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Effects of palladium coating on field-emission properties of carbon nanofibers in a hydrogen plasma

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ABSTRACT

Results from electron field-emission studies using arrays of patterned carbon nanofiber bundles are reported. We find that the desired field-emission characteristics were not compromised when a protective coating consisting of a layer of palladium of 5 and 30 nm thickness was applied. Following exposure to a hydrogen plasma for several hours we find that the coatings impede plasma damage significantly, whereas the field-emission properties of uncoated nanofibers degraded much more rapidly. The results demonstrate that carbon nanofibers with protective conformal metal coatings can be integrated into harsh plasma environments enabling a range of applications such as field-ionization ion sources and advanced (micro)-plasma discharges.

1. Introduction

Carbon nanofibers (CNFs) are promising electron field-emitters with high field-enhancement factors [1]. They can boost the performance of micro-plasmas [2] and enable ion formation in field-ionization-type ion sources, e.g., for integration in very compact neutron generators [3]. CNF-based field emitters can also increase the electron density and hence the atomic to molecular ion fraction in Penning-type plasma discharge ion sources [4]. Fabrication methods for the formation of CNF arrays are well established [5]. However, one major concern for these applications is possible etch damage to the CNFs caused by neutral atoms and ions, and physical sputtering by the latter, which can limit the lifetime of CNF-based emitters in harsh plasma environments [6,7]. Efficient protection of CNFs from plasma damage while preserving their favorable field-emission properties is thus critical to advance these promising applications. We are especially interested in the application of field emitters in neutron generators. In this article, we report on the coating of CNFs, the influence of the coating on field-enhancement factors, the effect of exposure to a harsh plasma environment on the structural integrity of nanofiber samples, and on the trends in electron field-emission properties for a series of plasma exposures.

2. Experimental details

The CNFs used in this work were grown by a plasma-enhanced chemical vapor deposition (PECVD) process as described in a previous publication [3]. The growth substrate consists of a silicon wafer with a copper (200 nm) and titanium (30 nm) layers as a base, and a patterned nickel layer as a catalyst. The copper and titanium layers are used to provide electrical contact and to prevent nickel diffusion. During the growth process the nickel catalyst forms the head of the CNF, where it absorbs carbon and forms nickel carbide. Carbon precipitation on the nickel-CNF interface leads to the growth of the CNF [8]. In our process bundles of three to five CNFs were grown on nickel catalyst patches (~3 μm^2) that had been patterned by standard optical lithography. The CNF bundles were formed in arrays with a spacing of 10 μm. As a protective coating for the CNFs we used palladium. Palladium is a favorable metal because it is known to form a uniform coating on CNFs [9,10] and because it also functions as a catalyst for deuterium dissociation [11], which can aid the formation of atomic hydrogen ions within the source, a desirable feature for our applications, e.g., for very compact neutron generators [3]. The coating was applied by palladium evaporation. The evaporation rate was monitored using a quartz crystal microbalance and a rate of 2 Å per second was implemented. After evaporation of 30 nm of Pd, the CNFs were investigated by transmission electron microscopy (TEM) using a Zeiss Libra 200MC operated at 200 kV. The TEM samples were prepared by removing the CNFs from the silicon substrate and transferring them onto a TEM grid. Chemical mapping, which was performed by plasmon-peak energy-filtered TEM spectrum-imaging in combination with principal component analysis [12], clearly shows a

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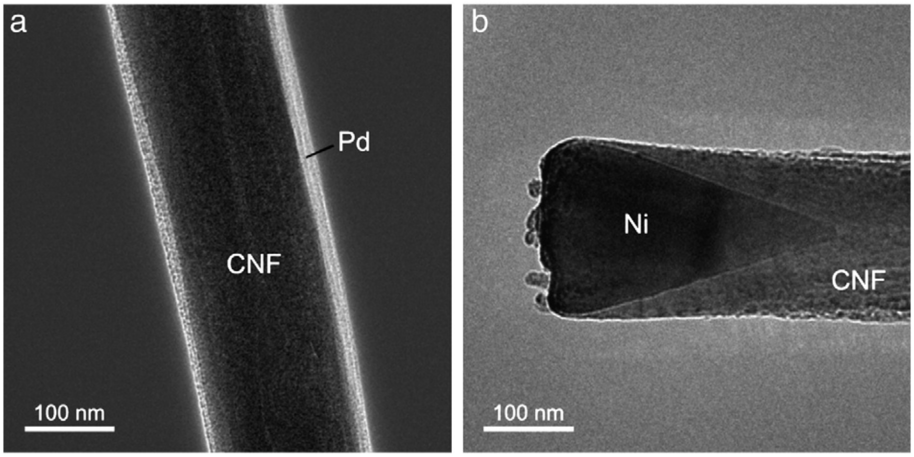

Fig. 1. a) TEM chemical analysis of a CNF with a Pd coating, showing a Pd layer along the sidewalls of the CNF, and b) a bright-field TEM image of the tip area of the CNF showing the nickel catalyst.

uniform coating, Fig. 1a), along the sidewall of the CNF, that is not observed for uncoated samples. The uniformity of the Pd layers was as expected [9,10]. For the TEM samples no island formation or clustering of Pd was visible on the surface of individual CNFs, which was not the case for evaporated gold coatings (not shown). In Fig. 1b), a regular bright-field TEM image shows the nickel at the tip of a CNF. Chemical mapping indicates that these nickel tips do not seem to have a Pd coating present. However, since the nickel will protect the CNF tip from etching by atomic hydrogen, the additional presence of a Pd layer on the tip is not required. Consequently, optimization of the coating process to include tip coverage was not pursued. In fact, having the tip not coated is beneficial for our data analysis, since we can assume that the work function at the tip (where the field emission takes place) has not changed and we can also assume that the tip radius has not changed as a result of the coating process. We note that some samples imaged with a Scanning Electron Microscope (SEM, Zeiss Ultra operated at 20 kV) do in fact appear to show Pd clustering, e.g. lower right inset of Fig. 3. However, unlike the TEM case, one cannot clearly ascertain from the SEM images whether or not the Pd coating covers the CNF tip as well as the side walls. As a result, assumptions regarding the tip work function and radius being unaffected by the Pd coating in the case of uniformly coated samples may no longer apply to those exhibiting Pd clustering. However, we believe that as long as the coating covers the entire length of the fiber, as is indeed observed for all samples, then the essential result that the Pd coating protects the CNFs in a harsh plasma environment should not be affected.

Since we have not observed clustering on our TEM samples, we cannot make a statement about the tip area of the samples that show clustering and therefore we still assume that the tip work function and radius are not affected by the coating. We believe that the different coating morphologies do not impact the results of this paper as long as the coating covers the CNF completely, which is what we observed for all of our samples.

In our experiments we placed coated (5 and 30 nm Pd) and uncoated CNF samples (size 1 cm^2) into the plasma chamber of a microwave-driven (2.45 GHz) electron cyclotron resonance (ECR)-type ion source [13]. The source was operated at a microwave power of 500 W and a hydrogen gas pressure of 0.15 Pa. This ECR source produces a hydrogen plasma with a high proton fraction of 95% [13] and a plasma electron density of ~10^{17} m^{-3} [14].

The setup for electron field-emission measurements was described in an earlier publication [3]. Samples were placed into a high-vacuum chamber (base pressure 1.3×10^{-5} Pa). The sample-to-bias-plate distance was controlled by a linear manipulator and field-enhancement factors, γ, were calculated from Fowler–Nordheim (FN) plots resulting from repeated voltage scans during which sample currents were recorded. Typical bias voltages where 10 to 40 keV for gaps of a few mm. In our calculations of effective emission-areas and field-

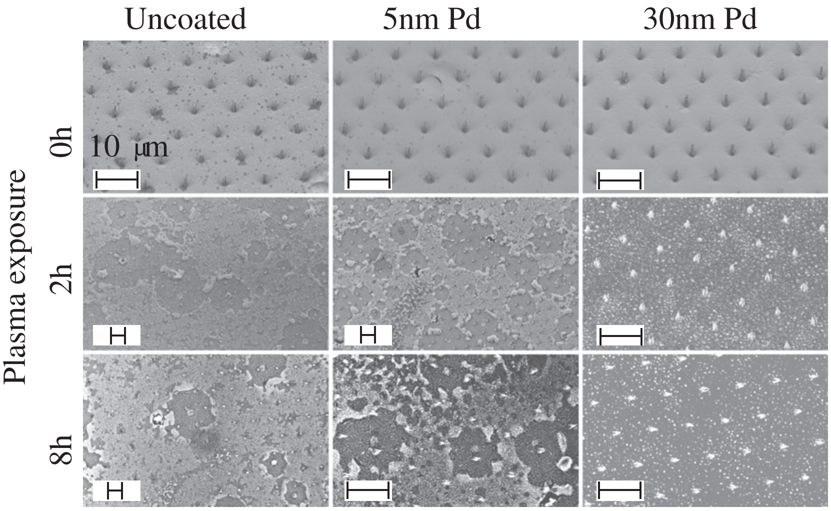

Fig. 2. SEM of CNF arrays. Distance between CNFs is 10 μm.

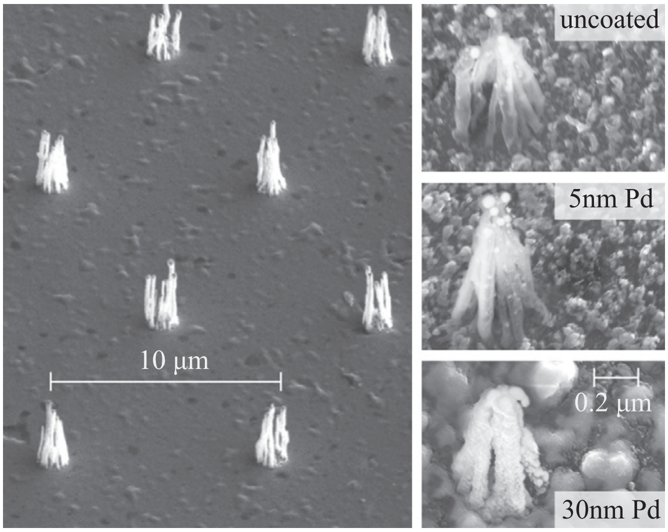

Fig. 3. SEM of single CNFs.

enhancement factors we assumed a constant value of the work function of 4.8 eV for all samples as discussed above. We recognize that this assumption can introduce a systematic error, e.g., due to work function changes during extended plasma exposures. While this limits the generality of our results, we believe that it does not impact the validity of our main findings when calculating field-enhancement factors and emitting areas. We also stress that these calculated values are used only as a measure to compare the samples. We therefore make use of the simple FN-equation without any correction factors, which fits out data very well. In order to extract absolute numbers one would have to include corrections to the FN-equation [15]. The results on threshold voltages and lifetimes are not affected by the assumptions discussed above, since they are measured directly.

In between plasma exposures and current–voltage (I-V) measurements, we imaged samples using an SEM in order to track structural damage induced during plasma exposures (Fig. 2). After a total of eight hours of plasma exposure we ran lifetime tests while increasing the emission currents on all samples.

3. Results and discussion

Inspection of the samples using an SEM reveals that the uncoated and 5 nm Pd-coated samples suffered severe substrate damage, while changes on the sample with a 30 nm Pd coating are very minor in comparison. Individual CNFs as shown in Fig. 3 do not reveal any visible etch damage. The origin of the damage to the substrate layers is probably thermal heating resulting from exposure to the hydrogen plasma. Following the PECVD growth process and the Pd coating step, there are three metal layers present on the silicon substrates — on the outside the Pd coating, then a titanium layer (30 nm), and below that a copper layer (200 nm). Comparing the melting temperatures in this tri-layer structure ($T_{Ti} = 1661$ °C, $T_{pd} = 1552$ °C, and $T_{Cu} = 1083$ °C), we argue that the 30 nm thick Pd layer probably protects the underlying copper layer from melting. This could be tested, e.g., in a study were the back side of samples is actively cooled during plasma exposures.

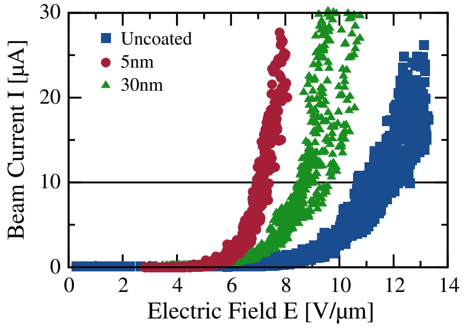

Fig. 4. Example I-V curve. This data was taken after 8 h of plasma exposure and 4 h of electron emission, cf. Fig. 7.

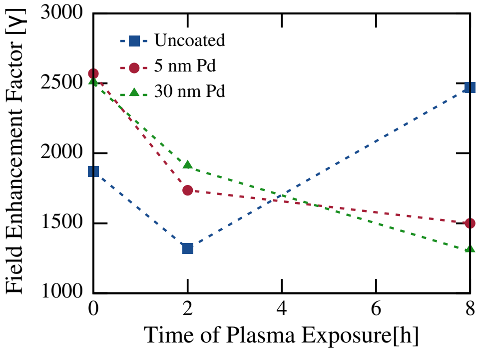

Fig. 5. Field-enhancement factors of uncoated and coated CNFs versus plasma exposure time.

In Fig. 4 we show electron field-emission plots of the extracted electron current as a function of the applied electrical field, E, for an uncoated sample and for samples with 5 and 30 nm Pd coatings.

This data was taken after exposure to a hydrogen plasma in the ECR source for samples with a total area of 1 cm^2 with ~10^6 CNF bundles. Similar data was taken in between plasma exposures and analyzed using FN-plots to extract field-enhancement factors and emission areas. The initial enhancement factors of all three CNF samples were between 1900 and 2500 (Fig. 5) with a slightly higher γs for both of the coated samples compared to the uncoated sample. It is an important first result that coating with a protective Pd layer does not degrade field emission properties of CNFs. The statistical error in this measurement is small, but the systematic error can be rather large. The major contribution to this large uncertainty stems from the small sub-ensemble of an estimated several hundred CNF tips that contribute dominantly to electron field-emission, out of a total of ~10^6 tips. This can lead to different fibers contributing with different γ factors in repeated runs. We did find that the field-enhancement factor remains constant for repeated runs on samples that were stored in situ for periods of several days. However, during the experiments samples underwent several vacuum cycles. The systematic errors are therefore hard to quantify and because of this error bars were not included in Figs. 5–7. Comparing the evolution of the field-enhancement characteristics after plasma exposure, we find that after two hours of plasma exposure, the field enhancement factor of all three samples went down by approx. 25% while the emitting area went up (see Fig. 6) with the coated CNFs still having higher γs. After eight hours of plasma exposure this trend continued for the coated samples, while γ of the uncoated sample went up and its emitting area decreased

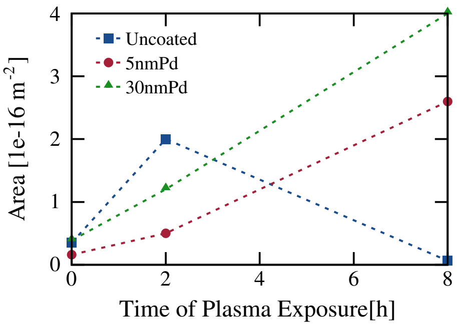

Fig. 6. Emitting area for uncoated and coated CNFs versus plasma exposure time.

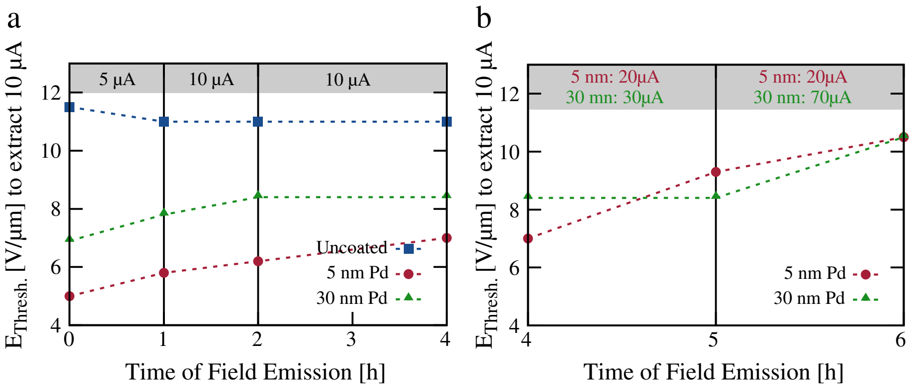

Fig. 7. Required electric field to extract 10 µA after 8 h of plasma exposure. Between these measurements the sample was run at a constant current as stated at the top of the graph. No higher current could be extracted from the uncoated sample after 4 h. (a) the first 4 h of field emission (b) the last 2 h using higher currents between measurements.

drastically. The moderate decline in field-enhancement factors and the increase in area during plasma exposure points to an etching effect of those tips with a high-field enhancement factor. By removing the sharpest tips from the distribution, more tips (and therefore a larger area) with a lower γ contribute to the current. The uncoated sample shows a strong decline in area at the end of the plasma exposure, which can be explained by a strong etching of most tips, so that only a small number of tips remain. This small number of tips would also lead to a larger variation in γ, a possible explanation for the high field-enhancement factor measured for this sample.

Even though surface damage on the wafer was observed, no correlation between the behavior of γ and the visible damage could be found. We also note that the possible change in field-enhancement factor due to etching is not visible in the SEM images. Here, one has to keep in mind that only a small subset of tips contributed to the current and therefore the SEM images do not necessarily represent the emitting tips.

After finishing the eight hours of plasma exposure, we mounted the samples again in our field-emission setup for more electron emission studies. The extracted current was now increased step-by-step over several hours and kept stable by a feedback loop. In between these steps, we compare the electric field, E_{Thresh}, required to extract 10 µA, see Fig. 7. The threshold electric field was derived from I-V curves, such as those shown in Fig. 4, which were acquired in between the constant current runs by switching the feedback loop off and automatically scanning the voltages over a time frame of several minutes and then continuing in constant current mode. We started extracting 5 µA for an hour, then extracted 10 µA for three hours. After this time, no higher currents could be achieved from the uncoated sample applying fields $E \leq 12$ V/µm, whereas the coated samples delivered 20 µA for two hours in the case of the 5 nm coating, and 30 followed by 70 µA for an hour each in the case of the 30 nm coating.

These results are consistent with our earlier interpretation that tips with high field-enhancement factors are severely damaged by etching. The coated samples show slow effects of burnout taking place for prominent emitters, which increases the threshold for the electric field that is needed to extract a constant current, e.g. 10 µA. In contrast, the uncoated sample only has very few tips left after plasma exposure, resulting in a much reduced maximum current that can be extracted from them.

We also expect a similar behavior of lower field-enhancement factors and a larger emitting area over time from conditioning of the samples. However, all samples were conditioned before plasma exposure and conditioning would not explain the difference between coated and uncoated samples.

Although the coated samples also show some degradation during plasma exposure, no reduction in emitting area was observed. A sufficient layer of Pd coating protects the CNFs. It also increases the amount of extractable current for a given electric field. The coating therefore improves the lifetime of CNFs in a hydrogen plasma environment.

4. Conclusions and outlook

In summary, the impact of a harsh hydrogen plasma environment and long-duration beam extraction on the field-enhancement factor of coated and uncoated CNFs were investigated. We showed that the field-emission properties of Pd-coated CNFs are comparable to those of uncoated ones. Although heavy degradation of the samples was observed, the field-enhancement factor was influenced only moderately by the plasma. Extracting a beam over a long period revealed differences between the coated and uncoated samples. The coated samples can deliver high currents for a longer time; the uncoated sample delivers a lower current only for a limited time (<4 h). Our results underpin the application potential of metal-coated CNFs for cold cathodes and for ion formation by field ionization in a harsh plasma environment.

For future experiments a similar study using heavier ions such as argon or oxygen will be interesting to investigate the possible use of this type of protection coating for a larger variety of plasma applications.

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References

[1] W.A. de Heer, A. Chatelain, D. Ugarte, Science 270 (1995) 1179.
[2] S.-J. Park, J.G. Eden, K.-H. Park, Appl. Phys. Lett. 84 (2004) 4481.
[3] A. Persaud, I. Allen, M.R. Dickinson, T. Schenkel, R. Kapadia, K. Takei, A. Javey, J. Vac. Sci. Technol. B 29 (2011) 02B107.
[4] A. Sy, Q. Ji, A. Persaud, O. Waldmann, T. Schenkel, Rev. Sci. Instrum. 83 (2012) 02B309.
[5] M. Meyyappan, L. Delzeit, A. Cassell, D. Hash, Plasma Sources Sci. Technol. 12 (2003) 205.
[6] J.D. Wnuk, J.M. Gorham, B.A. Smith, M. Shin, D.H. Fairbrother, J. Vac. Sci. Technol. A 25 (2007) 621.
[7] J. Yu, J. Chen, S. Deng, N.S. Xu, Appl. Surf. Sci. 258 (2011) 738.
[8] K.P. De Jong, J.W. Geus, Catal. Rev. 42 (2000) 481.
[9] Y. Zhang, N.W. Franklin, R.J. Chen, H. Dai, Chem. Phys. Lett. 331 (2000) 35.
[10] S. Lee, S.-J. Kahng, Y. Kuk, Chem. Phys. Lett. 500 (2010) 82.
[11] T. Mitsui, M. Rose, E. Fomin, D. Ogletree, M. Salmeron, Nature 422 (2003) 705.
[12] F.I. Allen, M. Watanabe, Z. Lee, N.P. Balsara, A.M. Minor, Ultramicroscopy 111 (2011) 239.
[13] O. Waldmann, B. Ludewigt, Rev. Sci. Instrum. 82 (2011) 113505.
[14] K.D. Vargheese, G.M. Rao, Rev. Sci. Instrum. 71 (2000) 467.
[15] R.G. Forbes, A. Fischer, M.S. Mousa, J. Vac. Sci. Technol. B 31 (2013) 02B103.