

project. A standard solution of NBS SRM 951 prepared in a CaCO_3 matrix yielded an average $^{11}\text{B}/^{10}\text{B}$ ratio of 3.9873 (± 0.3 per mil; $n = 30$) compared with a value of 4.0527 (± 0.2 per mil; $n = 105$) obtained for this standard by the Cs_2BO_2^+ method [J. K. Aggarwal and M. R. Palmer, *Analyst* 120, 1301 (1995)]. All data in Table 1 are reported as $\delta^{11}\text{B}$, where

$$\delta^{11}\text{B} = \left[\frac{(^{11}\text{B}/^{10}\text{B})_{\text{sample}}}{(^{11}\text{B}/^{10}\text{B})_{\text{standard}}} - 1 \right] \times 1000 \text{ and } ^{11}\text{B}/^{10}\text{B}_{\text{standard}}$$

= 3.9873. Seventeen analyses of 2 μl of open ocean water yielded a $\delta^{11}\text{B}$ value of $+39.7 \pm 0.3$ per mil. No results have been excluded and the average $\delta^{11}\text{B}$ values for each sample include all the data for that sample (Table 1).

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Low-Field Electron Emission from Undoped Nanostructured Diamond

W. Zhu,* G. P. Kochanski, S. Jin

Strong and sustained electron emission at low electric fields was observed in undoped, nanostructured diamond. Electron emission of 10 milliamperes per square centimeter was observed at applied fields of 3 to 5 volts per micrometer. These are the lowest fields ever reported for any field-emitting material at technologically useful current densities. The emitter consists of a layer of nanometer-size diamond particulates, which is heat-treated in a hydrogen plasma. These emission characteristics are attributed to the particles' high defect density and the low electron affinity of the diamond surface. Such emitters are technologically useful, because they can be easily and economically fabricated on large substrates.

Cold-cathode electron field emitters are potentially useful for field emission displays and other vacuum microelectronic devices (1). Although typical metal (such as molybdenum) or semiconductor (such as silicon) emitters have high work functions, diamond can possess a negative electron affinity (NEA) surface (2, 3) that, in principle, allows its surface to emit electrons under low electric fields (4–10). This eliminates the complicated and costly process of fabricating sharp microtips to provide geometric field enhancement. The excellent mechanical and chemical stability of diamond also yields highly durable and reliable emitters, even under extreme conditions.

It is generally thought that undoped diamond is unable to produce sustained electron emission due to its insulating nature. Electron emission from surface states in diamond can occur (11), but there are no obvious mechanisms by which electrons can be transported through the undoped bulk to the surface states. Either the bulk or the surface of diamond must be made conductive. Additional-

ly, the Fermi level must be near the conduction band to allow effective emission, which can be accomplished either by *n*-type doping as reported by Koizumi *et al.* (12) or by introducing defects into the diamond, as we have done here. Although *p*-type diamond can readily be made by boron doping, it does not emit well because the electrons reside deep (>5 eV) below the vacuum level.

We report that strong and sustained electron emission at low applied fields is obtained from undoped diamond using ultrafine, nano-

structured particulates. The emitters produce 10 mA/cm² at applied fields of 3 to 5 V/ μm , and 1 $\mu\text{A}/\text{cm}^2$ at 1 to 2 V/ μm . Such low field electron emission has been achieved at current densities that are of interest to major technological applications, such as field emission displays. We attribute this emission behavior to the inherently defective structure of nanostructured diamond and the low electron affinity of the diamond surface. As has been pointed out (7, 13), structural defects play an important role in lowering the required emission field for undoped or *p*-type doped diamond, because they form energy bands within the bulk band gap, thus elevating the Fermi level and reducing the energy barrier that electrons must tunnel through to be emitted.

We used commercially available, 10- to 100-nm micropolycrystalline diamond particles produced by explosive synthesis, which are available as dispersed aqueous suspension. X-ray diffraction patterns show broadened diamond peaks, and each of the particles actually consists of many 1- to 20-nm crystallites and associated grain boundaries. The material is defective because of the presumed rapid growth rate and the incomplete structural evolution limited by the size (14). These particles are smaller than the diamond grit used by Geis *et al.* (10) in their nickel/cesium-coated emitter experiments. We used no metals in our emitters.

The dispersed diamond was attached to an *n*-type silicon substrate as a thin, uniform layer by a simple spraying or brushing technique. The layer was dried at ambient temperature, then subjected to a hydrogen plasma treatment at a temperature of 650°C and a pressure of 20 torr for 1 hour. Neither the as-deposited layer nor the structure that was heat treated in a high-purity hydrogen or argon gas atmosphere gave any measurable emission at reasonable fields. A thin and

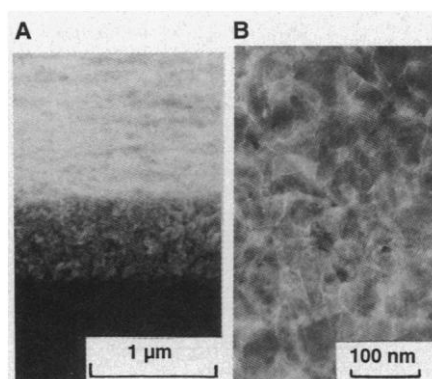


Fig. 1. (A) SEM taken at an angle to show both the top and the cross-section of the emitter and (B) TEM of the nanostructured diamond.

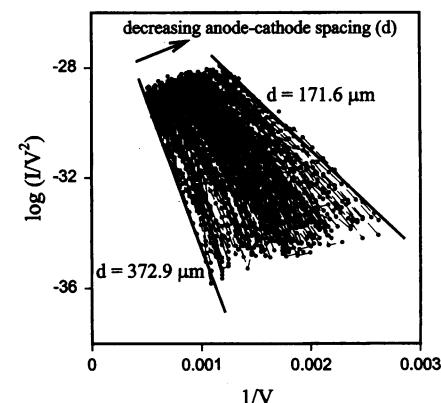


Fig. 2. Emission *I*-*V* curves from the nanostructured diamond emitters. This is a collection of many sets of data obtained over an anode-cathode distance range between 372.9 μm and 171.6 μm at a step size of 3.3 μm .

Bell Laboratories, Lucent Technologies, 600 Mountain Avenue, Murray Hill, NJ 07974, USA.

*To whom correspondence should be addressed. E-mail: wzhu@lucent.com

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conformal overcoating of homoepitaxial diamond by chemical vapor deposition (CVD) can optionally be applied on the particle layer immediately following the plasma treatment to further improve its structural integrity. A scanning electron micrograph (SEM) (Fig. 1A) shows the processed diamond emitter layer with a thickness of ~ 600 nm. The nanocrystalline nature and blocky configuration of the diamond particles are evident in a transmission electron micrograph (TEM) (Fig. 1B). Electron diffraction confirms the crystalline diamond structure of these particles.

The hydrogen plasma heat treatment is critical to activating the emitters. Without such a treatment, we are unable to observe any electron emission; instead, we see a catastrophic failure by arcing at fields greater than 100 V/ μm . Although the effect of the hydrogen plasma treatment is not completely understood, it is believed that it: (i) cleans the diamond surface by removing contaminants such as carbonaceous and oxygen- or nitrogen-containing materials and preferentially etches away graphitic or amorphous carbon present on the surface or along the particulate boundaries; (ii) saturates dangling bonds on the diamond surface with hydrogen, leading to a hydrogenated NEA surface; and (iii) improves particle-to-particle bonding and diamond-to-silicon interfacial bonding through vapor transport and diffusional reactions. The surface property of negative or low electron affinity coupled with the inherent defective structure are considered to be the main factors that make the nanostructured diamond such a low field emitter.

Emission current-voltage (I - V) curves from the nanostructured diamond particulates are shown in Fig. 2 (15). The data were collected over a range of anode-cathode distances and plotted as $\log(I/V^2)$ versus $1/V$ for $I > 1$ nA according to the Fowler-Nordheim

equation ($I = AV^2e^{-B/V}$), where A and B are constants. The voltage was raised from zero until the current density reached 10 mA/ cm^2 and then decreased to zero. After the anode moved one step (3.3 μm) closer to the cathode surface, the voltage cycle was repeated. The threshold fields derived from the curve fitting analysis of the data are approximately 1.5 V/ μm for an average current density of 1 $\mu\text{A}/\text{cm}^2$, and 4.9 V/ μm for 10 mA/ cm^2 (16). These represent almost an order of magnitude reduction from the fields required for many other types of emitters (see Table 1). There have been published studies reporting similarly low emission fields from diamond (4, 6, 9, 10, 17–19), but those results were often obtained at far lower current densities and did not show evidence of reproducible, stable emission. For example, Okano *et al.* (9) reported field emission at a low threshold field (~ 0.5 V/ μm at 10^{-7} A/ cm^2) from nitrogen-doped diamond, but the current density achieved was about 3×10^{-5} A/ cm^2 , which is two orders of magnitude lower than our current densities. Electron emission from CVD nanocrystalline diamond films has also been reported (20, 21), but with much lower current densities and higher threshold fields than we report here for particulate emitters.

In Fig. 3, the emission current densities are plotted against electric field for a variety of CVD diamond emitters as well as for the nanostructured diamond samples. The nanostructured diamond emitters show superior properties, with emission occurring at the lowest fields. The emission is sensitive to defect densities, because defects are the only viable mechanism of providing and transporting electrons in undoped diamond. Relatively perfect crystals with few defects have poor emission characteristics (high-quality, p -type diamond; Fig. 3). As the defect density increases (defective CVD diamonds; Fig. 3), the emission characteristics progressively improve. The best known emission is from the nanostructured diamond particulates, with

their many grain boundaries and presumed large defect densities.

Reproducibility tests from different locations of the same sample and from other batches consistently yield threshold fields within the range of 1 to 2 V/ μm for 1 $\mu\text{A}/\text{cm}^2$, and 3 to 5 V/ μm for 10 mA/ cm^2 . Emission was observed to be from a dense set of spots, each of different efficiency, as seen by placing a phosphor screen near the cathode. The emission site density was about $5 \times 10^4/\text{cm}^2$, which approaches the desirable level for display applications and is significantly higher than the 10^2 to $10^3/\text{cm}^2$ site density typically observed with CVD diamond emitters. The emission uniformity may be improved further by using smaller particles and optimizing the process conditions. We observed average current densities as high as 30 mA/ cm^2 . Assuming that the emission at each site comes from a single particle (~ 50 nm size), the local current density was estimated to be more than 10^4 A/ cm^2 .

The processed diamond particulates have remarkably stable emission characteristics. When a plasma-treated sample was exposed to air for more than 3 months, it exhibited essentially the same emission behavior as the freshly treated surface. Even an exposure to water (albeit high-purity, deionized water) did not alter the emission characteristics. We tested the emitter durability and observed a lifetime of 10 to 20 hours at relatively severe operating conditions of 10^{-7} torr and 10 mA/ cm^2 before the most efficient emitting spots fail or the required voltage doubles. This lifetime is consistent with estimates of ion bombardment damage that preferentially destroys the best emission regions.

For display applications, the nanostruc-

Table 1. Emission threshold fields (field required to generate an emission current density of 10 mA/ cm^2) for various emitter materials.

Material	Threshold field (V/ μm)
Mo tips (7)	50–100
Si tips (7)	50–100
p -type semiconducting diamond (13)	160
Undoped, defective CVD diamond (13)	30–120
Amorphous diamond (8)	20–40
Cesium-coated diamond (19)	20–30
Graphite powders (<1 μm size) (24)	17
Nanostructured diamond particles as-deposited	*
Heat-treated in H gas	*
Heat-treated in H plasma	3–5

*Arcing; no emission.

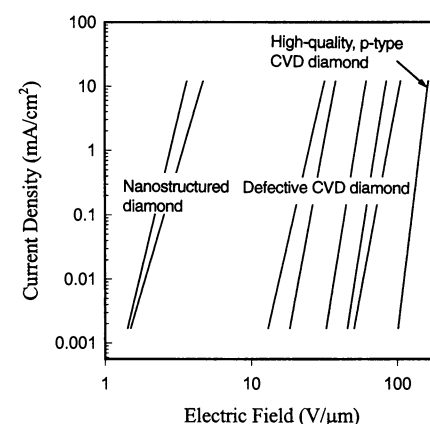


Fig. 3. Emission current density versus applied field for various diamond emitters.

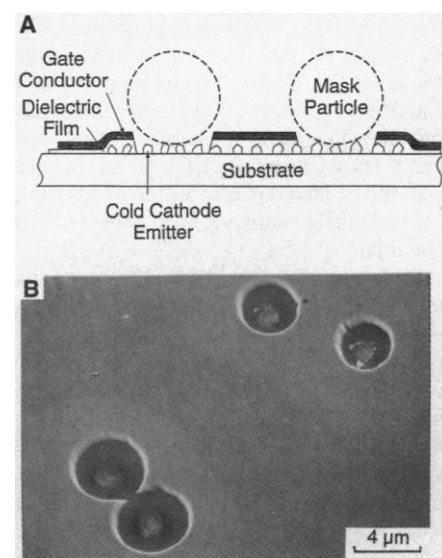


Fig. 4. (A) Schematic of, and (B) an SEM showing the formation of gate apertures by mask particles.

tured diamond emitter will most likely be used in the form of a thin coating, which can easily be applied to a large substrate by simple spray or printing techniques. The low threshold fields of 3 to 5 V/ μm also imply that a gate voltage of 10 to 20 V, conveniently available from off-the-shelf complementary metal-oxide semiconductor drivers, will be adequate to control and address the display pixels.

Further, on the diamond cathode surface, a gate structure can be constructed by employing a simple "particle-mask" approach without using lithography. Such a robust, lithography-free (and therefore inexpensive) gate structure can have important technological impact. A layer of diamond particulates is first deposited on a substrate and activated by hydrogen plasma treatment (Fig. 4A). Fine and loose mask particles are then sprayed randomly over the cathode surface. A dielectric thin film is then deposited, followed by the deposition of the gate metal film. The mask particles shadow the areas directly underneath so that no dielectric or gate material is deposited on the cathode surface. The mask particles are then either brushed or blown away to reveal the gate apertures. As an example, we mixed fine aluminum particles with acetone and spray-coated them on a glass substrate. A layer of copper, about 1 μm thick, was then evaporated on the substrate. After gently brushing off the mask particles, apertures of about 2 to 4 μm in diameter are left in the copper film (Fig. 4B). The size, density, and distribution of the apertures can be controlled by selecting proper mask particles and processing schemes.

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15. The field emission measurement was carried out in a vacuum chamber with a 10^{-8} torr base pressure at room temperature. As described previously (7), a voltage up to 2 kV was applied to a spherical-tipped molybdenum anode probe (tip radius of curvature $\approx$ 0.5 mm) to collect electrons emitted from the cathode diamond surface. A precision stepper controller (3.3 μm step size) was used to control the movement of the anode toward the cathode, and the emission current-voltage (*I-V*) characteristics were measured as a function of the anode-cathode distance. The obtained *I-V* data were analyzed using the Fowler-Nordheim theory (22), taking into consideration the variation of electrical field across the cathode surface and assuming a broad distribution in emission properties among the emitting tips (73). Capacitance was measured as the anode position changed to better determine the anode-cathode distance. A sphere-to-plane model was used to fit the capacitance data and estimate the position where the anode touched the cathode surface (73). The capacitance measurements also allowed problems—such as arcing, missteps of the probe, moving dust particles, or loose samples—to be detected, because they introduce discontinuities in an otherwise smooth capacitance-distance curve. The standard deviation of the capacitance about the fit corresponds to a 3 μm uncertainty out of a 100- μm spacing.
16. A sphere-on-cone model was adopted to derive the electrical field above the cathode surface (23), and a Fowler-Nordheim equation was then fit to the *I-V* data. The fitted parameters were used to interpolate or extrapolate the *I-V* characteristics of the emitters to a standard display pixel area (100 μm by 100 μm). The field required to produce an emission current density of 10 mA/cm² (that is, 1 μA over the pixel area, as is typically required for display applications) was then calculated and used as a figure of merit to compare various emitter samples. Note that we do not directly calculate the local fields on the tips of the emitters; instead, all of the field values are for the macroscopic electric field well above the cathode surface where the field is uniform and independent of the surface roughness. This macroscopic field is actually the relevant parameter for device applications. Using this field also allows us to avoid making strong assumptions about the emission physics, because the electronic properties of the emitters cannot be easily separated from the geometric field enhancement factors.
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Coherent Optical Control of the Quantum State of a Single Quantum Dot

N. H. Bonadeo, J. Erland, D. Gammon, D. Park,
D. S. Katzer, D. G. Steel*

Picosecond optical excitation was used to coherently control the excitation in a single quantum dot on a time scale that is short compared with the time scale for loss of quantum coherence. The excitonic wave function was manipulated by controlling the optical phase of the two-pulse sequence through timing and polarization. Wave function engineering techniques, developed in atomic and molecular systems, were used to monitor and control a nonstationary quantum mechanical state composed of a superposition of eigenstates. The results extend the concept of coherent control in semiconductors to the limit of a single quantum system in a zero-dimensional quantum dot.

Semiconductor quantum dots (QDs) are nanoscopic quantum structures (1) that allow electronic properties to be tailored through quantum confinement. Advances in optical spectroscopy techniques have revealed the distinctive features of these nanostructures, including atomic-like spectra with discrete and extraordinarily sharp spectral lines (2–4). However, the similarities between atoms and

QDs suggest the possibility of even greater opportunities. More specifically, we can consider the possibility of using coherent optical interactions to coherently engineer the wave function. Such proposals have been envisioned for implementation of various schemes for quantum computation and coherent information processing and transfer in which it is important to address and coherently control individual quantum units (5). In addition, it might be possible to extend earlier demonstrations of coherent control of semiconductor heterostructures such as photocurrent (6) and terahertz radiation (7) to a single quantum dot.

Coherent control of quantum mechanical processes and wave function engineering in atomic and molecular systems have reached an advanced level of understanding including control of molecular chemical reactions (8), selective photodissociation of molecules (9),

N. H. Bonadeo, Harrison M. Randall Laboratory of Physics and Center for Ultrafast Optical Science, University of Michigan, Ann Arbor, MI, 48109, USA. J. Erland, Harrison M. Randall Laboratory of Physics, University of Michigan, Ann Arbor, MI, 48109, USA. D. Gammon, D. S. Katzer, D. Park, Naval Research Laboratory, Washington, DC 20375, USA. D. G. Steel, Harrison M. Randall Laboratory of Physics and Electrical Engineering and Computer Science Department, University of Michigan, Ann Arbor, MI, 48109, USA.

*To whom correspondence should be addressed.