Progress Toward Diamond Power Field-Effect Transistors

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Diamond’s properties (highest thermal conductivity, high hole & electron mobilities, & high electric breakdown field) predict that diamond field-effect transistors (FETs) will have superior high-power high-frequency performance over FETs formed in other semiconductors. The development of diamond FETs is limited by a lack of quality substrates & the high ionization energy of the primary dopant, boron (B). This high ionization energy results in a resistance too high for FETs. Fortunately, recent developments are addressing these shortcomings. Single-crystal diamond substrates ~4 inches have been demonstrated. Further, two approaches address the dopant issue. When the surface of diamond is terminated in H, a surface p-type conductive layer forms. FETs made using this layer demonstrate competitive high-frequency performance, though manufacturability of this type of device has yet to be worked out. The second solution to doping uses delta doping by B. A thin <2-nm layer doped with B at >10²⁰ cm⁻³ is sandwiched within undoped diamond. This structure mitigates B’s high ionization energy by producing an acceptor subband with ~100% of the B is ionized. Recent reports of delta-doped diamond have channel resistances suitable for device applications. This article will review the state of the art for FET and substrate development.

1. Introduction

1.1. Comparison to Other Semiconductors

Diamond has a combination of electrical and thermal properties that make it unique among all the semiconductors for transistor applications. It has the highest room-temperature thermal conductivity, high hole and electron mobilities, high electric breakdown field, and a large bandgap (5.47 eV).[1] These properties are summarized in Table 1. Each of these properties contribute to desirable transistor properties. Thermal conductivity relates to the power dissipation a transistor can safely handle.

Desirable properties alone do not convey their relative importance. For this reason, researchers have developed a variety of figures of merit or weighted factors to allow materials to be compared directly, usually for a particular application or design criteria. The Huang chip area criteria, $HCA = \epsilon_2 \mu E_F$, is used to compare the size of transistors with similar properties. The larger the value, the smaller the transistor can be with the same power-handling properties.[2] The minimum power loss of a switching transistor is inversely proportional to the Huang switching criteria $= \sqrt{\epsilon_1 E_F}$.[2] Baliga’s figure of merit $= \epsilon_1 E_F$, which is applicable for low-frequency power applications, compares the semiconductors’ power switching properties, assuming power is only dissipated during the “on” state of the transistor.[3] For high frequency applications where the period of oscillation approaches the switching time of the transistor, the Johnson figure of merit $= v_{SAT} E_F/2r$ is used to compare the voltage-frequency product of a transistor.[2-4] Finally, due to the omission of thermal conductivity from any of the listed figures of merit and the established fact that the performance of present-day transistors is frequently limited by thermal effects, we present thermal conductivity alongside these figures of merit. Figure 1 summarizes the comparison of several semiconductors for these five figures of merit. If the intrinsic properties of diamond can be fully realized, the Johnson figure of merit, a metric favored by the authors, predicts diamond devices with performance triple that of as-yet-unrealized ideal GaN. The material properties of diamond plainly justify its development as a semiconductor.

1.2. Difficulty in Creating Charge Carriers in Diamond

Development of diamond as a semiconductor for field effect transistors (FETs) and radio frequency (RF) devices has been limited by a lack of diamond substrates and effective dopants, the latter having high ionization energies (B @ 0.36 eV, P @ \approx 0.57 eV, and N @ 1.7 eV).[1,5] These high ionization energies result in room-temperature charge-carrier densities that are
orders of magnitude below dopant concentration. Charge carriers (holes) at density \( p \), generated by a dopant, density \( N_A \), at temperature \( T \), and ionization energy \( E_A \) are related by Equation (1).

\[
p(p + N_D) = \left( \frac{2\pi m^* kT}{\hbar^2} \right)^{3/2} \exp \left(-\frac{E_A}{kT}\right)
\]

(1)

where \( m^* \) is the reduced mass of a hole, \( k \) is Boltzmann’s constant, \( \hbar \) is Plank’s constant, and \( N_D \) is the density of hole traps and donors (usually a small concentration of nitrogen or phosphorous present in the diamond). The hole density as a function of dopant density is shown by Figure 2.

From Equation (1) it can be seen that \( p \propto \exp(-E_A/2kT) \) if \( N_A \gg p \), which is nearly always the case at room temperature and \( N_D = 0 \). This means the carrier density increases by \( \exp(-0.18 \text{eV}/kT) \) or \( \approx 2 \)-fold for every 30°C. However, if donors are present in the diamond and \( N_D \gg p \) then \( p \propto \exp(-0.36 \text{eV}/kT) \) and carrier density increases by \( \approx 2 \)-fold for every 15°C. To the authors’ knowledge, for boron levels \( <10^{19} \text{cm}^{-3} \), reported carrier density as a function of temperature increases by \( \approx 2 \) for every 15°C, exhibiting a thermal activation energy of 0.36 eV instead of 0.18 eV, indicating the difficulty of removing donors in boron doped diamond. These low carrier densities make boron doped diamond too resistive to compete with other semiconductor transistors at room temperature. Diamond n-type dopants, like phosphorous and nitrogen, have even higher activation energies and resistances.

### 2. Conductive Diamond for FETs

This article discusses two solutions to the low carrier densities and the high resistance problem. The first exploits the unusual properties of a diamond surface that is terminated with hydrogen. In this case, a surface dipole is generated that lowers the energy required to pull an electron out of diamond’s valence band from 7.2 to 4.2 eV.[8] This enables electrons to leave the diamond and be captured by materials on the surface having higher binding energies than the H-terminated diamond. A resulting p-type conductive layer of holes forms just under the diamond surface that has sufficient conductivity to be used for competitive FETs. This process is referred to as surface transfer doping or activation, where the carriers are in the semiconductor and the dopants (electron-capture species) exist in an adjacent overcoating material matrix. Adsorbed gases on the diamond surface, \( \text{H}_2\text{O} \) with \( \text{pH} < 6 \) from atmospheric impurities,[9] \( \text{NO}_2 \),[10–13] \( \text{O}_3 \),[11] and solid metal oxides (\( \text{NH}_4\text{Ce(NO}_3)_6 \))[13] \( \text{Al}_2\text{O}_3 \),[14,15] \( \text{WO}_3 \), \( \text{MoO}_3 \), and \( \text{V}_2\text{O}_5 \)[16–18] all have demonstrated the ability to generate a diamond-surface-conductive layer. FETs fabricated using a combination of adsorbed \( \text{NO}_2 \) with \( \text{Al}_2\text{O}_3 \)[19] and \( \text{Al}_2\text{O}_3 \) with poly-tetra-fluoro-ethylene[20] have exhibited impressive device properties with current densities from 1.2 to 1.3 A mm\(^{-1} \). An example is shown in Figure 3. \( \text{Al}_2\text{O}_3 \) overcoated diamond devices have demonstrated a wide operational temperature range, \( -263 \) (10 K) to 400°C,[21] high voltage operation > 1 kV,[22] unity-current-gain frequency, \( f_T \), of 70 GHz,[23] and maximum frequency of oscillation, \( f_{\text{max}} \), of

| Parameter               | Diamond | c-BN | \( \beta-\text{Ga}_2\text{O}_3 \) | AlIn | GaN | SiC | GaAs | Si |
|-------------------------|---------|------|-------------------------------|------|-----|-----|------|----|
| \( \sigma_{\text{thermal}} \) \ (W/m-K) | 2,290 - 3,450 | 940 - 2,145 | 11 - 27 | 319 | \leq 253 | 370 | 55 | 145 |
| \( \epsilon^- \) mobility \ (cm\(^2\)/V\(s\)) | 4,500 | 825 | 180 | 426 | 2,260 | 900 | 8,500 | 1,450 |
| hole mobility \ (cm\(^2\)/V\(s\)) | 3,800 | 500 | -- | -- | 24 | 120 | 400 | 480 |
| \( E_{\text{breakdown}} \) \ (MV/cm) | \approx 13.0 | \approx 17.5 | \approx 10.3 | \approx 15.4 | \approx 4.9 | \approx 3.0 | \approx 0.4 | \approx 0.3 |
| \( v_{\text{sat}} \) \ (10\(^7\) cm/s) | 2.3 (\epsilon^-) | 1.4 (h^+ | 1.1 | 1.3 | 1.4 | 2.0 | 1.0 | 1.0 |
| Rel. permittivity | 5.7 | 7.1 | 10.0 | 9.8 | 10.4 | 9.7 | 12.9 | 11.8 |

Table 1. Summary of electrical and thermal properties of commonly used and future semiconductors. The higher thermal conductivities for diamond and cubic BN are for isotopically pure crystals. The last row indicates the semiconductor maturity, pink being less mature.[3]
120 GHz.\textsuperscript{[24,25]} The high voltage operation and inherent high thermal conductivity, \approx20 times that of Si, demonstrates the feasibility of a diamond FET superior to those formed in other semiconductors.

A second potential solution to the problem of diamond charge carriers uses boron in delta-doped layers. A very thin layer, \(<2\) nm, with sharp, well-defined boundaries of heavily boron-doped diamond, \(>10^{20}\) cm\(^{-3}\), is grown epitaxially within an undoped diamond layer. The wave functions of holes in the boron-doped layer extend into the nearby high-mobility intrinsic layer,\textsuperscript{[26,27]} thus increasing carrier mobility. Further, in such highly doped diamond, a dopant subband forms which raises the activation of the boron to nearly 100%. For comparison, if the boron was uniformly distributed, \(<1\)% of the boron atoms would contribute holes, making the material too resistive through both low carrier density and degraded mobility. There are numerous reports on delta-doped diamond, but the device quality of these layers has been disappointing until recently.\textsuperscript{[28–32]}

2.1. Generating Diamond Surface Conduction

As described above, when the H-terminated diamond surface is overcoated with a material that has a higher electron-binding energy, electrons leave the diamond and attach themselves to the overcoating material, thereby producing a conductive layer of holes in the diamond surface. Work with several of these materials – NO\(_2\), transition metal oxides, and Al\(_2\)O\(_3\) – is discussed below.

2.1.1. Transfer Doping With NO\(_2\)

The presence of NO\(_2\) in concentrations as small as 6 ppb makes H-terminated diamond conductive.\textsuperscript{[10,11]} At higher NO\(_2\) concentrations, the lowest reported surface resistance is \(\approx700\) Ω sq.\textsuperscript{[33]}

Figure 1. Bar chart showing a comparison of semiconductors using several figures of merit criteria.

Figure 2. Hole concentration at 298 K for several donor % concentrations as a function of boron doping. The donors can be either nitrogen or phosphorus and trap the charge carriers, removing them from the valence band and making the diamond more resistive. A commonly used carrier density for transistors, \(10^{19}\) cm\(^{-3}\), requires \(>10^{19}\) boron concentration. If even a small fraction of nitrogen donors are incorporated into the diamond at 0.25% of the boron concentration, then the carrier density can never exceed \(10^{19}\) cm\(^{-3}\) for any boron doping level. At doping densities \(>10^{19}\) cm\(^{-3}\) the boron atoms form a sub-band and Equation (1) is no longer applicable.\textsuperscript{[7]}

Figure 3. Drain current \(I_{DS}\) as a function of drain-source voltage \(V_{DS}\) of a 0.4-μm-gate-length diamond FET with a NO\(_2\) – Al\(_2\)O\(_3\) activation layer. The gate-source voltage was varied from \(V_{GS} = +11\) to \(-5\) V in \(ΔV_{GS} = -2\) V steps. The device was fabricated on a polycrystalline diamond substrate.\textsuperscript{[19]} Reprinted with permission from Jpn. J Appl. Phys., K. Hirama, H. Sato, Y. Harada, H. Yamamoto, M. Kasu, Diamond Field-Effect Transistors with 1.3 A mm\(^{-1}\) Drain Current Density by Al\(_2\)O\(_3\) Passivation Layer, 51 (2012) 090112.
and highest reported transistor drain current of 1.35 A mm$^{-1}$ were achieved. Initially, it was believed that adsorbed NO$_2$ was taking electrons from the diamond, forming NO$_2^-$. However, no NO$_2^-$ could be detected on the diamond surface, but instead NO$_3^-$ was found at concentrations approximately equal to the positive charge density in the diamond. Given the difficulty of accurately characterizing a sub-monolayer of adsorbed material, these results were obtained from the surface chemistry of diamond powder, < 250 nm in diameter, where the surface area is increased by $\approx$10$^4$ over a diamond plate. This increase in surface area allowed for infrared transmission to detect the surface chemistry. Figure 4 shows the diamond powder during H-termination, and the Fourier transform infrared spectroscopy, FTIR, measurements of diamond powder before and after H-termination are displayed in Figure 5. Details of H termination and FTIR procedures are presented in ref. The absorption peak corresponding to NO$_3^-$ at 1382 cm$^{-1}$ is off scale.

Figure 4. Diamond powder during H-termination in a hydrogen plasma at $\approx$60 Torr of H$_2$. The powder is initially heated by the plasma to $\approx$1000°C for 10 min to degas the powder and then H terminated for 60 min at $\approx$800°C.

Figure 5. Fourier transform infrared absorption, FTIR, of diamond powder before (“cleaned diamond powder”) and after H-termination.

Figure 6. FTIR of H-terminated diamond powder before and after NO$_2$ exposure. No absorption for NO$_2^-$ at 2557 and 1270 cm$^{-1}$ was measured. The absorption peak corresponding to NO$_3^-$ at 1382 cm$^{-1}$ is off scale.

Figure 7. Possible reaction of NO$_2$ with H-terminated diamond to form a negative ion on the diamond surface and a positive carrier in the diamond.
importantly there is no evidence of NO2 at 2557 and 1270 cm\(^{-1}\). Instead, a very strong absorption appears at 1382 cm\(^{-1}\), which is consistent with NO\(_3\). At atmospheric pressure and room temperature, NO2 is in equilibrium with its dimer, N\(_2\)O\(_4\). We speculate that the dimer reacts to remove an electron from the diamond and thus dissociates into NO and NO\(_3\) by the reaction shown in Figure 7.

Although absorption at 1382 cm\(^{-1}\) is consistent with NO\(_3\), further evidence is desirable to rule out that another carbon complex could be responsible for this absorption or that additional absorption peaks could be hidden at 1382 cm\(^{-1}\). To unequivocally determine that the absorption at 1382 cm\(^{-1}\) is only from NO\(_3\), isotopically enriched N\(^{15}\)O\(_2\) was used to replace the N\(^{14}\)O\(_2\) used in the experiments. Figure 8 shows the absorption of two H-terminated diamond powders, one exposed to N\(^{14}\)O\(_2\) and the other exposed to N\(^{15}\)O\(_2\). The shift in the resulting absorption peak from 1382 to 1352 cm\(^{-1}\) not only indicates that we are actually forming NO\(_3\) on the diamond surface, but that there is no hidden chemistry associated with absorption in the region of 1382 cm\(^{-1}\).

The concentration of NO\(_3\) was additionally measured by washing the NO\(_2\)-exposed powder with water. NO\(_3\) dissolved in the water and its concentration was measured both by electrospray spectrometer, Figure 9, and colorimetric techniques. Using the surface area of the diamond powder, 47.3 cm\(^2\) mg\(^{-1}\), determined by the (Brunauer, Emmett, and Teller) BET technique,\(^{[36]}\) the surface density of NO\(_3\) as determined by electrospray and colorimetry was 6.3 \(\times 10^{13}\) and 8.2 \(\times 10^{13}\) cm\(^{-2}\), respectively. Van der Pauw and Hall measurements of the carrier density for single-crystal H-terminated and NO\(_2\)-exposed (100) diamond plates yield 3 \(\times 10^{13}\)–9 \(\times 10^{13}\) cm\(^{-2}\). This agreement between surface density of NO\(_3\) and carrier density is well within the uncertainty of the measured NO\(_3\).

Conductive H-terminated diamond is commonly modeled by transfer doping where an electronegative overcoating pulls electrons out of the diamond, generating hole carriers. The model assumes that there are no chemical reactions between the H-terminated diamond and the overcoating material. When NO\(_2\) is applied to H-terminated diamond and reacts with the diamond surface to form NO\(_3\), the concentration of hydrogen bonded to the diamond surface is reduced by 2 to 10 times as measured by the FTIR signature of the C─H bond. Additionally, the O─H
atoms are removed and oxidized during transfer doping with NO$_2$ or that the FTIR C─H signature is suppressed by the presence of NO$_3^-$/C$_0$. One speculation is that the NO$_2$ reacts with some of the less strongly bonded H on the surface by Equation (2).

\[
\text{NO}_2 + \text{C} - \text{H} \rightarrow \text{HNO}_3 + \text{C}^ullet
\]

where the H is removed, additional chemical reactions would occur forming C─O─H. If this is the case then the surface conductance would vary with the local chemistry over a
submicron scale potentially reducing the hole mobility. In spite of the potential for locally non-uniform conduction, NO\textsubscript{2} activated diamond is one of the lowest resistive surfaces to date, \(\approx 700 \, \Omega \, \text{sq}^{-1}\). Only O\textsubscript{3} of the transfer doping gases has a lower resistance.\cite{11} Ley et al. reported that O\textsubscript{3} chemically reacts with the H-terminated diamond surface and the reaction enhances the transfer doping conductance.\cite{37} He speculated a small fraction of the diamond surface, \(\approx 1\%\), is oxidized by O\textsubscript{3} forming either ether groups, \(\text{C}\ldots\text{O}\ldots\text{C}\), or alcohols, \(\text{C}\ldots\text{O}\ldots\text{H}\). The other diamond transfer doping materials, \((\text{NH})\text{3Ce(NO3)}\text{6}, \text{MoO3}, \text{WO3},\) and \(\text{V2O5}\), are known for their oxidizing properties and may have similar chemical reactions. The simple models of transfer doping may require some additional modifications.

As discussed above, NO\textsubscript{2} on H-terminated diamond generates one of the lowest surface resistances of any diamond treatment and the highest reported drain current. We also observe that the resistance increases with time making it unusable for devices. Figure 10 shows the resistance of single crystal (100) H-terminated diamond in air, after NO\textsubscript{2} exposure, and NO\textsubscript{2} exposed and kept in dry N\textsubscript{2}. H-terminated diamond will become conductive in air by exposure to the O\textsubscript{3} and/or NO\textsubscript{2} in the atmosphere. However, this conductance is temporary and variable. In dry N\textsubscript{2}, the resistance, at the scale in Figure 10, appears stable over days but this is in part due to the anticorrelation between the carrier density and mobility as seen in Figure 11. Figure 11 also shows that the density logarithmically decreases in time, and the lithographic process used to make FETs is observed to increase the resistance (data not shown). Because of the instability of NO\textsubscript{2}-enhanced conductivity, other approaches are being pursued, including atomic layer deposition (ALD) of Al\textsubscript{2}O\textsubscript{3} and transition metal oxides like MoO\textsubscript{3}, WO\textsubscript{3}, and V\textsubscript{2}O\textsubscript{5}, which will be discussed next.

2.1.2. Transition Metal and Aluminum Oxides

Kueck\cite{14} first reported the use of ALD of Al\textsubscript{2}O\textsubscript{3} to stabilize diamond’s surface conductance. Metal-insulator field-effect transistors, MISFETs, made with this coating were stable in time over a wide range of temperatures and were reasonably stable under high voltage operation.\cite{21,22} However, the high surface resistance from 8 to 12 k\,\Omega\,sq\textsuperscript{-1} for (100) oriented diamond substrates limits the drain current.\cite{39} Looking for a coating that would both stabilize the diamond surface and generate resistances \(< 5 \, \text{k}\,\Omega \, \text{sq}^{-1}\), the transition metal oxides WO\textsubscript{3}, MoO\textsubscript{3}, V\textsubscript{2}O\textsubscript{5}, Nb\textsubscript{2}O\textsubscript{3}, and ReO\textsubscript{3} were considered. Some of these oxides had been previously used with organic solar cells because of their high electron work function.\cite{40} As the work function of these oxides increases in Figure 12, the energy difference (activation energy) between the diamond valence band and the oxide’s conduction band increases. As the activation energy increases, the carrier density in the diamond would be expected to increase also, which has been demonstrated by Verona et al.\cite{41} in Figure 13. These oxides are easily deposited by thermal evaporation on diamond and generate high sheet carrier densities approaching \(\approx 10^{14} \, \text{cm}^{-2}\) with surface resistances of 2.7 and 1.8 k\,\Omega\,sq\textsuperscript{-1} for (100) and (111) diamond surfaces, respectively.\cite{43} The stability of these transition metal oxide films is superior to that of NO\textsubscript{2}, but the level of stability found with Al\textsubscript{2}O\textsubscript{3} has not yet been demonstrated by them. V\textsubscript{2}O\textsubscript{5} on diamond exhibited surface conduction that varies \(< 10\%\) over temperatures of \(-200\) to \(-200\) \textdegree C in vacuum.\cite{43} Crawford\cite{44} found that when V\textsubscript{2}O\textsubscript{5} and MoO\textsubscript{3} are heated in air above \(100\) \textdegree C, a significant increase in...
diamond’s resistance occurs and remains high after cooling. However, encapsulating the films with a spin on glass, HSQ, stabilized the diamond resistance up to 300 °C.

There are also other concerns with transition-metal-oxide transfer doping. Although resistances of ≈2 kΩ sq⁻¹ can be obtained, the highest reported drain current is <0.4 A mm⁻¹, whereas the use of ALD Al₂O₃ yields surface resistances of 4 to 12 kΩ sq⁻¹[39] but obtains 0.8 to 1.2 A mm⁻¹[39,45]. These transition metal oxides are themselves semiconductors with a complex range of oxidation states. Under the operating conditions of a MISFET, current may pass through these films, potentially changing their oxidation states and resulting in a material with a lower electron affinity and a corresponding increase in surface resistance. Future efforts will elucidate the cause of the lower drain currents of transition metal oxide MISFETs.

2.1.3. ALD Aluminum Oxide

Another overcoating material, Al₂O₃, has resulted in low surface resistance as reported above. The classic transfer-doping model

Figure 17. a) Top view and (b) side view of silicon wafers being coated with a polycrystalline diamond film in a hot filament CVD reactor. Deposition areas as large as 400 × 1180 mm (0.5 m²) have been coated with this technology. Photo courtesy of Neocoat SA[51]
where the conduction band of the coating material is below diamond’s valence band does not apply in this case, as the conduction band of $\text{Al}_2\text{O}_3$ is $\approx 3 \text{ eV}$ above the valence band of diamond.\textsuperscript{46} However, $\text{Al}_2\text{O}_3$ can contain electron traps below diamond’s valence band.\textsuperscript{46} We speculate that these traps are responsible for the enhanced conduction with ALD $\text{Al}_2\text{O}_3$. By varying the ALD parameters and controlling impurities in the ALD deposition, we have obtained surface resistances between 1.5 and 2.5 kΩ sq$^{-1}$. Figure 14 compares the resistance of three H-terminated diamonds aged in air over many days – after being activated by air, NO$_2$, and ALD $\text{Al}_2\text{O}_3$, respectively. Overcoating with $\text{Al}_2\text{O}_3$ adds stability to the carrier density as shown in Figure 15 compared to NO$_2$-activated diamond in dry N$_2$ in Figure 11. However, the stability of these ALD $\text{Al}_2\text{O}_3$ films has not been evaluated under actual MISFET operation.

Reproducibility and stability of FETs with high drain currents $\geq 1 \text{ A mm}^{-1}$ has yet to be demonstrated. Thus, much of the remaining research in diamond is directed to developing a stabilizing layer on diamond that enables reproducible high-current, high-voltage FETs with practical lifetimes.

**Figure 18.** An example of homoepitaxial growth on different facets to increase the size of the starting substrate. Reproduced with permission.\textsuperscript{15} Copyright 2006, Elsevier B.V.

**Figure 19.** Fabrication procedure using smaller diamond substrates to manufacture a larger mosaic crystal. Schematic drawing courtesy of Excellent Diamond Products, EDP Corporation.\textsuperscript{17}
2.2. Boron Delta Doping

The second potential source of conductive diamond for FETs, delta doping, is obtained by embedding a very thin layer, ≤2 nm (<6 diamond unit cells), of high boron doping, >10^{20} cm^{-3}, into an otherwise undoped diamond. Modeling has predicted for these thin layers that the carriers are quantum confined\(^{[26,27]}\) and Kohn et al.\(^{[47]}\) have predicted that RF FETs made with the diamond structure shown in Figure 16 would have a current capacity of 2.5 A mm\(^{-1}\) and RF power generation from 34 to 75 W mm\(^{-1}\), depending on the gate structure and the desired frequency of operation. These remarkable properties are the result of the hole wave function being larger than the thickness of the delta layer which allows a portion of the wave function to exist in the undoped regions of the diamond where the hole mobility can be significantly higher than for a uniformly doped material. With a material doped uniformly at >10^{19} cm\(^{-3}\), voltage measurement of diodes cannot resolve the doping.

Secondary ion mass spectroscopy, SIMS, and capacitance-voltage measurement of diodes indicated a concentration of boron in the unintentionally doped regions. With a residual gas residence time of 5 s, this level was introduced into the growth chamber to obtain the adequate for high mobility. H\(_2\)S was added to the gas flow to getter residual boron during the growth of undoped diamond. Secondary ion mass spectroscopy, SIMS, and capacitance-voltage measurement of diodes cannot resolve the doping density of the delta layer, but estimates are ~4 × 10^{20} cm\(^{-3}\) boron in a 1 nm thick layer. The fabrication of FETs on these films will determine their potential for high power RF devices.

3. Large-Area Diamond Substrates

The full realization of diamond’s device performance heralded by the figures of merit in Figure 1 is also limited by the lack of large-area diamond substrates with device research limited to diamond substrates a few to 10 mm on a side. Naturally sourced crystals will not satisfy chemical purity nor geometric requirements and have significant shortcomings in reproducibility. High pressure, high temperature (HPHT) material is in ready supply in small, blocky shapes and serves the diamond

Figure 20. Process to self-align small faceted cubic high-pressure, high-temperature HPHT crystals. After alignment low-pressure homoepitaxial diamond growth is used to cement the crystals together.

Figure 21. Optical micrograph of self-aligned cubic HPHT crystals just before homoepitaxial growth. The crystal in-plane orientation is ±1° and the tilt off the axis normal to the substrate is ±0.5°.\(^{[58]}\)
tool-cutting and gemstone markets very well but the crystals are not large enough for good electronic development. The desire is strong for wafer-scale diamond, and multiple approaches are under simultaneous development worldwide.

3.1. Polycrystalline Wafers

Efforts are underway to determine which applications might be served by the far more immediately scalable polycrystalline diamond wafers. The highest FET current densities yet reported have been fabricated on polycrystalline diamond.\[50,19\] This is in part because the (110) oriented diamond, common to polycrystalline diamond substrates, has a higher electrical surface conductance than (100) oriented substrates when activated with similar technologies.\[39,50\] Since the grain boundaries are not shorts and the FETs’ drain to source distances, 0.5 to 10 μm, can be smaller than the crystals in the substrate, there are not significant compromises using polycrystalline films for small FETs for research work. Large area (110) oriented polycrystalline substrates are comparatively easy to grow or obtain. CVD-grown polycrystalline diamond is commercially available from a variety of sources up to 2 and as large as 6 inches from a few select providers. Hot filament (HF) growth tools have demonstrated scalable, cost-effective coating capability and can produce near-optical-quality microcrystalline material. An example of a HF system is shown in Figure 17. To date, neither HPHT diamond synthesis nor HF techniques have shown great progress toward producing wafer-scale monocrystalline diamond.

3.2. Homoeptaxial Single-Crystal Diamond Growth

A high atomic hydrogen flux is generally viewed as essential for CVD deposition of high-quality diamond.\[52,53\] As a result, plasma CVD has been shown to be a promising method to grow high-quality material, but has its own challenges and limitations. Chief among these are vacuum-chamber constraints, uniformity,
scalability, and the thermal engineering challenges associated with a high-energy plasma. There is only one plasma CVD method that does not require a vacuum chamber and has demonstrated scalability, the DC arc jet, but the material quality is low and the output is primarily used in mechanical applications where the optical and electrical properties of the diamond are unimportant.\[54\]

The challenges of homoepitaxial growth of diamond in plasma CVD have been largely mitigated, and there are many companies that have sprung into existence to leverage this knowledge. In general, homoepitaxy does not yield a useful surface larger than the initial substrate. However, some variations on homoepitaxy can increase the substrate size. Homoeptaxial growth on carefully selected rather small single crystals with minimum dislocation densities can be performed in such a way that the available area is increased step by step while the dislocation density is kept low, as depicted in Figure 18.\[55\] By such an approach, 4H-SiC has progressively been scaled over 20 years starting from small platelets to a 6-inch wafer size.\[56\]

### 3.3. Mosaic Tiling

The idea of tiling diamond substrates together and growing epitaxy to “glue” them together and make a cohesive epi-layer as illustrated in Figure 19 has seen decades of development. Despite the challenges of precisely aligning the substrates, the approach has seen some successes. Boundaries at crystal joints continue to contain a higher concentration of defects (and often impurities). Time will tell if these defects can be reduced to the point that the optical and electrical properties become unimportant.

Pending further development in tiling, and with homoepitaxy seemingly stalled at whatever sizes are available as substrates, we also look to heteroepitaxy to provide larger diamond areas, with deposition on silicon wafers as the holy grail of the field.

In a blend of heteroepitaxy and mosaic tiling, a related approach involves an arrangement of cube shaped HPHT diamonds, their orientations aligned by as-grown natural growth faces,\[58\] as shown in Figure 20 and 21.

If the HPHT diamonds are instead octahedrons, faceted by (111) planes, then alignment is accomplished with anisotropic etch pits faced with (111) planes in (100) Si wafers.\[59\] Both approaches use the natural facets of the crystals for alignment rather than human/machine precision. Although the approach has only been attempted via hot-filament growth, the approach may yet yield wafer-scale material.

### 3.4. Heteroepitaxial Diamond Growth

Two groups in the 1990’s began development of heteroepitaxial growth of diamond on single crystal silicon wafers\[60,61\] using a process that was developed to enhance random diamond nucleation.\[62,63\] Both groups used the same procedure with small variations. The starting Si wafer was cleaned and inserted into a diamond growth system having established diamond growth conditions, nominally via a plasma formed in a hydrogen-methane mixture. However, the wafer was DC biased from −100 to −300 volts with bias currents >100 mA. This results in an amorphous carbon layer instead of diamond growth. However, in this carbon layer diamond crystals nucleate heteroepitaxially on the Si crystal.\[63\] After a nucleation period, the bias voltage is removed and growth conditions for homoepitaxial diamond are established. The amorphous carbon etches away and diamond nuclei expand and merge to yield a continuous diamond film, pictorially shown in Figure 22.

In 1996, Ohshuka demonstrated heteroepitaxial diamond on an Ir film heteroepitaxially grown on a single crystal MgO substrate.\[64\] Professor Matthias Schreck, his students, and collaborators have used these previous 1990’s developments to deliver the largest single-crystal wafer seen to date.\[65\] The approach starts with a silicon wafer with an epitaxial layer of yttria-stabilized zirconia, YSZ, chosen as a reasonable lattice-match to diamond. Atop that, iridium, another reasonably good lattice-matched material (within 7%) provides the epitaxial surface, as shown in Figure 22. The final material stack, Figure 23, is the result of decades of research and experimentation and the precise mechanism of growth is an ongoing topic of research. The 3.6-inch wafer, shown in Figure 24, is a remarkable accomplishment given the lattice mismatch with iridium. The resulting diamond substrates are characterized in detail in ref. \[66\]

Another group has taken on the task of relieving the crystallographic and thermal mismatch between substrate and epitaxial layer with extensive etching of the initial diamond heteroepitaxial layer to produce a wafer of micro-needles upon which further epitaxy is strain-relieved relative to the substrate. An example is shown in Figure 25. Similar techniques have been used since the 1980’s for the epitaxial growth of GaN and Ge on Si.\[67,68\]

### 4. Conclusions

After significant worldwide research, the promise shown by the semiconductor properties of diamond is beginning to be realized in actual devices. Kawarada reported in 2010 a MISFET on (110)
Delta-doped FET models have shown high theoretical RF power levels of ≈70 W mm⁻¹. [47] In contrast, after much development, today’s state of the art industrial AlGaN/GaN HEMTs mounted on diamond heatsinks are at no higher than 19.9 W mm⁻¹. [75] and research devices have been reported with limited operational life and RF power levels of 41 W mm⁻¹. [76]

Delta doping requires precise control of the starting diamond substrate, the impurities, and the rapid switching of growth conditions in order to form the necessary atomically sharp boundary layers. Several groups have attempted this and after years of research recent reports have been published of delta-doped material with properties that could make competitive diamond FETs. To our knowledge, no FETs have been fabricated on this material as yet.

In spite of the early maturity stage of the diamond FETs described above, key building blocks and existence proofs have been demonstrated which show the promise of diamond FETs once all the key ingredients can be integrated into single devices. Indeed, all semiconductor-device technologies had to pass through this stage of maturation, including Si, GaAs, and GaN. These device building blocks, coupled with the recent demonstration of ≈4-inch single-crystal diamond wafers, opens the door to a diamond power-FET manufacturing capability someday.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
atomic layer deposition, diamond delta doping, diamond field effect transistors, diamond heteroepitaxy, NO₂

Distribution Statement
The authors declare no conflict of interest.

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