Influence of NiO ALD Coatings on the Field Emission Characteristic of CNT Arrays

Maksim A. Chumak 1,*, Leonid A. Filatov 1, Ilya S. Ezhov 1, Anatoly G. Kolosko 2, Sergey V. Filippov 2, Eugeni O. Popov 2 and Maxim Yu. Maximov 1

1 Institute of Metallurgy of Mechanical Engineering and Transport, Peter the Great Saint-Petersburg Polytechnic University, st. Politelchnicheskaya, 29, 195251 St. Petersburg, Russia
2 Cyclotron Laboratory, Ioffe Institute, st. Politelchnicheskaya, 26, 194021 St. Petersburg, Russia
* Correspondence: equilibrium2027@yandex.ru; Tel.: +7-(931)-382-63-46

Abstract: The paper presents a study of a large-area field emitter based on a composite of vertically aligned carbon nanotubes covered with a continuous and conformal layer of nickel oxide by the atomic layer deposition method. The arrays of carbon nanotubes were grown by direct current plasma-enhanced chemical vapor deposition on a pure Si substrate using a nickel oxide catalyst which was also deposited by atomic layer deposition. The emission characteristics of an array of pure vertically oriented carbon nanotubes with a structure identical in morphology, covered with a layer of thin nickel oxide, are compared using the data from a unique computerized field emission projector. The deposition of an oxide coating favorably affected the emission current fluctuations, reducing them from 40% to 15% for a pristine carbon nanotube and carbon nanotube/nickel oxide, respectively. However, the 7.5 nm nickel oxide layer coating leads to an increase in the turn-on field from 6.2 to 9.7 V/µm.

Keywords: atomic layer deposition (ALD); thin film structures; field emission cathode; composite structures; carbon nanotubes; direct current plasma-enhanced chemical vapor deposition (DC-PECVD)

1. Introduction

An analysis of the literature shows that the deposition of coatings of oxide metals at their optimal thickness improves the emission characteristics. Among them, such systems as TiO2 [1], ZnO [2,3], MgO [4], iron oxide [5], RuO2 [6,7], CuO [8], NiO [9], and HfO2 [10] were considered. Such oxides typically have a small positive electron affinity, which can reduce the effective work function of the emitters.

Metal oxides covering the surface of carbon nanotubes (CNTs) can exist in the amorphous and crystalline states with different stoichiometric compositions, which leads to a difference in electrical properties. This can significantly affect their field emission properties. The effect of oxygen in the NiO coating structure on improving the field emission of nanotubes was demonstrated by the authors of article [9]. Measurements of different samples confirmed that the field emission current measured at 5 V/µm can be improved from 0.25 mA/cm² to 0.8 mA/cm² by coating with NiO on CNT. A decrease in the turn-on voltage from 3.1 to 2.6 V/µm with the NiO coating was also found.

In addition, the difference in the stoichiometric composition can significantly affect the charge transfer in metal oxides. The electrically conductive properties of nickel oxide grown by the atomic layer deposition (ALD) method were studied in article [11]. The grown oxide film had an atomic ratio of oxygen to nickel smaller than in the stoichiometric oxide. For example, the atomic ratio of O/Ni is 0.77 for the film deposited at 250 °C. That is why the current NiO films exhibit dielectrics rather than p-type semiconductors.

The growth of NiO oxides on CNT was shown in [12–14]. They managed to obtain a continuous and high-quality coating on nanotubes. In [13], the ALD process was performed...
with bis(cyclopentadienyl) nickel (Cp2Ni) and O3 as the Ni precursor and oxygen source, respectively. The deposition was conducted with a substrate temperature of 140 °C.

Nickel oxide, as shown in the review, is used to coat CNTs in order to improve emission characteristics. In this work, we demonstrated the investigation and analysis of the microstructural features of the NiO/CNT nanocomposite obtained by ALD and its field emission capabilities using a computerized method with multichannel collection and processing of field emission data.

2. Materials and Methods

Before fabricating composite structures, the KEF 7.5 grade Si substrate was cleaned of natural oxide in HF acid, washed in distilled water to remove residues of etching products, and boiled in an acetone solution to remove organic contaminants. Then, a NiO catalyst layer was deposited. The NiO precipitation process was carried out in a Picosun R-150 closed-type ALD reactor with hot walls. NiCp2 and O3-H2O were chosen as precursors for growing NiO, and high-purity N2 (99.999%) was used as both carrier and purge gas. NiO was deposited by sequential exposure of CNTs to NiCp2 and O3-H2O. The pulse durations for NiCp2 and O3-H2O were 1 s and 6 s, respectively, and the N2 gas purge time was 10 s. One cycle is NiCp2/purge/O3/purge = 1.0/10.0/6.0/10.0 s. The deposition temperature was maintained at 250 °C, and the sublimation temperature of NiCp2 was 110 °C. A similar growth method was used in [15,16]. Experimentally, it was found that the preferred oxide thickness for growing a dense and uniform array of tubes is 3.8 nm.

The arrays of carbon nanotubes were grown by direct current plasma-enhanced chemical vapor deposition on a pure Si substrate. During the growth of vertically aligned carbon nanotube (VACNT) arrays, the reactor was equipped with the following system of electrodes: a graphite washer acted as the cathode. A stainless-steel disk (ø 45 mm) served as the 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 of 100 sccm. Samples obtained after NiO deposition served as substrates. 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 [17–20]. The NiO coating for CNT was deposited under the same process parameters and conditions as the nanotube growth catalyst. The areas of both cathodes are 1 cm².

Scanning electron microscopy (SUPRA 55-25-78 microscope) was used to analyze the results of growth of short VACNT arrays. SEM revealed the presence of extended structures. Transmission electron microscope (TEM) microphotographs were implemented by Carl Zeiss Libra 200FE. X-ray diffraction (XRD) analysis was implemented by Rigaku SmartLab setup.

The field emission study was carried out by a computerized method with multichannel collection and processing of field emission data [21]. The method uses flat electrodes and fast high-voltage scanning mode (one IVC in 20 ms). The interelectrode distance was 300 µm, and the measuring chamber was in a technical vacuum (~10⁻⁷ Torr).

3. Results

Figure 1a,b show SEM images of a general view of the cathodes used in this study. There were short tubes with an average length of 300 nm. The sample in Figure 1b has a 7.5 nm thick NiO coating, while the other witness sample has no coating (Figure 1a). It should also be noted that there are rather high tubes in the array, which are at least twice as long as the rest of the mass of tubes. According to SEM, all CNTs have a catalyst in their heads. Figure 1c,d show TEM images of pure CNT and CNT/NiO samples, respectively. The image for pure CNTs (Figure 1c) clearly shows their internal structure, showing the number of internal layers reaching 20, and internal wall growth defects that have arisen due to the passage of catalyst particles during their growth. In Figure 1e the detailed image shows that the Ni catalyst located at the free ends of the tube has an elongated shape and
a single crystal structure, since the periodicity in the arrangement of Ni atoms is clearly visible. As can be seen from Figure 1d, CNTs are coated with a continuous layer of NiO. Figure 1g shows the XRD spectrum of NiO-coated CNTs, which indicates that the oxide has a cubic Fm-3m crystal structure, and direct measurement of the lattice parameter from the TEM images shows that the oxide is in the bunsenite phase.

However, the photographs show areas on the coatings that have no periodicity in the arrangement of atoms. A clearly distinguishable boundary between the outer walls of the tubes and the oxide layer makes it possible to estimate its thickness as 7–8 nm (Figure 1f).

Figure 1. SEM images for pristine (a) and NiO-coated (b) CNTs. TEM images for pristine (c) and NiO-coated (d) CNTs, detailed TEM image of pristine CNT (e), detailed TEM image of NiO-coated CNTs (f,g) and XRD spectrum of NiO-coated CNTs.
Thus, we come to the conclusion that the oxide layer has a polycrystalline structure with an amorphous phase present in its composition.

At the first stage of the measurements, the sample was subjected to high-voltage training, which resulted in the activation of new emission centers and the destruction of some of the most unstable and strongly protruding tips. Figure 2a,d shows the time dependences of voltage pulse amplitudes and corresponding emission current pulses (voltage and current levels) for pristine CNT and CNT/NiO samples, respectively. This method makes it possible to carry out a gradual training of tips, to fully study and compare the characteristics of the emitters over the entire operating range.

![Figure 2a](image1.png) ![Figure 2b](image2.png) ![Figure 2c](image3.png) ![Figure 2d](image4.png) ![Figure 2e](image5.png) ![Figure 2f](image6.png)

**Figure 2.** Training of cathodes by voltage steps for pristine CNT (a) and CNT/NiO (d), IVCs for samples (corresponding to the step numbers and glow patterns (c,f)) and corresponding IVC in Fowler–Nordheim coordinates (in inserts) for pristine CNT (b) and CNT/NiO (e).
On the stepwise dependence of the current on time (Figure 2a,d), saturation of the emission current is observed, i.e., the current after each increase in voltage drops sharply to a certain constant level. In the opinion of the authors of [22], such saturation is an adsorption effect, which is not observed in clean nanotubes without ascorbates.

Figure 2b,d show the emission current IVCs for pure CNTs and CNT/NiO, respectively, measured from zero to the current-stage current level in fast measurement mode (one IVC per 20 ms). The IVC numbers correspond to the numbers of the steps during the training. Each IVC is also represented in Fowler–Nordheim coordinates in the insets. The IVCs were treated using the Fowler–Nordheim-type equation applying Elinson–Schrednik approximation [23]:

$$I = S_{\text{eff}} A_{\varphi} \left( \frac{U \beta_{\text{eff}}}{d} \right)^2 \exp \left( - \frac{B_{\varphi} d}{U \beta_{\text{eff}}} \right),$$  \hspace{1cm} (1)

where $A_{\varphi} = \frac{1.4 \times 10^{-6}}{\varphi} \exp \left( \frac{10.11}{\sqrt{\varphi}} \right)$ [AeVV$^{-2}$], $B_{\varphi} = 6.49 \times 10^9 \varphi^{3/2} [\text{eV}^{-3/2}\text{V}^{-1}\text{m}^{-1}]$ are constants, $\beta$ is a local field enhancement factor at the emitter tip, $U$ is an applied voltage, and $\varphi$ is the work function of a material. In our studies, the work function for CNT was assumed to be $\varphi = 4.6 \text{ eV}$ [24], and for the NiO oxide film $\varphi = 5.3 \text{ eV}$ [25].

As a result of the approximation procedure for each of the IVCs, the effective field gains $\beta_{\text{eff}}$ of the emitters were determined. Characteristics such as the inclusion field $E_{\text{on}}$ and the threshold field $E_{\text{th}}$ are also defined from the IVC. The turn-on field, $E_{\text{on}}$, is defined as the applied electric field required to obtain an emission current density of 10 $\mu$A/cm$^2$ from emitters, and for the threshold field, $E_{\text{th}}$, is 1 $\mu$A/cm$^2$. The measured IVCs for pristine CNT and CNT/NiO at numbers 8 and 5, respectively, showed that $E_{\text{on}}$ was 6.16 V/μm for clean nanotubes and 9.66 V/μm for 7.5 nm thick NiO-coated CNTs. An increase in $E_{\text{th}}$ from 4.85 V/μm to 7.49 V/μm was also found upon coating with oxide. The maximum recorded emission current densities were 2.86 mA/cm$^2$ and 0.86 mA/cm$^2$ for clean and coated tubes, respectively. As can be seen, to achieve the same current level for the CNT/NiO structure, it is necessary to apply a higher voltage. This indicates a negative effect of NiO coating with a thickness of 7.5 nm. Due to the technical difficulties in obtaining a large batch of samples with initial CNT arrays of the same morphology, our study is limited to only one NiO-coated sample at a preselected thickness of 7.5 nm.

Figure 2c,f show the luminescence patterns of the phosphor screen for pure CNTs and CNT/NiO, respectively (1 and 2 were obtained using light filter). Each picture of the glow of the phosphor corresponds to the number of the step in the process of training. The patterns of luminescence of the phosphor show how the number of emission sites increases with increasing voltage. Both samples showed a fairly uniform distribution of sites over their entire area. The brightness of the glows in both samples differ greatly due to the strong difference in the height of the nanotubes. The highest ones give more current, since the focusing of the electric field occurs more strongly on them. To achieve uniformity in current output, it is necessary to manufacture structures with a minimum spread in the height of the tips.

To calculate statistical distribution of the effective field enhancement factor ($\beta_{\text{eff}}$) and emission area ($A_{\text{eff}}$), the standard IVC regression analysis in semi-logarithmic Fowler–Nordheim coordinates, according to Equation (1), was applied. Figure 3a shows histograms of fluctuations of the mentioned effective parameters. The average values were for pristine CNT $<\beta_{\text{eff}}>$ = 1380, $<A_{\text{eff}}>$ = 260 nm$^2$ and for CNT/NiO $<\beta_{\text{eff}}>$ = 1040, $<A_{\text{eff}}>$ = 3000 nm$^2$ at the maximum current levels 2.86 mA and 0.86 mA, respectively.
As we can see, $\beta_{eff}$ for pristine CNT is larger than for the sample with NiO. The decrease in $\beta_{eff}$ is probably caused by an increase in the diameter of the nanotubes, due to which the aspect ratio of the tips involved in the emission decreased. The reasons for its difference can be due not only to the geometric factor, but also to the oxide material itself and its deposition quality. However, the emission areas, on the contrary, have smaller values than those of CNT/NiO. Obviously, the disadvantage in terms of the field enhancement factor on the sample with oxide is compensated by a larger emission area.

The high $\beta_{eff}$ (more than 1000) found in both structures indicates a significant length of the emitting CNTs. SEM shows that the bulk of the CNTs do not have the necessary length to achieve strong field focusing at the ends, therefore, it can be concluded that the current is provided by individual nanotubes that protrude strongly above the emitter surface, which are visible on the SEM images.

Figure 3b shows the time dependences of the current at 1.8 mA and 0.5 mA at 2.9 kV and 2.3 kV for pristine CNT and CNT/NiO, respectively. Measurement of statistics within a minute is sufficient to obtain an estimate of the average value of the effective parameter. Further data collection does not lead to a significant change in this parameter. Small current ripples are observed for the two analyzed structures. The coated structure keeps the average current level fairly stable over the entire time interval under consideration, while the sample with pure nanotubes gives a gradual decrease in the current level. Probably, in the first case, the oxide prevents the tubes from being bombarded by ions from the residual atmosphere, so the overall current level does not decrease with time. The emission current fluctuations are estimated according to a simple expression on a relatively stable areas determined empirically:

$$S_t = \frac{I_{max} - I_{min}}{I_{aver}} \cdot 100\%$$ (2)

where $I_{max}$ is the maximum, $I_{min}$ is the minimum, and $I_{aver}$ is the average current. They are equal to 39.9% and 15.3% for pristine CNT and CNT/NiO, respectively. The decrease in emission current fluctuations due to the coating of NiO nanotubes may be due to the lower susceptibility of tips to ion bombardment in the residual atmosphere, when uncoated tubes experience it more strongly, which can lead to their sputtering. A similar phenomenon was observed by the authors of [26]. Thus, according to the experimental data, the introduction of an oxide coating on the tubes showed a slight deterioration in the emission characteristics. However, another result was shown in [9], in which NiO formed an inhomogeneous coating from closely spaced crystal clusters, demonstrating an increase in the field emission current of nanotubes. Such a difference in the results could be due to the difference in coating morphologies, since in our case the ALD method of oxide coating was used, which gives a
continuous uniform coating of tubes, and in [9] Ni nanoparticles deposited on an array of CNTs were oxidized. Probably, the effect of strengthening the focusing of the field on NiO particles decorating carbon nanotubes took place here.

4. Discussion

Among the reasons that led to the deterioration of the emission characteristics may be a geometric factor: an increase in the radius of the tips, due to which the focusing of the electric field decreased. In addition, among the possible reasons may be an increase in the work function of NiO to a value greater than that of nanotubes. It is noted in the literature that this value can be approximately 5.3 eV [22]. The appearance of an additional energy barrier for electrons at the point of contact between the oxide and the tube cannot be ruled out. In addition, among the reasons for the decrease in currents, one should consider a decrease in the electric field on the surface of the tubes passing through the oxide, which possibly has a sufficiently high concentration of free charge carriers in its structure, which endows NiO with the ability to screen the external electric field, which leads to its decrease when passing to the tubes. To more accurately establish the mechanism for reducing emission currents, additional studies of the electronic structure, conductivity, concentration, and type of charge carriers of NiO films obtained by the ALD method should be carried out with the same technological growth parameters.

Obviously, the uniformity of the current output over the cathode area is low. To achieve greater uniformity, it is necessary to manufacture structures with a smaller spread of tips in height. In addition, for a more detailed analysis of the effect of different NiO thicknesses, it is necessary to prepare a batch of samples with the same geometric characteristics and separate tips, which is a technically difficult task. Carrying out such studies is beyond the scope of this work, since it is only in the nature of preliminary tests. However, this type of array shows a good result in terms of overall current output and current stability at low operating voltages. This type of cathode with short tubes is a suitable basis for a comparative analysis of the effects on field emission of various coatings and a promising candidate for the manufacture of electron sources in various technical applications.

5. Conclusions

In this work, we studied the influence of NiO on the field emission characteristics of CNT arrays in terms of key parameters over the entire operating range. Analysis of the data showed that the deposition of an oxide coating on CNTs slightly worsened their emission characteristics. The measured IVCs for pristine CNT and CNT/NiO showed that turn-on fields were 6.16 V/µm for clean nanotubes and 9.66 V/µm for 7.5 nm thick NiO-coated CNTs. An increase in $E_{th}$ from 4.85 V/µm to 7.49 V/µm was also found upon coating with oxide. The maximum recorded emission current densities were 2.86 mA/cm² and 0.86 mA/cm² for clean and coated tubes, respectively. This could be caused either by an increase in the radius of the tips, due to which the focusing of the electric field decreased, by an increase in the work function to a value greater than that of nanotubes, or by a decrease in the electric field on the surface of the tubes passing through the oxide, which possibly has a rather high concentration in its structure of free charge carriers, which give NiO the ability to screen the external electric field, which leads to its decrease when passing to the tubes. To more accurately establish the mechanism for reducing emission currents, additional studies of the electronic structure, conductivity, charge concentration, and type of charge carriers should be carried out.

However, the deposition of an oxide coating favorably affected the emission current fluctuations. They are equal to 40% and 15% for pristine CNT and CNT/NiO, respectively. Improving the emission stability due to the coating of nanotubes with NiO may be due to the lower susceptibility of tips to ion bombardment in the residual atmosphere.

**Author Contributions:** Conceptualization, M.A.C., L.A.F.; methodology, E.O.P., L.A.F., M.Y.M., I.S.E., A.G.K., S.V.F.; validation, E.O.P.; formal analysis, M.A.C., M.Y.M., L.A.F., I.S.E., E.O.P.; investigation, M.A.C., L.A.F., I.S.E., M.Y.M., A.G.K., S.V.F.; resources, M.Y.M., L.A.F.; writing—original draft...
Funding: Authors M. Maximov and I. Ezhov thank the strategic academic leadership program 'Priority 2030' of the Russian Federation (Agreement 075-15-2021-1333 dated 30 September 2021) for partial financial support of the work.

Data Availability Statement: All data generated or analyzed during this study are available within the article.

Acknowledgments: The author thanks Maksim Valerievich Mishin for discussing the results of the research.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Gurylev, V.; Chin, T.K.; Useinov, A. Charge transfer and field emission characteristics of TiO2@CNTs nanocomposite: Effect of TiO2 crystallinity. J. Alloys Compd. 2021, 857, 157598. [CrossRef]
2. Li, C.; Fang, G.; Yuan, L.; Liu, N.; Ai, L.; Xiang, Q.; Zhao, D.; Pan, C.; Zhao, X. Field emission from carbon nanotube bundle arrays grown on self-aligned ZnO nanorods. Nanotechnology 2007, 18, 155702. [CrossRef]
3. Yan, X.; Tah, B.K.; Miele, P. Field emission from ordered carbon nanotube-ZnO heterojunction arrays. Carbon 2008, 46, 753–758. [CrossRef]

4. Chakrabarti, S.; Pan, L.; Tanaka, H.; Hokushin, S.; Nakayama, Y. Stable field emission property of patterned MgO coated carbon nanotube arrays. Jpn. J. Appl. Phys. 2007, 46, 4364. [CrossRef]
5. Yang, C.; Li-Gang, Y.; Ming-Sheng, W.; Qi-Feng, Z.; Jin-Lei, W. Low-field emission from iron oxide-filled carbon nanotube arrays. Chin. Phys. Lett. 2005, 22, 911. [CrossRef]
6. Lian, H.B.; Lee, K.Y.; Chen, K.Y.; Huang, Y.S. Growth of needle-like RuO2 nanocrystals on carbon nanotubes and their field emission characteristics. Diam. Relat. Mater. 2009, 18, 541–543. [CrossRef]
7. Chen, C.A.; Lee, K.Y.; Chen, Y.M.; Chi, J.G.; Lin, S.S.; Huang, Y.S. Field emission properties of RuO2 thin film coated on carbon nanotubes. Vacuum 2010, 84, 1427–1429. [CrossRef]
8. Sreekanth, M.; Ghosh, S.; Srivastava, P. Highly enhanced field emission current density of copper oxide coated vertically aligned carbon nanotubes: Role of interface and electronic structure. arXiv 2018, arXiv:1811.10951.

9. Yang, C.J.; Park, J.I.; Cho, Y.R. Enhanced Field-Emission Obtained from NiO Coated Carbon Nanotubes. Adv. Eng. Mater. 2007, 9, 88–91. [CrossRef]
10. Il Song, Y.; Yang, C.M.; Ku Kwac, L.; Ahm Kim, H.; Ahm Kim, Y. Atomic layer coating of hafnium oxide on carbon nanotubes for high-performance field emitters. Appl. Phys. Lett. 2011, 99, 153115. [CrossRef]
11. Xie, L.Y.; Xiao, D.Q.; Pei, J.X.; Huo, J.; Wu, X.; Liu, W.J.; Ding, S.J. Growth, physical and electrical characterization of nickel oxide thin films prepared by plasma-enhanced atomic layer deposition using nickelocene and oxygen precursors. Mater. Res. Express 2020, 7, 046401. [CrossRef]
12. Tong, X.; Qin, Y.; Guo, X.; Moutanabib, O.; Ao, X.; Pippel, E.; Zhang, L.; Knez, M. Enhanced catalytic activity for methanol electro-oxidation of uniformly dispersed nickel oxide nanoparticles—Carbon nanotube hybrid materials. Small 2012, 8, 3390–3395. [CrossRef] [PubMed]
13. Li, X.; Yu, L.; Wang, G.; Wan, G.; Peng, X.; Wang, K.; Wang, G. Hierarchical NiAl LDH nanotubes constructed via atomic layer deposition assisted method for high performance supercapacitors. Electrochem. Acta 2017, 255, 15–22. [CrossRef]
14. Zhao, L.; Yu, J.; Yue, S.; Zhang, L.; Wang, Z.; Guo, P.; Liu, Q. Nickel oxide/carbon nanotube nanocomposites prepared by atomic layer deposition for electrochemical sensing of hydroquinone and catechol. J. Electroanal. Chem. 2018, 808, 245–251. [CrossRef]
15. Koshtyal, Y.; Nazarov, D.; Ezhov, I.; Mitrofanov, I.; Kim, A.; Ryumyantsiv, A.; Lyutakov, O.; Popovich, A.; Maximov, M. Atomic-layer deposition of NiO to produce active material for thin-film lithium-ion batteries. Coatings 2019, 9, 301. [CrossRef]
16. Koshtyal, Y.; Mitrofanov, I.; Nazarov, D.; Medvedev, I.; Kim, A.; Ezhov, I.; Ezhov, L.; Ryumyantsiv, A.; Popovich, A.; Maximov, M.Y. Atomic-layer deposition of Ni-Co-O thin-film electrodes for solid-state liibs and the influence of chemical composition on overcapacity. Nanomaterials 2021, 11, 907. [CrossRef]
17. Chen, J.G.; Huang, Z.P.; Wang, D.Z.; Chen, J.H.; Yang, S.X.; Ren, Z.F.; Wang, J.H.; Calvet, L.E.; Chen, J.; Klemic, J.F.; et al. Growth and characterization of aligned carbon nanotubes from patterned nickel nanodots and uniform thin films. J. Mater. Res. 2001, 16, 3246–3253. [CrossRef]
18. Jonsson, M.; Nerushev, O.A.; Campbell, E.E. Dc plasma-enhanced chemical vapour deposition growth of carbon nanotubes and nanofibres: In Situ spectroscopy and plasma current dependence. Appl. Phys. A 2007, 88, 261–267. [CrossRef]
19. Chhowalla, M.; Teo, K.B.K.; Ducati, C.; Rupesinghe, N.L.; Amaratunga, G.A.J.; Ferrari, A.C.; Roy, D.; Robertson, J.; Milne, W.I. Growth process conditions of vertically aligned carbon nanotubes using plasma enhanced chemical vapor deposition. *J. Appl. Phys.* **2001**, *90*, 5308–5317. [CrossRef]

20. Jeong, K.Y.; Jung, H.K.; Lee, H.W. Effective parameters on diameter of carbon nanotubes by plasma enhanced chemical vapor deposition. *Trans. Nonferrous Met. Soc. China* **2012**, *22*, S712–S716. [CrossRef]

21. Popov, E.O.; Kolosko, A.G.; Filippov, S.V.; Terukov, E.I.; Ryazanov, R.M.; Kitsyuk, E.P. Comparison of macroscopic and microscopic emission characteristics of large area field emitters based on carbon nanotubes and graphene. *J. Vac. Sci. Technol. B Nanotechnol. Microelectron. Mater. Process. Meas. Phenom.* **2020**, *38*, 043203. [CrossRef]

22. Dean, K.A.; Chalamala, B.R. Current saturation mechanisms in carbon nanotube field emitters. *Appl. Phys. Lett.* **2000**, *76*, 375–377. [CrossRef]

23. Shrednik, V.N. Field emission theory, Chap. 6. In *Unheated Cathodes*; Elinson, M.I., Ed.; Sovietskoe Radio: Moscow, Russia, 1974; pp. 165–207. (In Russian)

24. Gao, R.; Pan, Z.; Wang, Z.L. Work function at the tips of multiwalled carbon nanotubes. *Appl. Phys. Lett.* **2001**, *78*, 1757–1759. [CrossRef]

25. Irwin, M.D.; Servaites, J.D.; Buchholz, D.B.; Lee, B.J.; Liu, J.; Emery, J.D.; Zhang, M.; Song, J.-H.; Durstock, M.F.; Freeman, A.J.; et al. Structural and electrical functionality of NiO interfacial films in bulk heterojunction organic solar cells. *Chem. Mater.* **2011**, *23*, 2218–2226. [CrossRef]

26. Chen, P.H.; Huang, Y.S.; Su, W.J.; Lee, K.Y.; Tiong, K.K. Characterization and enhanced field emission properties of carbon nanotube bundle arrays coated with N-doped nanocrystalline anatase TiO$_2$. *Mater. Chem. Phys.* **2014**, *143*, 1378–1383. [CrossRef]