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AMORPHOUS DIAMOND FLAT PANEL DISPLAYS

Final report of ER-LTR CRADA Project

Lawrence Berkeley National Laboratory and SI Diamond Technology

LBNL BG 95-34, 10/94 - 3/97

ABSTRACT OF FINAL TECHNICAL REPORT

The objective of this project was to determine why diamond-based films are unusually efficient electron emitters (field emission cathodes) at room temperature. Efficient cathodes based on diamond are being developed by SI Diamond Technology (SIDT) as components for bright, sunlight-readable, flat panel displays. When the project started, it was known that only a small fraction (<1%) of the cathode area is active in electron emission and that the emission sites themselves are sub-micron in size. The critical challenge of this project was to develop new microcharacterization methods capable of examining known emission sites. The research team used a combination of cathode emission imaging (developed at SIDT), micro-Raman spectroscopy (LBNL), and electron microscopy and spectroscopy (National Center for Electron Microscopy, LBNL) to examine the properties of known emission sites. The most significant accomplishment of the project was the development at LBNL of a very high resolution scanning probe that, for the first time, measured simultaneously the topography and electrical characteristics of single emission sites. The increased understanding of the emission mechanism helped SIDT to develop a new cathode material, "nano-diamond," which they have incorporated into their Field Emission Picture Element (FEPix) product. SIDT is developing large-format flat panel displays based on these picture elements that will be brighter and more efficient than existing outdoor displays such as Jumbotrons. The energy saving that will be realized if field emission displays are introduced commercially is in line with the energy conservation mission of DOE. The unique characterization tools developed in this project (particularly the new scanning microscopy method) are being used in ongoing BES-funded basic research.

The project was begun with the signing of the Cooperative Research and Development Agreement (CRADA) in 10/94 (beginning of FY95). The project was substantially complete by the end of FY96 (9/30/96). A small project carryover was spent in FY97 and the project was closed out on 3/31/97.

There is no Proprietary or Protected CRADA Information in this report.

BACKGROUND AND APPROACH

The flat panel display market is currently valued at \$5 billion/yr and is projected to be as high as \$20 billion/yr by 2000 - U.S. companies have less than 5% of the market at present. Displays based on field emission cathodes are a promising alternative technology in which the U.S. currently has a technological head start over the Japanese. SI Diamond Technology (SIDT) is a small, publicly held company based in Houston, Texas. SIDT has been developing flat panel displays based on field emission from their patented Amorphous Diamond™ material. Although the technology is promising — SIDT has recently demonstrated a working 3x4” monochrome display — SIDT must solve critical materials problems in their cathode before they can bring mass-produced flat panel displays to market. In this two-year CRADA project, a team of five MSD PIs worked with SIDT scientists and engineers to understand the structure of their material and its field emission mechanism.

The scientific objective of this project was to determine the physical mechanism for the unexpectedly low electric field threshold for electron emission into the vacuum found in films of “amorphous diamond” (produced by laser ablation by SIDT) and “nanodiamond” (produced by chemical vapor deposition by SIDT). There are two important underlying scientific issues. (1) It has been known since the 1930’s that field emission usually occurs at a lower threshold than expected from the work function of a material. This effect is caused by a geometrical enhancement of the electric field at surface imperfections such as spikes and steps. This effect is being exploited in another field emission display technology, which is based on lithographically manufactured arrays of “tips” of Si or metal. At the beginning of the project the surface roughness of SIDT’s “amorphous diamond” material as measured at SIDT by AFM and profilometry was considered too small to explain the field emission through geometrical enhancement alone. (2) It has been known since the mid-1980’s that under certain conditions the (111) surface of crystalline diamond displays negative electron affinity (NEA). That is, electrons in the conduction band of diamond incident on the diamond surface can go downhill in energy into the vacuum. Numerous attempts have been made to exploit this effect to make an efficient diamond field emitter -- most have been stopped by the lack of effective *n*-type doping in crystalline diamond. At the beginning of the project it was conjectured by SIDT that diamond NEA was a factor in the efficient field emission from their “amorphous diamond” cathode.

PROJECT GOALS AND TASKS

Scientific Goal

The overall objective of this CRADA project was to elucidate the physics that enable SIDT’s films to emit electrons into vacuum at low threshold fields.

At the beginning of the project, the mechanism responsible for field emission in these materials was completely unknown. Our first specific objective was to develop suitable characterization methods for examining single, known emission sites and determining the crystalline state, the band structure, the chemical bonding, and topography

of the emission areas. Only a small fraction (<1%) of the cathode area is electron emitting; for this reason bulk characterization approaches are of limited use because they do not look specifically at the emission sites, which are known to be 1 micron or smaller in size. Our second objective was the development of a theoretical framework for use in interpreting characterization results and relating them to potential emission mechanisms.

Project Tasks

TEM and EELS studies were used to determine the bonding, composition and microstructure of the cathode materials. Raman spectroscopy provided complementary bonding information. However, because only a small fraction (<1%) of the cathode area is electron emitting (see Fig. 1), bulk characterization approaches are of limited use because they do not look specifically at the emission sites. An experimental methodology was developed jointly by SIDT and LBNL to identify and map emission sites in such a way that subsequent microcharacterization procedures can find them. As part of their in-kind contribution to this project, SIDT developed a scanning field emission/SEM instrument (\$50K capital investment). With this instrument, maps of emission site locations in a 300 x 300 μm area could be

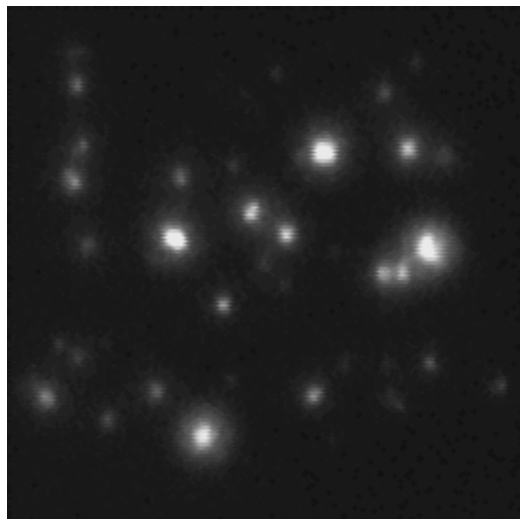


Fig. 1. Electron emission image showing less than 30 active emission sites in one 300x300 μm pixel area in an "Amorphous Diamond" cathode.

generated. A system of fiducial marking was developed such that the emission sites could be located at LBNL with sub-10- μm accuracy for spatially resolved Raman and scanning microscopy studies. As a result, we were able to use maps of emission sites provided by SIDT to obtain Raman spectra of known emission sites in both amorphous diamond and nanodiamond material, which allows their bonding structure to be determined.

Our theoretical approach has been to design experiments that can distinguish contributions to the enhanced field emission emanating from the geometrical and NEA factors discussed above. The basic equations governing simple field emission caused by tunneling of electrons through a surface barrier under the influence of a large applied electric field were derived by Fowler and Nordheim in the late 1920's. In the case of geometrical enhancement only, the surface barrier is expected to be several eV, on the order of the material's work function, and the field emission is not expected to be enhanced by elevated temperature. In the case of a NEA surface, or multistep processes involving several interfaces, more complex, "non-Fowler-Nordheim" behavior is expected. In the case of "nanodiamond" our model involved two interfaces: graphite/nanodiamond and nanodiamond/vacuum. Our barrier calculations revealed that increasing the cathode temperature by 200 C or more should have observable effects on the current-voltage behavior of the emission sites.

PROJECT RESULTS

At the beginning of the project, the detailed microstructure and the emission mechanism of SIDT “amorphous diamond” cathode material were not known. During the course of the project, much of what has been assumed about the structure of the SIDT films was found to be inaccurate. The first accomplishment of the project was elucidating the correct microstructure of the material through a combination of transmission electron microscopy, electron energy loss spectroscopy, and Raman spectroscopy studies. The material consists of an amorphous matrix with a 60/40 sp^3/sp^2 bonding ratio. Various amounts of graphitic inclusions are found depending on process conditions. There is no crystalline diamond in this material. Raman results on known emission sites in “amorphous diamond” revealed that some emission sites are graphite inclusions while others have the same composition as the bulk matrix.

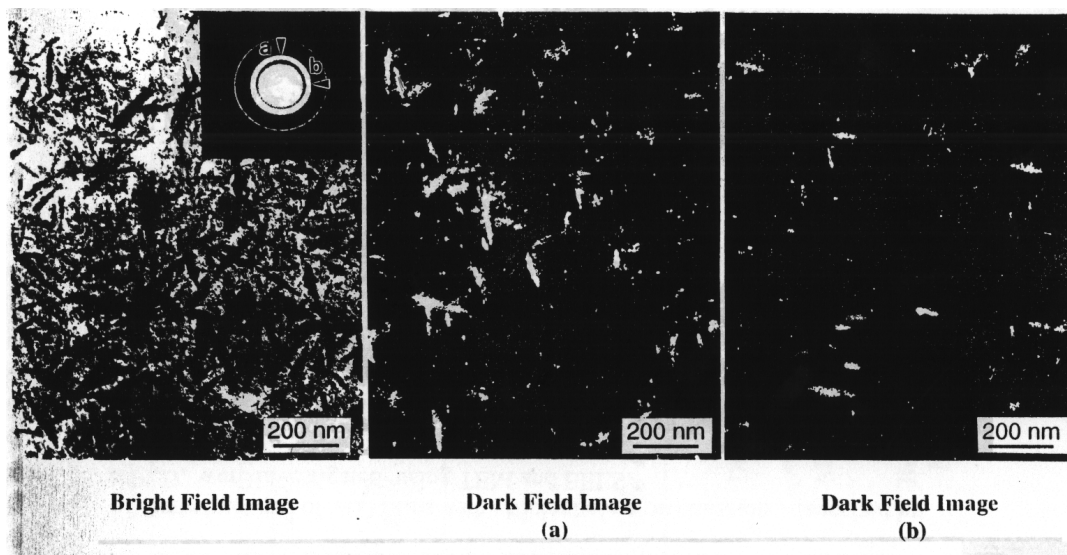


Fig. 2. TEM images of “nanodiamond” material. Dark field images reveal ca. 100 nm scale areas of oriented crystalline diamond.

At the mid-way point of the project, SIDT introduced a new cathode material, “nanodiamond,” that is made with a different process than the “amorphous diamond.” This material has 10x the emission site density of the “amorphous” diamond. TEM analysis (Figs. 2 and 3) done at LBNL elucidated the microstructure of this material, which consists of ca. 10 nm crystalline diamond nodules embedded in an amorphous, highly sp^2 -bonded matrix. Micro-Raman studies of known emission sites in this material revealed that averaged over a 1 micron area, emission sites have the same chemical structure as non-emitting areas. As shown in Fig. 4, the emission performance of the nanodiamond material was far superior to that of the “amorphous diamond” material.

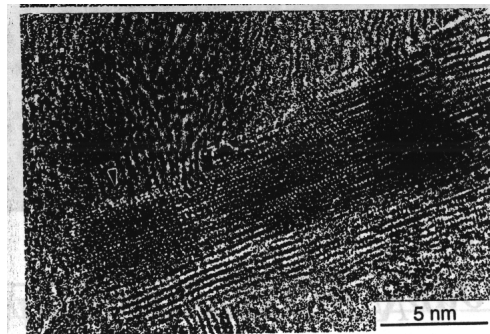


Fig. 3. Individual diamond crystallites are ca. 5 nm in size.

In order to measure the current-voltage curves of individual emission sites and

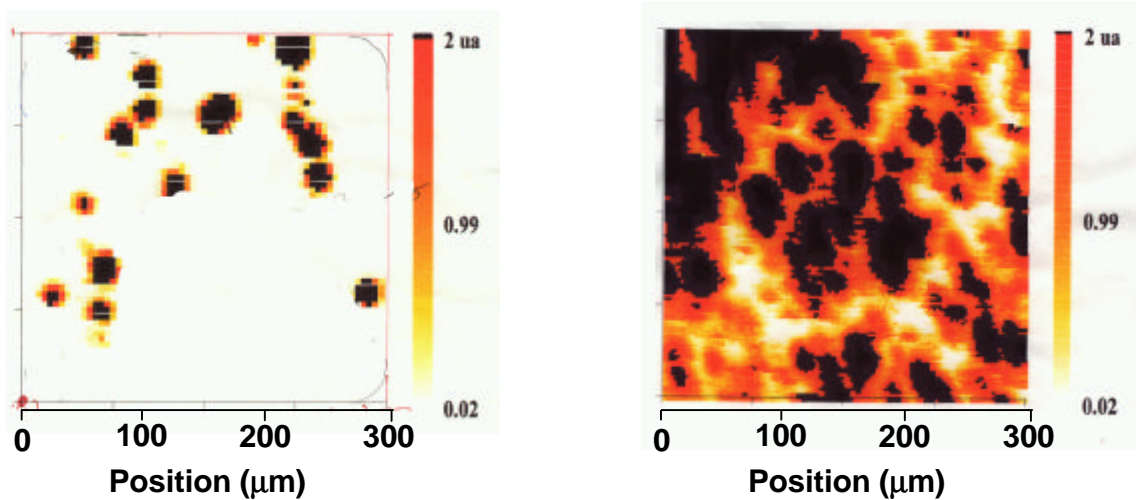


Fig. 4. Emission maps generated by SIDT's emission site locator. Dark area correspond to areas of high electron emission. The nanodiamond cathode (right) has a much higher emission site density than the amorphous diamond cathode (left). Individual emission sites can be located to within 10 microns using this instrument.

measure their topography, we constructed an atomic force microscope that can operate in high vacuum. The microscope is equipped with piezoelectric scanners designed for an extended scan range of $40\ \mu\text{m} \times 40\ \mu\text{m}$. By biasing a metal-coated AFM tip and feeding back on the force produced by the induced dipole in the material, it is possible to fly the tip at a controlled distance above the surface without touching it at constant tip-sample electric field. Simultaneous monitoring of current allows emission sites to be found. Emission sites were found on SIDT's "nanodiamond" material (Fig. 5). The current-

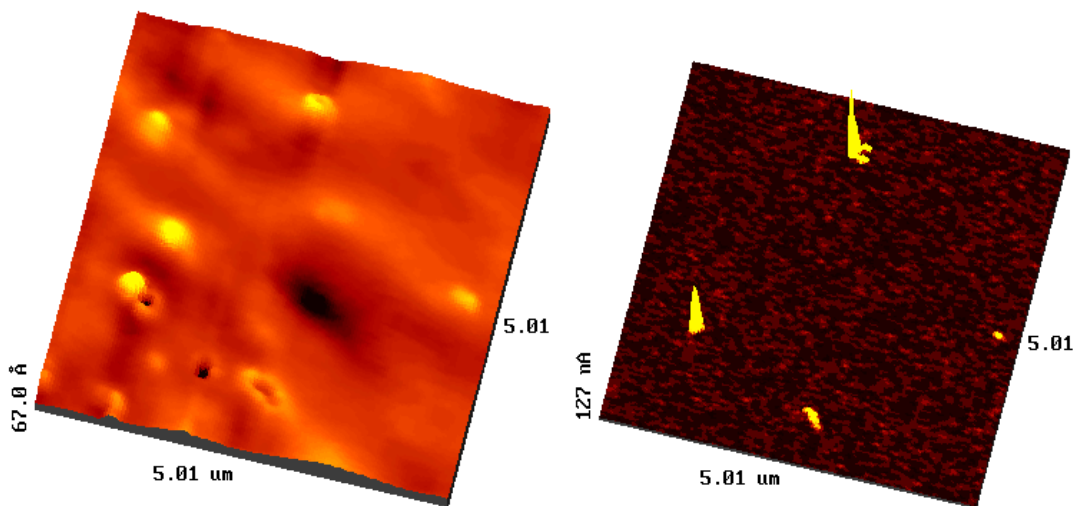


Fig. 5. "Topography" (left) and field emission (right) images collected simultaneously from SIDT nanodiamond cathode by flying biased AFM tip over sample at a height of 100 nm. Spikes in right-hand image are field emission sites. I-V curves (see Fig. 6) from these sites match those generated by lower-resolution equipment. Distinctive "volcano" pattern observed in topography map was related to local areas of low dielectric constant (insulating inclusions).

voltage curves matched those generated by lower resolution instruments (Fig. 6). The topography of the site can be estimated from the force map and we were able to place an upper limit on the emission site size of 100 nm. The emission sites appear to be fairly flat, which limits significantly the degree to which the emission is geometrically enhanced. In addition, we determined that the emission sites were insulating inclusions in a conducting matrix. To our knowledge, this was the first electrical measurement of an individual emission site. This result is a major achievement of the project.

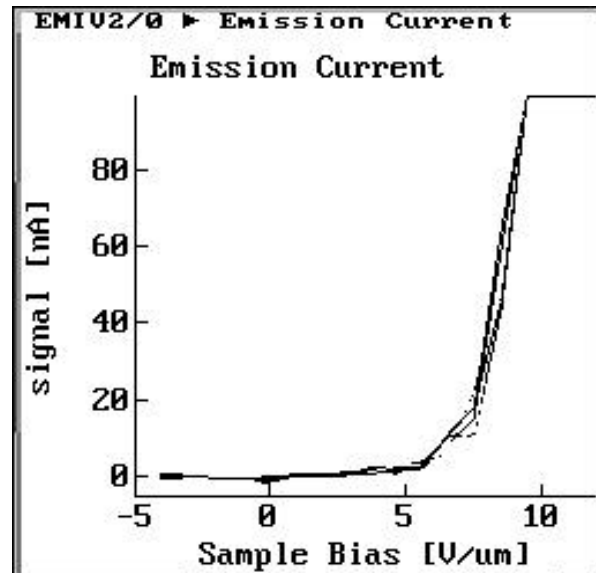


Fig. 6. I-V curve of single emission site.

At the beginning of the project several speculative mechanisms had been proposed to explain the enhanced emission of carbon-based cathodes. Some elements common to these theories include the known negative electron affinity of the diamond (111) surface, the large (5.5 eV) band-gap of diamond, and the relative chemical stability of carbon surfaces. Late in 1995, work at MIT on single crystal diamond suggested that if electrons can be injected into the conduction band of *n*-type diamond through an appropriate metal contact, efficient transport of the electrons to the surface and into vacuum is possible. We predicted that if such a “back-side-injection” mechanism is responsible for the emission in either of SIDT’s cathode materials, the current-voltage characteristics of the emission should display a strong and distinctive temperature dependence. A high-temperature field emission test station was built at LBNL and both cathode materials were tested. The “nanodiamond” emission characteristics were observed to change in the predicted way with at elevated temperature. The emission mechanism in “nanodiamond” was shown to be consistent with a three step mechanism: (1) tunneling of electrons from the conducting graphitic matrix phase into the conduction band of diamond nanocrystals, (2) transport of electrons in the diamond conduction band to the surface, and (3) electron emission into the vacuum with a low barrier. In contrast, the “amorphous diamond” emission characteristics remained unchanged at elevated temperature. In addition, the lack of any crystalline diamond in the material, led us to conclude that field emission in this material is not enhanced by NEA behavior of the surface.

SUMMARY OF SCIENTIFIC RESULTS

The project has succeeded in identifying the field emission mechanism in a class of materials being developed for use as cathodes in flat panel displays. This is of considerable technical importance. Field emission displays have the potential to replace liquid-crystal-based displays in much of the flat panel display market. Prototype field emission displays are brighter and more energy efficient than active matrix liquid crystal displays used currently in laptop computers. In the case of the flat cathodes being

developed by SIDT, additional advantages include scaling to very large sizes and a simplified manufacturing process.

PROJECT BENEFITS

Benefits of CRADA to LBNL and DOE

The discovery of the anomalously low threshold for field emission in “amorphous diamond” was a surprise. At the beginning of the project, there was no plausible explanation for amorphous diamond’s “effective” work function of 0.5 eV, which is one-tenth of the expected value based on the work functions of graphite and diamond, and much lower than that of any bulk material. Our determination of the mechanism responsible for this phenomenon advanced the fundamental understanding of the field emission in multi-phase materials, which is consistent with the commitment of the Office of Energy Research to basic research in materials science. The project supports indirectly the energy-efficiency mission of DOE. Flat panel displays based on field emission technology are expected to use significantly less energy display area than either existing CRTs or active matrix liquid crystal displays (AMLCDs). For example, at a given brightness level, the energy use of a field emission FPD is 10% compared to a CRT and 60% compared to an AMLCD.

Benefits of CRADA to SIDT

At the beginning of the CRADA project, SIDT had a specific technical problem. Although their prototype displays had an acceptable overall brightness, the low density of emission sites gave the display a “grainy” appearance. Identification of the emission mechanism, which is the major accomplishment of this project, has enabled SIDT to improve their “nanodiamond” process and to develop improved cathode materials. The emission uniformity of SIDT’s new cathodes has improved by over an order of magnitude compared to their earlier material, which enables them to produce a bright display with less graininess. More improvement is expected as SIDT works to increase the concentration of emitting structures.

PROJECT PUBLICATIONS

H. Sohn, K. M. Krishnan, and R. Fink, “Microstructures of Amorphous Diamond films grown by laser ablation method,” in *Diamond for Electronic Applications, Proceedings of the Fall 1995 MRS Conference*, ed. D. Dreifus, A. Collins, C. Beetz, T. Humphreys, K. Das, and P. Pehrsson (Materials Research Society, Pittsburgh, PA, 1996), pp. 455-460.

ACKNOWLEDGMENT

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