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論文内容の要旨

Carbon nanotubes (CNTs) are found to have a potential as excellent field emitters because of their remarkable electrical and mechanical properties. In spite of the work carried out in the CNT emitters field, achieving a high current density along with a total high emission current from a CNT emitter is still said to be a challenging job. It is because at a high current operation of an emitter, an emission current is in general limited by disappearance of CNTs from a substrate under a high electric field due to a weak bonding between CNTs and a substrate, a high contact resistance and a low thermal conductivity of CNT junction. Along with this a screening effect provoked by proximity of CNTs on an emitter also results in the limitation of a high emission current.

The work carried out in this thesis was focused on two main goals. One is to overcome these obstacles by improving a quality of rooting of CNTs into a substrate. The other is to enhance an edge effect, in which a higher emission current is expected to achieve from CNTs located at edges of an emitter as compared to that in the center because CNTs located at edges might experience a weak screening effect. In order to achieve this enhancement of the edge effect, fabrication of a field emitter array containing many small equidistant circular emitters was proposed.

Fabrication techniques of mainly two kinds of CNT field emitters, viz., a continuous film emitter (CFE) and a field emitter array (FEA), were developed in this work. A CFE was fabricated by depositing a titanium (Ti) thin film on a tantalum (Ta) base followed by dispersion of CNTs on Ti/Ta using a falling drop method and rooting of dispersed CNTs into a Ti film at a high temperature. However the small number of CNT coverage of around 50%, which is a ratio of an effective emission area to a total area of a substrate, was found in the CFE fabrication due to non-uniform dispersion of CNTs with the falling drop method.

In order to improve the CNT coverage and uniformity, an electrospray technique, in which CNTs are electrostatically charged and attracted towards a grounded substrate, was tried for CNT dispersion. As a result of it, the coverage was improved to ~70% and uniform CNT film could be obtained with a

small size of CNT bundles, isolated and longer CNTs. This technique was applied to make a CNT emitter for the first time worldwide.

In fabrication process of a FEA, equidistant small circular Ti islands were deposited instead of a Ti film by setting a mask on a Ta base and CNTs were rooted at a high temperature into the Ti islands to form circular emitters of CNTs. The CNTs were dispersed using the falling drop method. However it was found that at a high temperature CNTs were strongly rooted not only into Ti islands but also into a Ta base where CNT rooting had to be avoided. To avoid rooting of CNTs into Ta it was attempted that a FEA was fabricated at a comparatively low temperature. However, a low temperature rooting showed reduction of CNT coverage down to ~15% on Ti islands. In order to solve this antinomy and root CNTs only into Ti islands at a high temperature, a substrate was modified.

A substrate for a FEA was modified by depositing a TiN film on a Ta base followed by deposition of Ti islands on TiN/Ta. A TiN coating allowed rooting of CNTs into Ti islands at a high temperature and stopped rooting of CNTs into a Ta base. A TiN film was used in FEA fabrication for the first time in the world.

The all kinds of emitters prepared under the different conditions discussed above were tested under an applied DC voltage. An emission current of 20.4 mA with an effective current density of 1.2 A/cm^2 calculated by considering an effective emission area only was measured from a CFE prepared by the falling drop method. An emission current was significantly improved in case of a CFE prepared by the electrospray technique due to easy erection of CNTs. Reasons for the easy erection might be that the electrospray brought existence of more isolated and free-end CNTs and consequently longer and flexible CNTs although many CNTs lying on a substrate surface were found in the falling drop method.

A significantly better current density of ~13 A/cm^2 at 7 V/μm compared to 1.2 A/cm^2 for the CFE at the same field of 7 V/μm was achieved from both the FEAs prepared on a Ta base at high and low rooting temperatures. However a lower emission was achieved from a FEA rooted at a low temperature due to the small CNT coverage. The achieved high current density above in a FEA gave an evidence of the successful enhancement of the edge effect.

A series of FEAs on the TiN coated substrates were fabricated at a high temperature to optimize both pitch and diameter of circular emitters so as to get an adequate combination of the strong edge effect and an effective emission area in a FEA. According to experimental results of pitch optimization, the strongest edge effect corresponding to the highest effective current density was observed when the edge-to-edge distance between circular emitters was ≥150 μm. A diameter of 50 μm was found better than other bigger diameters of 100 and 200 μm to achieve a high emission current. The highest emission current was achieved from the FEA having circular emitters in a diameter of 50 μm and a pitch of 120 μm. A high emission current of 47 mA with a current density of 30.5 A/cm^2 was measured at 7 V/μm from this FEA. The FEA with circular emitters in a diameter of 50 μm and a pitch of 120 μm was accompanied by an adequate combination of an effective emission area and the strong edge effect.

The finite element method was tried to perform electrostatic simulation for evaluation of electric field distributions on modeled FEAs in different diameters and pitches. The field distribution on different FEA pitches shows negligible interference of circular emitters on each other for the edge-to-edge distance of ≥150 μm that was matching with the experimentally optimized distance for the strongest edge effect. Simulated electric field distributions on circular emitters of different diameters in a distance also expressed that a smaller circular emitter itself acts as a macroscopic sharp emitter.

Excellent stability of a CFE, a FEA rooted at a low temperature and a FEA with a TiN coated substrate was demonstrated by performing lifetime tests in a constant current mode for over 2020, 1007 and 2948 hours, respectively. Electric fields were increased by 3.5% and 15% during elapsed time in case of the CFE and the FEA rooted at a low temperature, respectively, whereas in case of the modified FEA, an electric field was decreased to 2.5%. The decrease of the electric field might be a result of slow erection of CNTs.

In addition to above achievements CFEs and FEAs were tested in a pulse mode in a combined diode-RF electron gun at Paul Scherrer Institute (PSI). Field emission of CNT emitters was observed at 5-30 V/μm, using a 250 ns FWHM long pulse with a peak voltage of 80-470 kV. A nano Coulomb of charge was extracted from a CFE and an emittance of 4 mm mrad was measured with a 2 pC electron beam.

As a conclusion, the electrospray technique was found to be a better technique for dispersion of CNTs applied in case of a CFE to improve CNT coverage and film uniformity. A FEA could be fabricated with improved rooting technique and quality at a high temperature owing to modification of a substrate by depositing a TiN film on a Ta base. Excellent field emission results were achieved from a FEA, which were much better than that for a CFE, were achieved as a consequence of the strong edge effect based on optimized values of a diameter and a pitch of circular emitters. A CFE tested in the diode-RF electron gun showed good field emission stability and a charge of a nano Coulomb was drawn from the CFE. A beam emittance of 4 mm mrad was measured at 2 pC charge.

博士論文の審査結果の要旨

CHOUHAN VIJAY氏の提出論文は、カーボンナノチューブ(CNT)を用いた大強度フィールドエミッターの製作技術の開発に関するものである。CNTは発見以来、電子の電界放出物質として注目され、様々な研究がなされてきたが、CNTとベース金属との接合に難があり剥がれ易い、また、CNTエミッターの面積を実用的な大きさにすると、電流密度が著しく低下する等の難点が克服すべき課題としてあった。

CHOUHAN氏の研究は、これらの課題に様々なアプローチで挑戦するもので、

1）　一様分布型CNTエミッターの製作と特性測定
2）　アレイ型CNTエミッターの優位性を示す実験的検証
3）　CNTとTi/Ta基体間の結合（根付）を向上させる技術の開発
4）　CNTを一様に分散させる電気分散法の開発
5）　アレイ型の作成工程の開発と作成工程の最適化
6）　アレイ型のアレイ最適化とシミュレーションによる定性的な検証
7）　CNTエミッターの寿命測定
8）　CNTエミッターによる500kV電子銃からビーム引き出し試験

など多岐にわたっている。

最初に一様分布型CNTエミッターを製作し、その放出電流特性から、高い放出電流を得るには、電界が集中しやすいエミッターのエッジの効果を有効に利用すべきであることを示し、アレイ型CNTエミッターの研究に移行した。

小円のCNTエミッターを多数配列するアレイ型の製作にあたり、Tiの小円以外の所(Ta基体）にCNTが付かないように、最初にTa基体にTiNの薄膜を付けてからその上にTiの小円を蒸着し、そこにのみCNTを根付する方法を開発した。CNTを一様に分散させる技術開発とあいまって、CNT被覆率を70%程まで向上させた。

アレイ型に於ける小円CNTエミッターの直径とアレイピッチを変えて実験的に最適条件を求め、それぞれ50 μmと120μmのときに電流が最大となることを示した。そのときの値は最大電流47mA、有効電流密度30.5A/cm^2（7V/μm）である。また、シミュレーションを行い、上の最適条件とよく一致することを示した。

2種類のアレイ型CNTエミッターについて、放出電流を一定に保つ長時間のDC寿命測定を実施し、極めて安定であることを確認した。低温根付（1000℃）の未使用エミッターを5A/cm^{2}で1007時間の連続試験し、加速電界は2.6%/週の微増に留まることを示した。また、電界電子放出特性を繰り返し行った高温根付（1200℃）のエミッターを2.3A/cm^{2}で2948時間試験し、この間の加速電界はむしろ減少（2.5%）することを実証した。（後者では、エミッター上のCNTが消失する効果よりも起立する効果が勝り、その結果として必要な電界強度が少し下がったと考えられる。）

本論文は、上で述べたように新しく開発した技術を含んでおり、加速器への応用にも有用な寄与をすると考えられる。

以上により審査委員全員が、CHOUHAN氏の研究は博士論文に値すると判断した。