is a potential possibility of controlling the nucleation process: control of the density and size of metal islands. An additional advantage of the technique can be the technological possibility of carrying out sequential stages of catalyst deposition and nanotube growth in one CVD reactor. This will eliminate the stage of reloading the samples, and hence the uncontrolled aging of the catalyst. The reproducibility of the process of obtaining finished structures will increase significantly. The technique is being developed at the Higher School of Physics and Technology of Peter the Great University. To characterize the emission properties of the LAFE a computerized technique for multichannel registration and online processing of the field emission data was used. This technique was developed at the Ioffe Institute.

2. Sample fabrication

The same CVD setup was used for sequential formation of Fe layers and VACNT arrays on a silicon substrate (figure 1). Each process was carried out with its own internal equipment of the general reactor. The reactor belongs to the type of vertical cold-wall reactors, consists of a quartz tube 60 mm in diameter and 500 mm long, equipped with end-face vacuum seals.

In the case of obtaining Fe layers, the reactor is organized according to the principle of a two-zone system according to the operating temperature. In the upper region, the first in the gas flow, there is a diffusion evaporator with ferrocene (bis (η -cyclopentadienyl) iron) serving as a metal source. The evolved reagent vapors are transferred by an argon flow to the underlying deposition area, where a quartz pedestal with a built-in heater is located. On the pedestal there is a graphite washer 45 mm in diameter with substrates, which were polished (100) silicon wafers doped by phosphorous with resistivity of 5 Ωm · cm with a native SiO₂ layer. For the sample presented in this work, deposition was carried out for 30 min at a pedestal temperature of 700 °C and a total pressure of 700 Pa. The consumption of argon and ferrocene was 50 and 0.27 sccm, respectively. No morphological features were observed on the smooth surface of the obtained Fe layer (with a nominal thickness of ≈ 30 µg/m²).

In the case of VACNT arrays, the reactor was equipped with an electrode system. The above-mentioned graphite washer acted as the cathode. A stainless-steel disc (ø 45 mm) served as an anode. The gap between the electrodes was 40 mm. The sample presented in this work was obtained by deposition for 10 min at a pedestal temperature of 740 °C and a total pressure of 300 Pa. The working medium was created from ammonia supplied with a flow rate of 200 sccm, and acetylene - 100 sccm. Samples obtained after iron deposition served as a substrate. The discharge was characterized by a current of 7.5 mA and an anode voltage of 480 V. A similar growth method was used in [23-26].

Scanning electron microscopy (SUPRA 55-25-78 microscope) was used to analyse the results of growth of VACNT arrays. SEM revealed the presence of extended structures (figure 2). The SEM image taken at an angle of 30 ° to the sample surface showed the CNT to have a slightly conical shape and a small variation in height (figure 2 (a)). The pictures show that the vast majority of CNTs are vertically aligned. Their average diameter is more than 20 nm, the average CNT length is ~ 200 nm, and the placement density is ~ 1.7 × 10¹⁰ cm². Separate CNT groups are visible on the surface, which is probably because of the initial Fe islands in these regions underwent agglomeration. In figure 2 (b), CNTs of much longer length (> 400 nm) are observed, lying on the substrate surface or bent.
3. Field emission investigation

The technique of multichannel collection and online processing of field emission data uses a plane-parallel arrangement of electrodes and registers: current-voltage characteristics of LAFE, patterns of distribution of emission sites over the surface (glow patterns), as well as the vacuum level in the interelectrode space. A detailed description of the setup for studying the emission properties was presented in [32]. In the experiments presented below, the interelectrode distance $d_{sep}=370 \, \mu m$, and the vacuum level $P \approx 10^{-7}$ Torr.

The main features of the technique for measuring emission properties are following: the use of a fast scanning mode of a sample with a high voltage (recording fast-IVC in 20 ms), online processing of fast-IVC with obtaining effective emission parameters (field enhancement factor $\gamma_{eff}$ and emission area $A_{eff}$), registration of luminescence patterns with processing them online. The program controlling the experiment has a built-in some modules: a module that allows to test the correspondence of the recorded IVC to the classical theory of field emission (so called «ortodox» test [33]), a module for detecting emission sites and plotting an emission surface profile (local field enhancement factors), a module for registering and statistically evaluating fluctuation oscillations of effective parameters.

At the first stage of measurements, the sample was subjected to high voltage training, while new emission sites were activated, and some of the most unstable, strongly protruding above the surface, were also destroyed (burned out in a vacuum discharge). The emission current during training reached 250 $\mu A$. Figure 3 shows the time dependences of the amplitudes of the voltage pulses and the corresponding pulses of the emission current (voltage and current levels). After training, the current level of 150 $\mu A$ was stable. An increase in the current above 250 $\mu A$ led to dramatical change in the emission surface: additional emission sites appeared in the pictures of a field projector located at the periphery of the sample, which indicates the inclusion of the edges of the silicon substrate in the emission. In this case, a strong change in the IVC was observed (see figure 4), a decrease in the effective emission area by two orders of magnitude, as well as a departure of the «ortodox» test criteria beyond the permissible values.
that the current is provided by individual nanostructures that protrude strongly above the emitter surface. From the SEM it is seen that the bulk of the CNT does not have the required length, so it can be concluded that the effective radius of emitting CNTs is ~ 1 nm.

The luminescence patterns showed the result of the analysis of the luminescence patterns. The number of emitting sites turned out to be about: $N_{es} = 44$. The emission area of one emission site was estimated by dividing the effective area of the entire emitter by the number of sites found from the luminescence patterns: $A_{eff} = <A_{eff}> / N_{es} = 400 \text{ nm}^2$. This area is close to the area of the CNT top, the dimensions of which we estimated earlier from SEM (hemisphere area 628 nm$^2$).

Using the area $A_{eff}$ and data on the current load at each emission site, the corresponding field enhancement factors ($\gamma_{eff}$) were calculated and their histogram was plotted (see the histogram in figure 6). The technique of this calculation was described by us in [32]. The $\gamma_{eff}$ values spanned the range from 965 to 1015, which includes the effective value $<\gamma_{eff}>$.

Such a high field enhancement factor (~ 1000) indicates a significant height of emitting CNTs: a simple estimate of the height $h = \gamma \cdot r / 0.7$ yields values greater than a micrometer, even under the assumption that the radius of emitting CNTs is ~ 1 nm. A more accurate theoretical estimate of the field enhancement factor depending on the geometry of the tip (in the HCP model) is given in [34]. It can be seen from the SEM that the bulk of the CNT does not have the required length, so it can be concluded that the current is provided by individual nanostructures that protrude strongly above the emitter surface.
4. Conclusion
The paper considers the fundamental possibility of using the CVD method to form an island catalyst film on the substrate surface. The prototype was created on a silicon substrate with a layer of dioxide. A study of the field emission properties of this sample showed a fairly stable current level of 150 µA. The corresponding IVC were measured. Evaluation of the dimensionless field along the trend line showed that it meets the requirements of the «orthodox» test for classical field emission. Raising the current to a level of 250 µA leads to the inclusion of the sample edges in the emission process and a sharp change in the shape of the IVC along with its exit from the acceptable ranges of the «orthodox» test. The inclusion of edges is clearly visible in the pictures of a field projector, which indicates the need to use it when investigating new types of emitters. The work also estimated the effective microscopic parameters – the field enhancement factor and the emission area. The emission patterns were used to estimate the emission area of one site and calculate the field enhancement factors for each site. The values of the field enhancement factors found from the IVC and luminescence patterns indicate that only the longest CNTs that can be seen in the SEM patterns are involved in the emission process. To include the main array in the emission, further optimization of the technology is required: lengthening the CNT and increasing the distance between them.

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