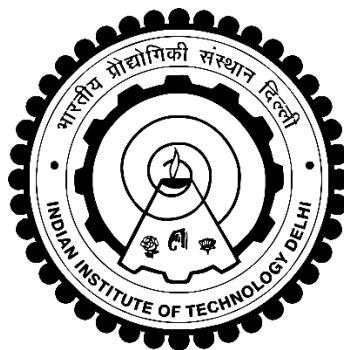


FIELD EMISSION PROPERTIES OF PATTERNED AND METAL-DECORATED CARBON NANOTUBES

GULSHAN KUMAR



**DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY DELHI
JANUARY 2025**

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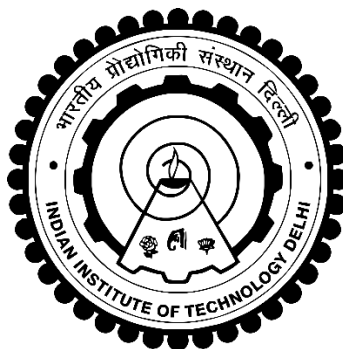
FIELD EMISSION PROPERTIES OF PATTERNED AND METAL-DECORATED CARBON NANOTUBES

by

Gulshan Kumar

Department of Physics

*Submitted in fulfilment
of the requirements of the
degree of Doctor of Philosophy to the*



**DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY DELHI
JANUARY 2025**

Dedicated to...

My family and friends

Certificate

*This is to certify that the thesis entitled “**Field emission properties of patterned and metal decorated carbon nanotubes,**” being submitted by **Gulshan Kumar** to the Indian Institute of Technology Delhi, New Delhi, for the award of the degree of **Doctor of Philosophy** in physics is a record of bonafide research work carried out by him under our supervision and guidance. To the best of our knowledge, he has fulfilled the requirements for the thesis submission, which has reached the requisite standard.*

The material in the thesis has not been submitted in part or in full to any other University or Institute for awarding any degree or diploma.

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ABSTRACT

A carbon nanotube (CNT) is a one-dimensional cylindrical carbon nanostructure synthesized synthetically. Since their ground-breaking discovery, carbon nanotubes have been one of the era's miraculous materials due to their exceptional properties such as high electrical and thermal conductivities, high aspect ratio, high mechanical strength, and chemical stability, as well as their widespread application in a variety of fields of science and technology. CNTs may be used as nano-interconnects in integrated circuits, electron sources, hydrogen storage, solar cells, gas sensors, lightweight and high-strength composites, and tissue engineering, among other uses. Due to their unusually high aspect ratio, excellent electrical conductivity, nanoscale tip, high mechanical stiffness, and ability to grow on a variety of substrates, tremendous effort has been made to replace conventional thermionic sources with CNT-based cold cathodes for applications such as field emission displays (FEDs), field emission microscopes, miniature X-ray tubes, microwave amplifiers, and e-beam lithography. An FE source's critical characteristics for device applications are low turn-on and threshold fields, a high current density, and temporal stability. Although carbon nanotubes are the best field emitters till date in terms of high emission currents at relatively low applied electric fields, a few issues remain, including low adhesion and high contact resistance between the substrate and the CNTs, poor device temporal stability, large field screening effects between adjacent CNTs, ion bombardment and space charge effect on the emitting tip during the field emission (FE) process.

The present thesis focuses on resolving unresolved issues, such as the screening effect between adjacent CNTs. The screening effect substantially impacts field emission properties since it decreases the effective electric field on the surface of the emitter. This

results in reduced emission currents, non-uniform emission, and changes in the F-N plots. The screening effect may be mitigated by ensuring that emitters are spaced appropriately. Comprehending and managing this phenomenon is essential for maximizing the efficiency of field emission devices. It has been proven that the use of interlayer impacts the adhesion of CNTs with substrate. Adhesion between the emitters and the substrate is critical for cold cathode applications, particularly FEDs. Due to a deficiency of catalytic metals on the substrate, producing metal silicide between the substrate and the CNT layer impairs CNT growth. So, there is a need to find a straightforward and cost-effective method for creating patterns of vertically aligned carbon nanotubes (VACNTs) with the help of interlayer and enhancing their field emission (FE) characteristics.

The first section of the thesis is based on the growth of patterned vertically aligned carbon nanotube (VACNT) films without the use of lithography-assisted deposition. A systematic change in the FE current density of the patterned CNT films grown at different temperatures was observed. This can be attributed to the less amorphous carbon over the film surface and optimum growth of patterned CNTs at 900 °C. The use of interlayers is to create pattern like pillars of VACNTs of various shapes, as well as enhancing the CNT substrate adhesion. The current density for the CNT film produced at 900 °C on the non-patterned substrate is 3.2 mA/cm², which rises to 16.1 mA/cm² at 3V/μm of the electric field, when VACNT bundles are arranged in a circular pattern.

Ultra-thin film-coated or decorated vertically aligned carbon nanotubes (VACNTs) have improved field emission parameters, including the effective emission area and the number of active emitters. However, on this topic, there are very few studies available. Examining FE images may assist in identifying changes in FE parameters before and after metal decoration on CNTs. The effect of electronic structure on decorated carbon

nanotubes field emission (FE) capabilities has been the subject of several studies, with a particular emphasis on the density of states (DOS) in the 0–10 eV energy band at the Fermi level. It will be intriguing to investigate, how the electronic structure affects the field emission properties of VACNTs decorated with various transition metals and how the occupancy of d- and s-states in some cases, can play the most prominent role in governing the field emission properties.

सारांश

कार्बन नैनोट्यूब (सीएनटी) एक आयामी बेलनाकार कार्बन नैनोस्ट्रक्चर है जिसे कृत्रिम रूप से संश्लेषित किया जाता है। उनकी अभूतपूर्व पश्चात, कार्बन नैनोट्यूब उच्च विद्युत और तापीय चालकता, उच्च पहलू अनुपात, उच्च यांत्रिक शक्ति और रासायनिक स्थिरता जैसे असाधारण गुणों के साथ-साथ विभिन्न क्षेत्रों में उनके व्यापक अनुप्रयोग के कारण युग की चमत्कारी सामग्रियों में से एक हैं। सीएनटी का उपयोग एकीकृत सर्किट में नैनो-इंटरकनेक्ट के रूप में, इलेक्ट्रॉन स्रोतों, हाइड्रोजन भंडारण, सौर सेल, गैस सेंसर, हल्के और उच्च शक्ति वाले कंपोजिट और ऊतक इंजीनियरिंग में किया जा सकता है। उनका असामान्य उच्च पहलू अनुपात, उत्कृष्ट विद्युत चालकता, नैनोस्केल टिप, उच्च यांत्रिक कठोरता, और विभिन्न प्रकार के सबस्ट्रेट पर उत्पत्ति की क्षमता के कारण, पारंपरिक थर्मिओनिक उत्सर्जकों को सीएनटी-आधारित कोल्ड कैथोड उत्सर्जकों के द्वारा बदलने के लिए व्यापक प्रयास किए गए हैं जैसे कि फील्ड उत्सर्जन डिस्प्ले (एफईडी), क्षेत्र उत्सर्जन माइक्रोस्कोप, लघु एक्स-रे ट्यूब, माइक्रोवेव एम्पलीफायरों, और ई-बीम लिथोग्राफी जैसे अनुप्रयोगों के लिए। डिवाइस अनुप्रयोगों के लिए एक फील्ड उत्सर्जन स्रोत की महत्वपूर्ण विशेषताएं कम टर्न-ऑन और थ्रेशोल्ड फ्रील्ड, एक उच्च विद्युत धारा घनत्व और लौकिक स्थिरता हैं। हालांकि कार्बन नैनोट्यूब अपेक्षाकृत कम लागू विद्युत क्षेत्रों में उच्च उत्सर्जन धाराओं के मामले में आज तक का सबसे अच्छा क्षेत्र उत्सर्जक हैं, कुछ मुद्दे बने हुए हैं, जिनमें सबस्ट्रेट और सीएनटी के बीच कम आसंजन और उच्च संपर्क प्रतिरोध, खराब डिवाइस लौकिक स्थिरता, आसन्न सीएनटी के बीच बड़े क्षेत्र स्क्रीनिंग प्रभाव, आयन बमबारी और क्षेत्र उत्सर्जन (एफई) प्रक्रिया के दौरान उत्सर्जक टिप पर अंतरिक्ष प्रभार प्रभाव, इत्यादि प्रमुख हैं।

वर्तमान थीसिस अनसुलझे मुद्दों को हल करने पर केंद्रित है, जैसे कि आसन्न सीएनटी के बीच स्क्रीनिंग प्रभाव। स्क्रीनिंग प्रभाव क्षेत्र उत्सर्जन गुणों को काफी सीमा तक प्रभावित करता है क्योंकि यह उत्सर्जक की सतह पर प्रभावी विद्युत क्षेत्र को कम करता है। इसके परिणामस्वरूप उत्सर्जन धाराएं कम हो जाती हैं, असमान उत्सर्जन होता है और F-N भूखंडों में परिवर्तन होता है। स्क्रीनिंग प्रभाव को उत्सर्जकों के बीच उचित दूरी सुनिश्चित करके कम किया जा सकता है। क्षेत्र उत्सर्जन उपकरणों की दक्षता को अधिकतम करने के लिए इस घटना को समझना और प्रबंधित करना आवश्यक है। यह प्रमाणित हो गया है कि इंटरलेयर का उपयोग सब्सट्रेट के साथ सीएनटी के आसंजन को प्रभावित करता है। उत्सर्जक और सब्सट्रेट के बीच आसंजन ठंड कैथोड अनुप्रयोगों, विशेष रूप से फील्ड उत्सर्जन डिस्प्ले के लिए महत्वपूर्ण है। सब्सट्रेट पर उत्प्रेरक धातुओं की कमी के कारण, सब्सट्रेट और सीएनटी परत के बीच धातु सिलिसाइड का उत्पादन सीएनटी उत्पत्ति को बाधित करता है। इसलिए, इंटरलेयर की मदद से लंबवत संरेखित कार्बन नैनोट्यूब (VACNTs) के पैटर्न बनाने और उनके क्षेत्र उत्सर्जन (FE) विशेषताओं को बढ़ाने के लिये एक आसान और लागत प्रभावी विधि खोजने की आवश्यकता है।

थीसिस का पहला खंड लिथोग्राफी-सहायता प्राप्त निक्षेप के उपयोग के बिना पैटर्न वाले लंबवत संरेखित कार्बन नैनोट्यूब (वीएसीएनटी) फिल्मों के विकास पर आधारित है। विभिन्न तापमानों पर उगाई जाने वाली पैटर्न वाली सीएनटी फिल्मों के एफई विद्युत धारा घनत्व में एक व्यवस्थित परिवर्तन देखा गया। यह फिल्म की सतह पर कम अनाकार कार्बन और 900 °C पर पैटर्न वाले सीएनटी के इष्टतम विकास के लिए जिम्मेदार ठहराया जा सकता है। इंटरलेयर्स का उपयोग विभिन्न आकृतियों के वीएसीएनटी के स्तंभों की तरह पैटर्न बनाने के साथ-साथ सीएनटी सब्सट्रेट आसंजन को बढ़ाने के लिए है। गैर-पैटर्न वाले सब्सट्रेट पर 900 °C पर निर्मित CNT फिल्म के लिए विद्युत क्षेत्र 3V/μm पर विद्युत् धारा घनत्व 3.2 mA/cm², जब VACNT बंडलों को एक

गोलाकार पैटर्न में व्यवस्थित किया जाता है पर तब यह बढ़कर 16.1 mA/cm^2 तक बढ़ जाता है ।

अति पतली फिल्म-लेपित या सजाए गए लंबवत संरेखित कार्बन नैनोट्यूब (VACNTs) ने प्रभावी उत्सर्जन क्षेत्र और सक्रिय उत्सर्जकों की संख्या सहित क्षेत्र उत्सर्जन मापदंडों में सुधार किया है। हालांकि, इस विषय पर, बहुत कम अध्ययन उपलब्ध हैं। एफई छवियों की जांच सीएनटी पर धातु सजावट से पहले और बाद में एफई मापदंडों में परिवर्तन की पहचान करने में सहायता कर सकती है। धातु से सजाए गए कार्बन नैनोट्यूब क्षेत्र उत्सर्जन (एफई) क्षमताओं पर इलेक्ट्रॉनिक संरचना का प्रभाव फर्मी स्तर पर 0-10 eV ऊर्जा बैंड (DOS) के घनत्व पर विशेष जोर देने के साथ कई अध्ययनों का विषय रहा है। यह जांच करना दिलचस्प होगा कि इलेक्ट्रॉनिक संरचना विभिन्न संक्रमण धातुओं से सजाए गए वीएसीएनटी (VACNT) के क्षेत्र उत्सर्जन गुणों को कैसे प्रभावित करती है और कुछ मामलों में डी- और एस- स्तरों की अधिभोग, क्षेत्र उत्सर्जन गुणों को नियंत्रित करने में सबसे प्रमुख भूमिका कैसे निभा सकती है।

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