Fabrication and Theory of Diamond Emitters

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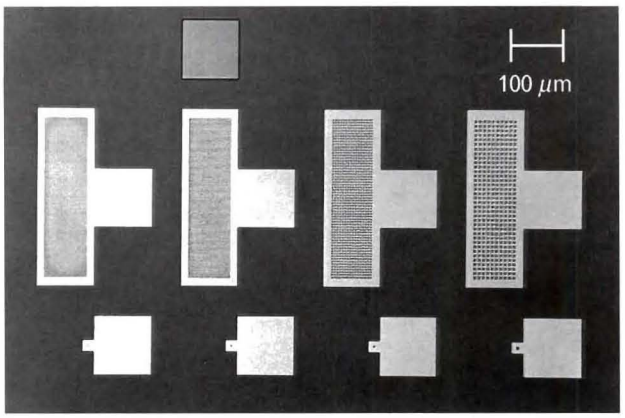
■ **This article describes the fabrication of gated diamond field-emission cathodes and discusses a theory of their operation. These cathodes are made by using commercial diamond grit with added nickel and cesium salts to enhance emission. The resulting structure resembles a Spindt-type field-emission cathode with the internal metal cone replaced by a layer of diamond grit approximately one hundred nanometers thick. Emission of electrons from these cathodes occurs at the lowest reported gate voltage of any field-emission device and is unaffected by operation at pressures of over 100 Pa of nitrogen. Operation in oxygen and hydrogen sulfide at pressures of 6×10^{-2} Pa degrades emission, but the cathodes recover once the ambient pressure is reduced to below 1×10^{-4} Pa. The emission current noise is 2.5% rms over an eight-hour period and 1% rms over a three-millisecond period. These cathodes suffer from high gate current that varies from 0.2 to 10^4 times the emitted current. The high gate current is known to be process dependent and is not inherent to the cathodes.**

The emission performance is explained by the stable negative electron affinity of diamond, which allows for injection of electrons from diamond into vacuum with little to no electric field. Cathode operation is limited by the injection of electrons into the diamond at the back metal-diamond interface, which depends on the doping of the diamond and the roughness of the interface.

DIAMOND MAY BE THE ULTIMATE material for cold-cathode field emitters. It is chemically inert, it has an oxygen-stable negative electron affinity (NEA) surface [1], and it is commercially available at an acceptable price (less than four dollars per gram), making it ideally suited for field-emission applications. This article describes a diamond field-emission cathode-fabrication process that produces robust cathodes with one of the lowest operating voltages of any field-emission device. The article then discusses the theory of operation of the cathode. The cathode performance is shown to be limited by the injection of electrons into diamond from the back metal-diamond contact. The subsequent emission of electrons from the diamond into vacuum requires little to no electric field (0 to 1 V μm^{-1}) because of the NEA property of diamond. This theory is similar to the analysis used to explain dielectric breakdown [2], which was later used by R.V. Latham et al. to develop a theory of field emission from insulators and composite structures [3]. M.E. Kordesch et al. applied the theory to electron emission from chemical-vapor-deposited diamond films [4].

The development of diamond cathodes is driven by potential applications. The cathodes discussed in this article not only operate at low voltages, but they also have the commercial advantage of being easily and inexpensively fabricated. Large-area cathodes have potential applications for use in flat-panel displays, power vacuum tubes to switch thousands of amperes, and fluorescent lighting. Other uses that require a small energy spread of the emitted electrons (less than 0.1 eV), which can be formed into a well-defined beam for use in scanning and transmission electron microscopes, are probably not potential applications for the cathodes discussed here.



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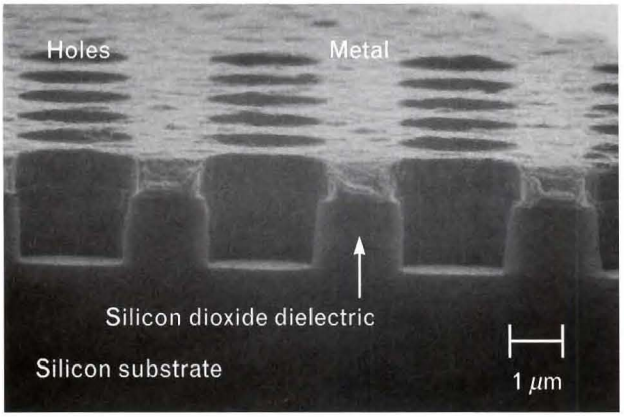


(b)

FIGURE 1. Photographs of a gated emitter array. (a) This optical image shows a top view of four emitter arrays, each 100 × 300 μm in size, with emitter holes that are 1, 2, 3, and 5 μm in diameter. Below each array is a single emitter hole. Contact pads 100 × 100 μm in size are shown to the right of each of the eight devices. (b) This scanning electron micrograph shows a cross section of a gated emitter array through the 2-μm-diameter holes in the emitter array. The silicon substrate forms the contact to the diamond, and the top metal layer serves as the gate electrode. The diamond will be deposited into the holes in a subsequent processing step.

Cathode Fabrication Process

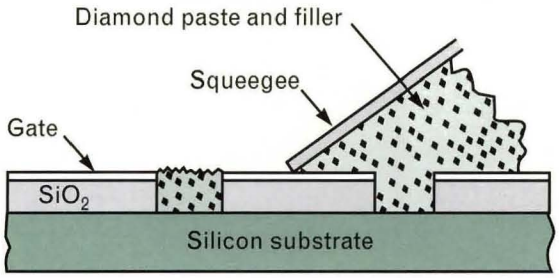
Our diamond cathode-fabrication technique is based on conventional integrated-circuit technology. The process begins with a silicon wafer on which a dielectric layer is deposited, followed by a metal gate electrode. The electrode metal is patterned into 100 × 300-μm isolated pads. Arrays of holes 1 to 5 μm in diameter are then etched through the metal and dielectric layer down to the silicon substrate, as shown by the photograph in Figure 1(a) and the scanning electron micrograph of a 2-μm emitter array in Figure 1(b). A number of processing variations have been studied, including the doping of the silicon substrate and the thickness and composition of the dielectric and gate metal. Our discussions, however, concentrate on n-type silicon wafers, less than 1 Ω cm^{-1}, with thermal- or chemical-vapor-deposited silicon-dioxide dielectric and a sputtered gate-metal alloy of titanium and tungsten.

Once the substrates have been fabricated, diamond grit up to 0.1 μm in diameter is deposited into the holes to form the cathode. Electrophoresis and other techniques using pastes, sprays, and slurries have all proven effective in depositing the diamond grit. Figure 2 shows an example of how diamond grit is deposited in the holes, along with a scanning electron micrograph of a diamond emitter. Figure 2(a) illustrates how we use a squeegee to distribute diamond paste and filler across the substrate. With this technique the amount of diamond deposited can be adjusted by adding specific amounts of filler to the paste. After the diamond grit has been deposited, the substrate is heated to 1080°C in a reducing ambient, which is usually a mixture of hydrogen and argon, to form electrical and mechanical contact between the diamond and the silicon substrate.

Figure 2(b) shows a typical diamond emitter. The contacts are improved by coating the diamond with nickel, which at elevated temperatures results in the formation of etched pits in the diamond. A process has been developed for adding nickel, in the form of a nickel salt, to the diamond grit prior to deposition and heating. In the final processing steps the cathodes are conditioned in a plasma formed from helium and oxygen, and cesium is deposited on the cathode either by direct evaporation or by the application of cesium salts in solution. The use of cesium is the key to low threshold operation because it lowers the electric field required to pull electrons from the diamond.

Emission Results

We performed a variety of experiments to obtain some optimum cathode performance. The standard



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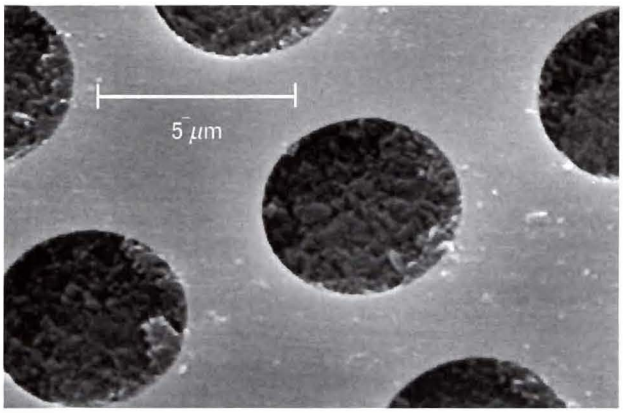

(b)

FIGURE 2. (a) Using the squeegee technique to deposit diamond grit. (b) Scanning electron micrograph of a 5-μm-diameter, squeegee-deposited diamond emitter after annealing at 1080°C. The filler evaporates during the anneal, leaving a layer of diamond grit at the bottom of the structure.

paste was a mixture of diamond grit, a nickel salt, and stearic acid as a filler. When the nickel salt was removed from the cathode-fabrication process, the devices were not operational. A variety of powdered materials, including graphite, type-Ia diamond (natural diamond), type-Ib diamond (synthetic diamond), explosively formed diamond, silicon carbide, and aluminum oxide were used as potential cathodes. Of all the materials we tried, only type-Ib diamond, explosively formed diamond, and silicon carbide resulted in emitting cathodes. Silicon-carbide cathodes, however, did not have the stable emission of the diamond-based cathodes.

The best emission was obtained from synthetic nitrogen-doped diamond grit and explosively formed diamond grit, both combined with the nickel salts and cesiation. Figure 3 shows emitted current as a function of gate voltage for one of the better gated cathodes. The emitted current was collected on an anode consisting of a tungsten wire approximately two hundred microns in diameter placed one to two millimeters above the gated diode. These cathodes have a threshold voltage as low as 5 V and achieve operating current levels for flat-panel displays with a gate bias of less than 15 V.

Cathode longevity has been tested by operating the emitters continuously for one hundred hours at high current densities, approximately 0.3 A cm^{-2}, and a vacuum pressure of approximately 6×10^{-5} Pa of nitrogen. The short-term emission fluctuations were 2.5% rms over an eight-hour period and 1% rms over three milliseconds. These results are quite remarkable, since no resistor is incorporated into the structure to stabilize the emission. In comparison, Spindt-type field-emission cathodes have 1 to 40% rms current noise over a ten-minute period [5].

Conventional field-emission cathodes typically require ultrahigh vacuum conditions for reliable operation, and cesiated cathodes are usually even more sensitive. These diamond cathodes, however, can operate with anode voltages of 400 V at pressures in excess of

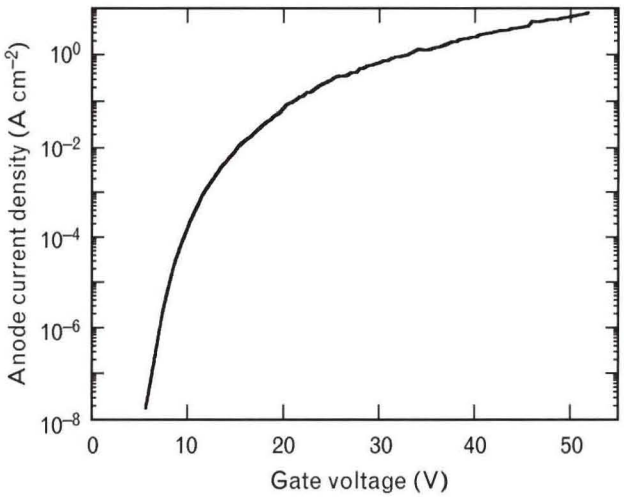

FIGURE 3. Measured emitted anode current versus voltage for a diamond gated cathode comprising an array of seven hundred 3-μm-diameter gated emitters. The cathode was seeded with 50-nm diamond grit and activated with cesium carbonate.

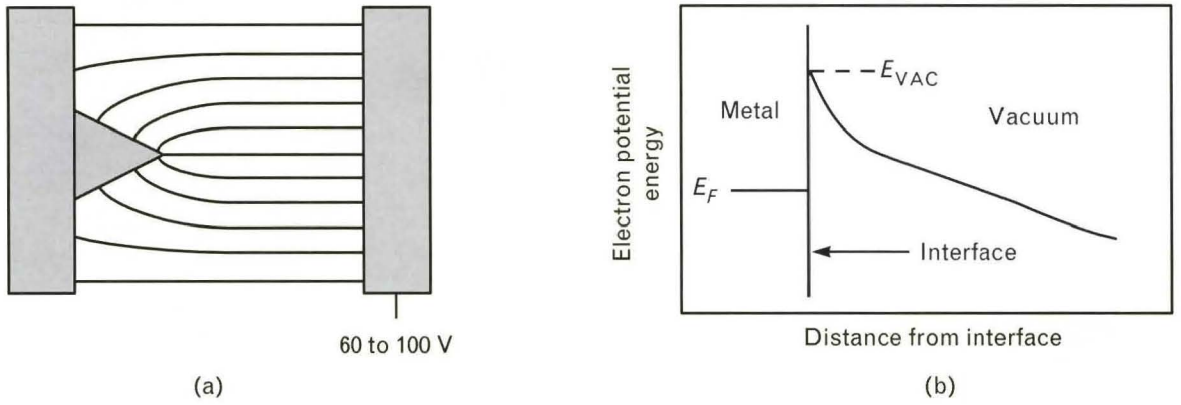

FIGURE 4. (a) Illustration of a metal-cone field-emission cathode. The electric field lines of force are concentrated at the tip, as shown. Typical anode or gate voltages necessary for emission with spacing of approximately one micron vary from 60 to 100 V. (b) The electric potential near the metal cone, where E_F is the Fermi energy in the metal and E_{VAC} is the minimum energy of electrons in the vacuum at the metal-vacuum interface.

100 Pa without damage, an environment that would cause erosion damage and limit device performance by ion bombardment (or *sputtering*) for most other cathodes. Operation in more reactive ambients, such as 6×10^{-2} Pa of oxygen or hydrogen sulfide, does in fact degrade the diamond cathode performance, but the emission recovers after several tens of minutes if the pressure is reduced to 1×10^{-4} Pa.

Although the diamond devices have demonstrated low threshold voltage, high current density, low emission noise, and robust operation, these cathodes exhibit excessive amounts of gate current. The gate current varies from 0.2 to 10^4 times greater than the anode current. The gate current was found to depend primarily upon the deposition technique of the diamond grit. We have found that the squeegee technique provides both the highest anode current and the highest gate-current-to-anode-current ratio.

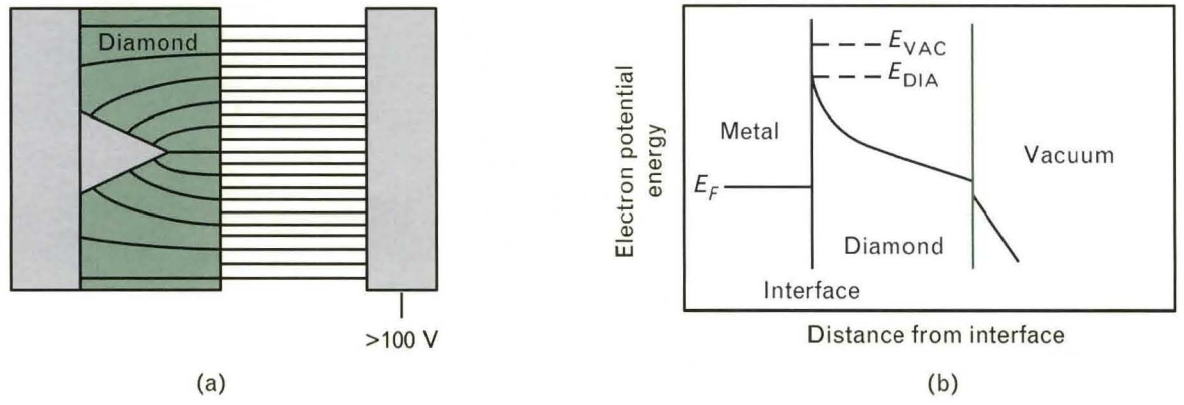

FIGURE 5. (a) Illustration of a field-emission cathode with a metal cone imbedded in undoped diamond. Estimated anode or gate voltages necessary for emission with spacing of approximately one micron is greater than 100 V. (b) The electric potential near the metal cone. The discontinuity of the potential at the diamond-vacuum interface is due to the negative electron affinity (NEA) of the diamond. The quantity E_{DIA} is the minimum energy of electrons in the diamond conduction band and E_{VAC} is the minimum energy of electrons in vacuum at the metal-diamond interface.

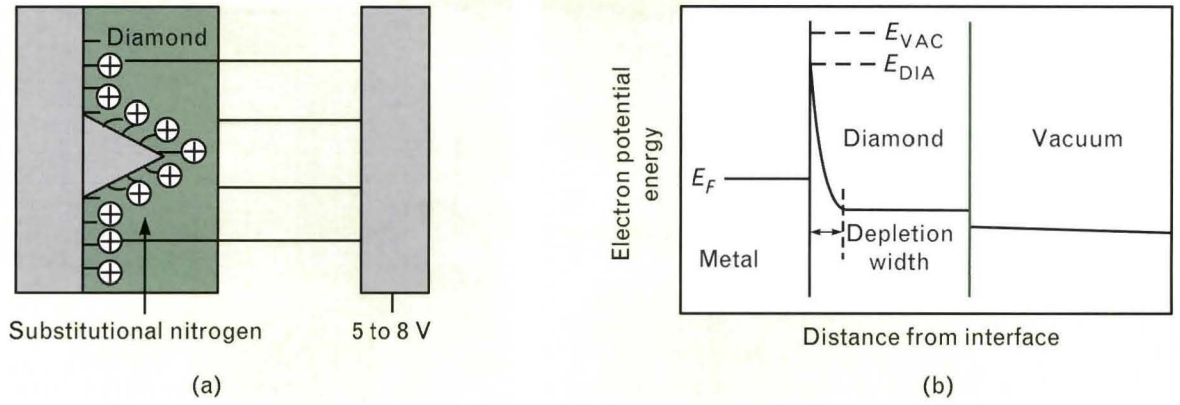

FIGURE 6. (a) Illustration of a field-emission cathode with a field-enhancement metal cone imbedded in nitrogen-doped diamond. Gate voltages necessary for emission with diamond-gate spacing of approximately one micron varies from 5 to 8 V. (b) The electric potential near the metal cone. The discontinuity of the potential at the diamond-vacuum interface is due to the NEA of diamond. The narrow depletion width allows us to obtain the necessary electric field at the tunneling barrier with a bias of only a few volts. The quantity E_{DIA} is the minimum energy of electrons in the diamond conduction band and E_{VAC} is the minimum energy of electrons in the vacuum at the metal-diamond interface.

Theoretical Comparison of Diamond and Field-Emission Spindt-Type Cathodes

Let us compare the emission mechanisms of diamond cathodes with the more established metal-cone field-emission cathodes [6]. Figure 4 shows an illustration of a conventional field-emission cathode that uses the electric-field enhancement at a sharp-tipped metal cone to increase the tunneling of electrons from the metal into vacuum. Figure 4(a) illustrates the field lines around the metal cone of this cathode, and Figure 4(b) shows the electric potential near the metal-vacuum interface, where E_F is the Fermi energy in the metal and E_{VAC} is the minimum energy of electrons in vacuum.

If this metal cone is imbedded in undoped diamond, as shown in Figure 5(a), then the electrons in the metal have to tunnel into diamond's conduction band before they can be emitted into vacuum. Figure 5(b) shows that the minimum energy of electrons at the metal-diamond interface is smaller for diamond than for vacuum. The tunneling barrier for electrons at the metal-diamond interface, as determined from Schottky barrier measurements, is estimated to be 3.5 to 4.0 eV [7]. This energy is just below the 4-to-5-eV barrier for electron tunneling into vacuum from most metals. Diamond's dielectric constant—which is 5.7—lowers the field in the diamond and results in lower emission than the equivalent structure in vacuum. In this case the back contact prevents us from exploiting the NEA property.

Now let us consider the case in which the diamond is doped with an electron donor. Figure 6(a) depicts ionized nitrogen dopants near the metal-diamond interface, and Figure 6(b) illustrates the resulting potentials. Substitutional nitrogen forms a deep trap 1.7 eV below the conduction band [8]. In this case, the average field near the metal-diamond interface can be increased above that obtained at conventional metal-vacuum interfaces by virtue of the reverse-biased Schottky diode formed at the metal-diamond interface. The probability of electrons tunneling into the conduction band and subsequently into vacuum is increased when compared with electron tunneling from the same metal structure in vacuum. For diamond doped to 10^{19} cm^{-3} nitrogen, the depletion width shown in Figure 6(b) is only a few tens of nanometers. This narrow depletion width makes it possible to obtain the necessary electric field at the tunneling barrier with a bias of only a few volts instead of the fifty to a hundred volts required for vacuum emission. Experimentally, the minimum voltage necessary

to obtain emission of electrons from metal into vacuum is 5 to 8 V, which is one of the lowest published operational voltages of any field-emission device.

Detailed Analysis of Diamond Cathode Operation

For purposes of analysis, the model of the cathode can be divided into five regions of interest: the metal-diamond interface, the diamond transport region, the diamond-vacuum interface, the vacuum transport region, and the vacuum-metal interface, as illustrated in Figure 7. In this article we are primarily concerned with the metal-diamond interface and the diamond-vacuum interface.

Metal-Diamond Interface

Electron injection from the metal into the diamond and the operational characteristics of our cathodes are largely determined by the behavior of the metal back contact. The diamond doping and localized field enhancement (due to roughening at the interface) play significant roles in the operation of the contact.

Figure 8 illustrates the effects of doping for three different types of diamond. Figure 8(a) shows the energy levels for n-type diamond where the Fermi energy E_F is near the conduction band. This configuration would be best for cold cathodes, but to date no n-type dopant suitable for cold cathodes has been demonstrated. Figure 8(b) shows the energy levels for aggregated nitrogen dopant [9], which is commonly found in natural type-Ia diamond. In this case the nitrogen forms a deep donor below the Fermi energy of most metals. This donor cannot form a stable depletion region in the diamond because, if the donor is positively charged, electrons will tunnel from the metal to the donor and neutralize it. Figure 8(c) shows the energy levels for synthetic type-Ib diamond containing substitutional nitrogen, which forms a comparatively shallow trap. Since the donor energy of the nitrogen is well above the Fermi energy of most metals, a depletion region will form in equilibrium. This result is consistent with Figure 6 and is both a desirable and obtainable condition for emission.

When the metal-diamond interface illustrated in Figure 8(c) is positively biased, electrons can tunnel into the conduction band. Figure 9 illustrates the tunneling of electrons from the metal into the diamond conduction band under a positive bias of 6 V.

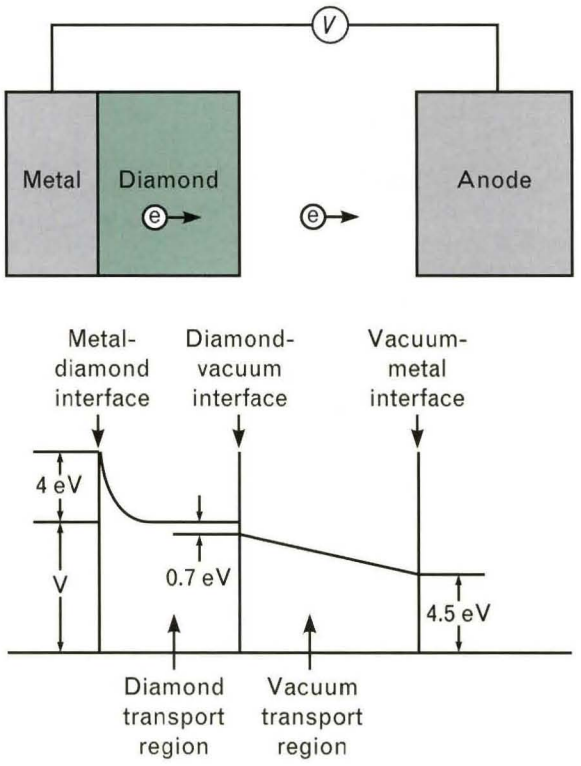

FIGURE 7. Diagram of a diamond cathode in a diode structure. This figure illustrates the five regions of interest: the metal-diamond interface, the diamond transport region, the diamond-vacuum interface, the vacuum transport region, and the vacuum-metal interface. The anode is biased approximately five volts above the cathode back contact. This figure also shows the estimated energy levels associated with the junctions between the different regions.

This model of conduction through the metal-diamond interface is supported by various experimental observations. In our gated cathodes, natural type-Ia diamond containing aggregated nitrogen will not emit electrons, while substitutionally doped type-Ib diamond does emit electrons. These experimental observations correspond with the theory depicted in Figures 8 and 9. Furthermore, in a diode emitter configuration, boron-doped p-type diamond emits electrons only at electric fields greater than 10 V μm^{-1}, while the type-Ib diamond emits electrons at electric fields less than 1 V μm^{-1} [10].

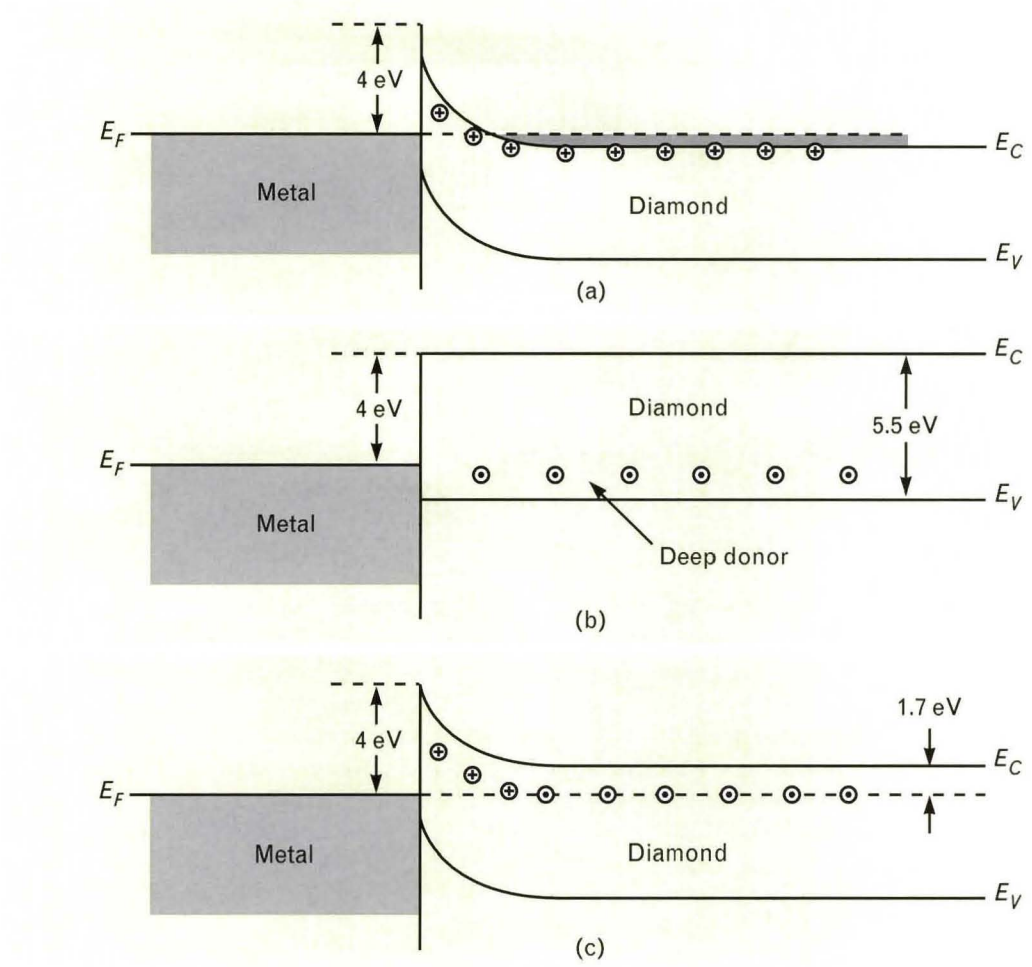

FIGURE 8. (a) The metal-diamond interface for n-type diamond. A depletion region forms at the metal-diamond interface in equilibrium. (b) The metal-diamond interface for type-Ia diamond doped with aggregated nitrogen. Donors are approximately 4 eV below the conduction band. In this case no depletion will form. (c) The metal-diamond interface for type-Ib diamond with substitutional nitrogen. Donors are approximately 1.7 eV below the conduction band. In equilibrium a depletion region forms at the metal-diamond interface. In this figure, E_C is the minimum energy of electrons in the conduction band, and E_V is the maximum energy of electrons in the valence band. The circles, which represent the energy positions of the donors, indicate electrons (minus signs), positively charged impurities in diamond (plus signs), and neutral impurities that potentially can be positively charged (dots).

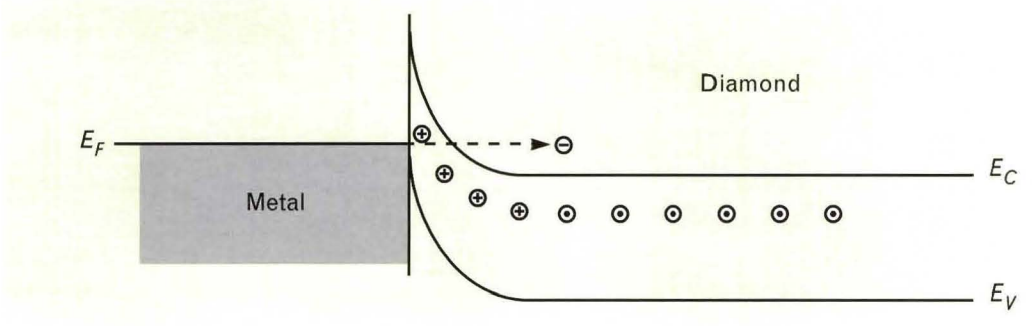

FIGURE 9. Energy levels for a metal-diamond interface with the diamond biased with respect to the metal. In this bias condition, electrons from the metal can tunnel into the diamond conduction band.

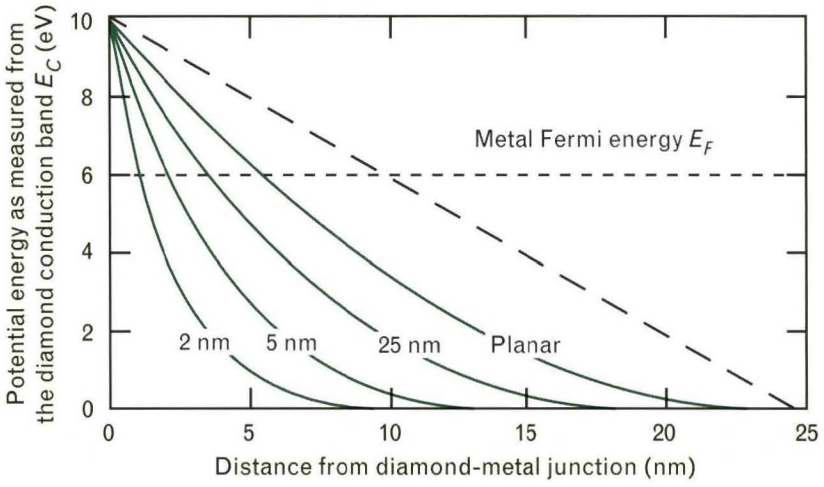

FIGURE 10. The potential energy as a function of distance into the diamond from spherical metal-diamond interfaces of different radii. Each solid curve is labeled with the radius of the metal sphere. The diamond is doped to 10^{19} cm^{-3} with substitutional nitrogen, and the metal Fermi energy E_F is 4 eV below the minimum energy of the diamond conduction band. The field extends 25 nm into the diamond for the planar case. The solid curves are obtained by reverse-biasing the metal-diamond junction by 6 V. The inclined dashed line is for a planar junction on undoped diamond with an electric field of 450 V μm^{-1}. The horizontal dashed line represents the Fermi energy of electrons in the metal.

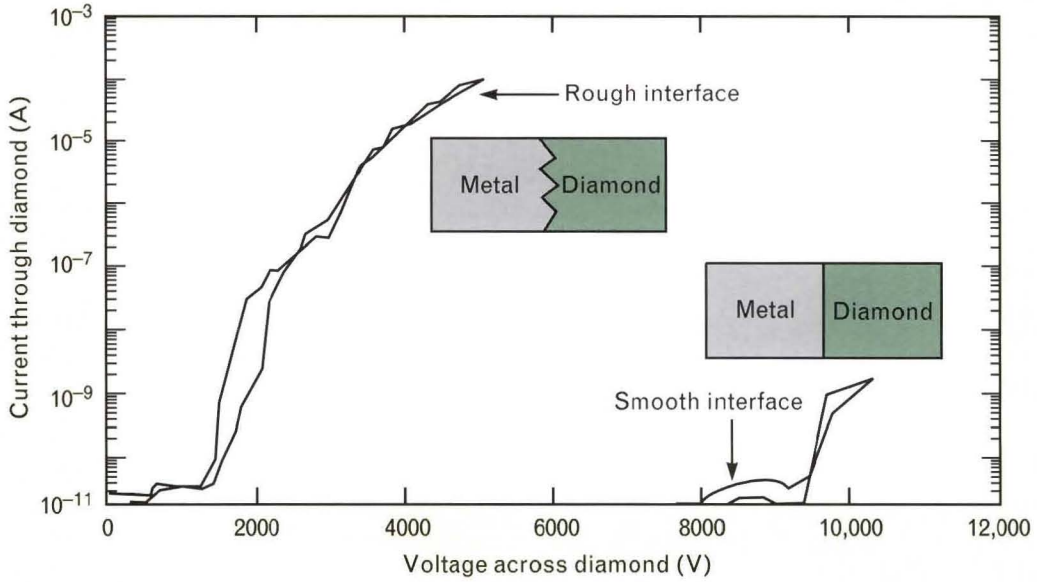

FIGURE 11. Comparison of conductivity through a synthetic type-Ib diamond approximately 1.3 mm thick, as a function of roughness at the interface. Conduction through diamond is clearly greater for a rough diamond-metal interface than for a smooth interface.

Electrons are injected into the conduction band in the diamond by tunneling, as illustrated in Figure 9. The degree of tunneling depends on the electric field at the metal-diamond interface, which is determined by the nitrogen doping and the roughness of the interface. If the interface is smooth, the probability of tunneling is too small to explain the experimental current densities. If the interface is roughened, however, then the emission probability is increased, just as a sharp metal cone enhances emission with Spindt-type field-emission cathodes, as shown in Figure 4.

Figure 10 shows the potential energy as a function of distance from the metal-diamond interface for several levels of interface roughness. The roughness is approximated by assuming spherical metal surfaces of different radii surrounded with type-Ib diamond doped to 10^{19} cm^{-3} nitrogen. The degree of tunneling increases with the reduction of the tunneling distance. This distance is determined by the intersection of the potential energy curves with the metal Fermi energy. For example, with the planar interface the tunneling distance is approximately 5 nm, whereas with a roughened interface with a radius of curvature of approximately 2 nm the tunneling distance is reduced to less than 2 nm. This reduced tunneling distance results in an orders-of-magnitude increase in the degree of emission of electrons from the metal into the diamond.

Figure 11 shows the effect of back-interface metal-diamond roughness on conduction through synthetic type-Ib diamond; the figure compares conduction through diamond for both rough and smooth interfaces. The smooth surface was obtained by evaporating nickel on a polished diamond substrate. The rough surface was obtained by first depositing nickel salts on the diamond and then heating the substrate to 1100°C in a gas mixture of argon and hydrogen. The nickel is reduced and roughens the diamond surface by catalyzing a reaction between diamond and hydrogen to form methane [11]. Examination with a scanning electron microscope indicates that the roughness is on the order of 10 nm or less. Additional nickel is then evaporated on the roughened surface to ensure electrical contact.

Conduction through the diamond was obtained by mounting the nickel-coated diamond surface in silver epoxy and contacting the other top clean diamond surface with a rod one millimeter in diameter. We measured the current through the diamond as the positive bias on the rod was increased from 0 V to 4000 V and then decreased back to 0 V. This process resulted in two curves—one for increasing bias voltage and one for decreasing bias voltage. Figure 11 clearly shows that conduction through diamond is greater for a rough metal-diamond interface than for a smooth interface.

The rough surface formed by annealing nickel salts on diamond in hydrogen, either for single-crystal diamond as in Figure 11 or for gated metal diodes as in Figure 1, is believed important for the emission of electrons from the metal into the diamond. Gated metal diodes and single-crystal diamond diodes made without a nickel salt will not emit.

Transport through Diamond

Transport through the diamond region begins by injection of electrons with high electric field (10^7 V cm^{-1}) at the metal-diamond interface followed by transport through the remaining diamond at lower fields. For the diamond-grit-based cathodes discussed in Figures 1 and 2, conduction of electrons through less than 100 nm of nitrogen-doped diamond does not limit emission of electrons into vacuum.

Diamond-Vacuum Interface

The diamond-vacuum interface has been extensively studied [1, 12–14]. As shown previously, some crystal planes of diamond such as the (111) have an NEA, while others such as the (100) have a positive electron affinity (PEA) [1].

The variations in the work function of different surfaces result in contact potentials and fields in the vacuum close to the surface of the cathode, as depicted in Figure 12. These fields compromise the NEA property of the diamond [15]. To minimize this effect, we can treat the diamond with a plasma that contains oxygen, and then coat the diamond with cesium, resulting in an oxygen-cesium surface termination that lowers the work function of the PEA surfaces and enhances emission of electrons into the vacuum [16]. Alternatively, the cesium can be added to the diamond surface as a cesium salt. The plasma

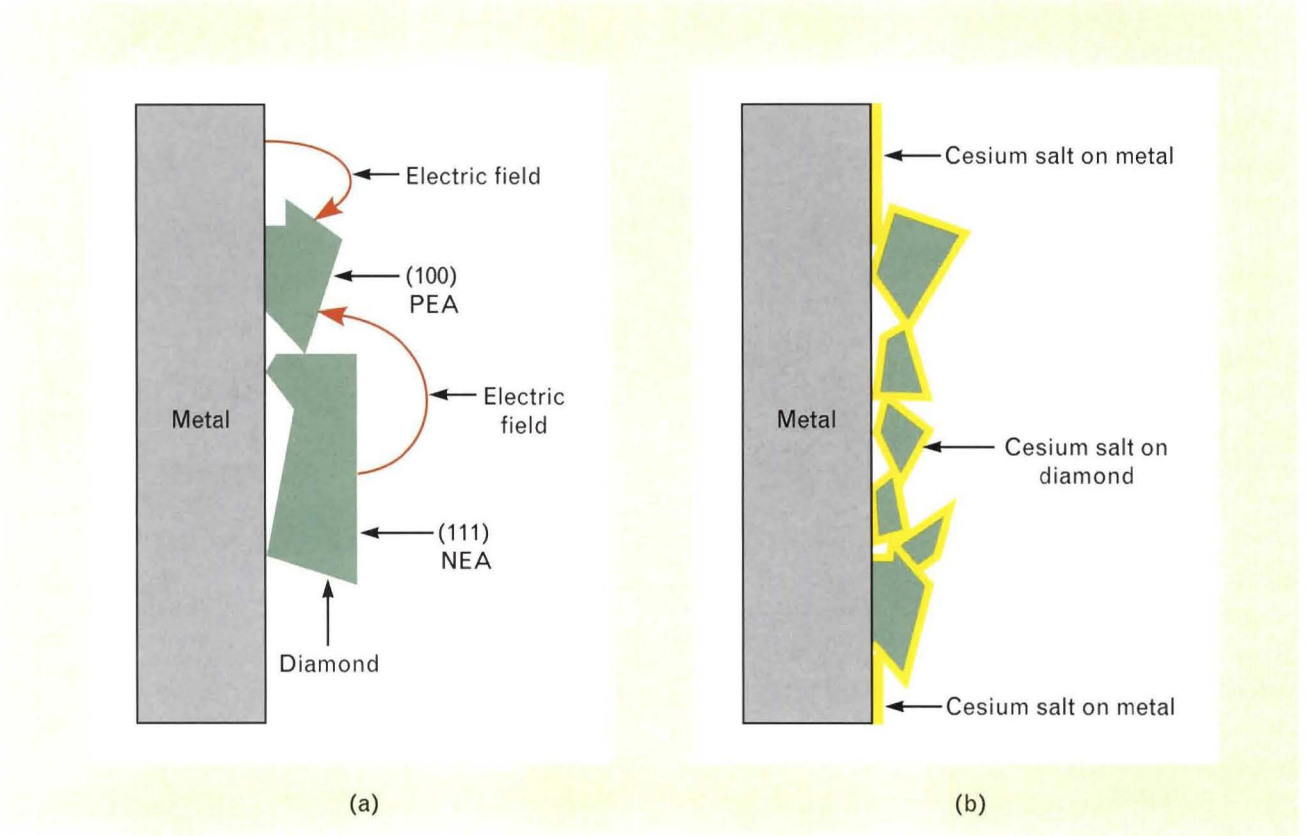

FIGURE 12. Diagram of diamond grit in the cathodes showing the built-in electric field between diamonds of different crystal planes and between the diamond and a metal surface. (a) Diamonds with an NEA (111)-oriented surface exposed next to a diamond with a positive electron affinity (PEA) (100)-oriented surface on a large metal substrate have electric fields that bend into the (100)-oriented surface, which inhibits the emission of electrons from the (111)-oriented surface. (b) Continuous, oxygen-cesium-coated diamond on a metal surface reduces the effect of the built-in fields from the PEA diamond and metal surfaces.

containing oxygen and the addition of a cesium salt (usually cesium chloride or cesium carbonate) is necessary for the low voltage emission of the gated metal diodes, as shown in Figure 3.

Transport through Vacuum

The electric field required for transport through vacuum depends on the field required for conduction through the diamond and any charge at the diamond-vacuum interface. Additional electric field in the vacuum is required to overcome any built-in electric field from PEA surfaces. Therefore, even if the diamond has an NEA surface, the electric field at the surface is not necessarily zero. Experimentally we have measured the required field for emission to be 0 to 1 V μm^{-1} with single-crystal diamonds [10].

Vacuum-Metal Interface

Since both the metal anode shown in Figure 7 and the metal gate shown in Figure 1(b) have a work function of 4 to 5 eV, the effective potential between the diamond cathode and the metal anode is reduced by the work function of the metal. This result is consistent with the minimum gate voltage of 5 V for emission, as shown in Figure 3. If we used a metal anode with a lower work function, then the minimum gate voltage for emission could be reduced.

Summary and Conclusions

We have fabricated diamond-grit cathodes with excellent emission performance. These devices exhibit a lower emission threshold than cesium-coated Spindt-

type cathodes [17], and reach current densities required for flat-panel displays at gate voltages of 10 to 15 V. Temporal uniformity of a few percent has been demonstrated. The emission is also tolerant of poor vacuum conditions. The stability of these cathodes is partly due to the inherent stability caused by the NEA property of diamond, which allows the emission-limiting metal-diamond interface to be protected from the vacuum environment. Other field-emission cathodes in which emission is limited by the metal-vacuum interface can be damaged by ion bombardment, arcing, and chemical reactions. Diamond cathodes have been operated successfully at high current levels continuously for approximately a hundred hours, which simulates ten years of operation in a flat-panel display.

These cathodes have a number of drawbacks as well. The primary operational shortcoming is the high gate current. In addition, the lack of uniformity and reproducibility in the production of these cathodes has plagued device performance. These problems are directly related to the deposition techniques of the diamond grit. We believe that further developments in reducing gate current and standardizing production will improve the cathode properties. Finally, high processing temperatures and the use of cesium are potential problems. The high processing temperatures—900 to 1100°C—limit the use of cathodes to applications in which high-temperature processing is acceptable. The addition of cesium salts to the cathodes could potentially corrode the cathodes because of the hygroscopic nature of these salts. This problem does not exist if the cathodes are kept in a vacuum or in a dry environment.

Acknowledgments

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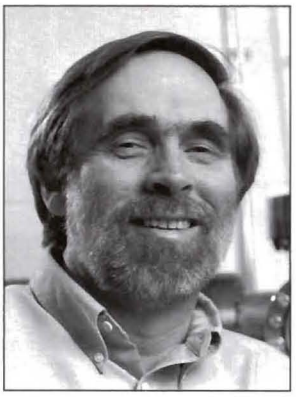

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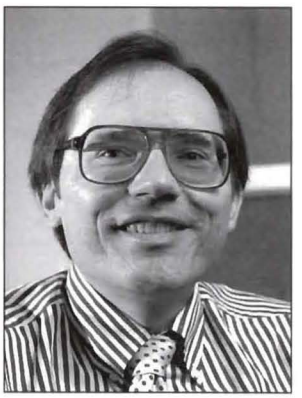

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