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Growth, Characterization and Device Development in Monocrystalline Diamond Films

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13. ABSTRACT (Maximum 200 words)

The effects of hydrogen on cluster binding energy and growth mode of diamond, the determination of the Schottky barrier height for Ti on (111) diamond and models for MESFET devices in diamond have been the subjects addressed in this reporting period. Capillarity and atomistic formulations for determining diamond thin film growth modes have been compared. Arguments are presented based on simple atomistic cluster binding energy calculations that suggest hydrogen should play an important role in stabilizing the 2-dimensional cluster configuration and thus promote layered diamond growth, assuming that the interfacial strain and misfit energies are not too high. Assumptions which may cause this model to break down experimentally are also discussed. The Ti-natural IIb(111) diamond interface has been investigated using UV photo-emission produced by a 21.2 eV light source. The chemically cleaned diamond showed a sharp (0.5 eV FWHM) peak at the position of the conduction band indicating a negative electron affinity surface. By determining the relative positions of the diamond valence band edge and the titanium Fermi level, the Schottky barrier height of titanium on diamond (111) was measured and found to be 1.0 ± 0.2 eV. A model for the observed titanium induced negative electron affinity is proposed, based on the Schottky barrier height of titanium on diamond, and the work function of titanium. A detailed, theoretical model for p-type diamond MESFETs is being developed. The model formulation contains the development of a complete and accurate description of the semiconductor surface between the gate and drain electrodes. The initial formulation of the model is complete and some test simulations of an ultra short gate length device have been performed.

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I. The Effects of Hydrogen on Cluster Binding Energy and Resulting Growth Mode During Chemical Vapor Deposition of Diamond*

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Abstract

Capillarity and atomistic formulations for determining diamond thin film growth modes are compared. Arguments are presented based on simple atomistic cluster binding energy calculations that suggest hydrogen should play an important role in stabilizing the 2-dimensional cluster configuration and thus promote layered diamond growth, assuming that the interfacial strain and misfit energies are not too high. Assumptions which may cause this model to break down experimentally are also discussed.

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It is generally agreed that in order for diamond to be fully utilized as an electronic material, single crystal diamond thin-films over large areas must be realized¹⁻⁴. Ideally one would prefer to grow the single crystal diamond two-dimensionally (Frank-van der Merwe growth) on economic, easily obtained non-diamond substrates. However, due to diamonds high surface energy it is often considered that CVD diamond should grow in a 3-D, or Volmer-Webber, mode on most foreign substrates, and this is in fact what has been observed. Justifications for the 3-D growth mode are based on Youngs Equation;

$$\cos(\theta) = (\gamma_s - \gamma_i) / \gamma_c \quad (1)$$

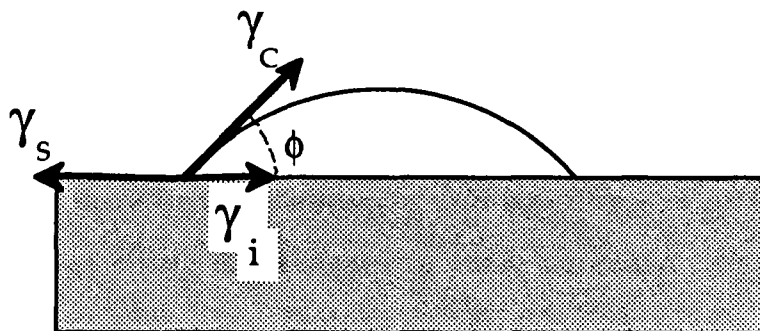


Figure 1. Capillarity model, showing the relationship between surface energies and condensate contact angle, θ .

Where γ_s , γ_c , and γ_i are the surface free energies of the substrate, condensate (diamond), and the interface between the two respectively (Refer to figure 1). From this relationship, in order to obtain 2-D growth ($\theta = 0$) the following inequality must occur;

$$\gamma_s \geq \gamma_i + \gamma_c$$

Since diamond has a surface energy higher than all other known materials, γ_s should always be $< (\gamma_i + \gamma_c)$, and therefore 3-D growth should always be the

preferred mode. This is not surprising when one considers the high bond strength of diamond.

However, the previous statement, that ' γ_s should always be $< (\gamma_i + \gamma_c)$ ', assumes that γ_c is equal to that of a freshly cleaved diamond surface and, in the case of vapor phase diamond the surface energies are not affected or altered during the chemical vapor deposition process. Surface energies are often determined by measuring the cleavage energy on a particular plane. The high energy associated with that surface is due to the unaccommodated bonds created as a result of the cleaving process. If some of those bonds are subsequently satisfied, either by forming a C=C double bond with another carbon or by bonding with a foreign atom on the surface, the result is a lowering of the overall free energy associated with that diamond surface. In this article the authors will present arguments based on cluster binding energy calculations that suggest 2-D growth of diamond on foreign substrates should be possible under certain conditions.

The following is concerned with cluster binding energy calculations and how they relate to the equilibrium shape and resulting growth mode of small diamond clusters. For more general discussions on thin film nucleation and growth several excellent reviews are recommended.⁵⁻⁸ There are two formulations typically used in the determination of the equilibrium shape of a cluster of atoms, or nuclei, on the surface. The first and most commonly used, is referred to as the capillarity method, and the second is the atomistic method. In the present arguments, the atomistic formulation will be utilized because it has been shown to be more accurate in the determination of the equilibrium shapes of microscopic clusters of atoms⁹.

The atomistic formulation is used to calculate the binding energy of a cluster of atoms. For a given cluster size, the configuration with the highest binding energy will be the most stable^{9, 10}. So while the capillarity method⁹ looks at the nuclei macroscopically as a droplet on a surface, the atomistic method will sum the binding energies of every atom in the cluster in order to determine the most stable configuration. For the following formulation, the energy changes due to relaxation of interfacial strain are neglected. Thus, the binding energy of the cluster is approximated as the sum of all bond energies in that cluster, including those between cluster and substrate atoms.

Consider clusters of atoms on a hexagonal close packed plane (see figure 2). If E_a and E_b represent the adsorption energy of a single atom on the substrate, and the bond strength of two cluster atoms, respectively, then the binding energy (E_i) for a cluster of i -atoms may be expressed as follows;

$$E_i = \sum(E_a) + \sum(E_b) . \quad (2)$$

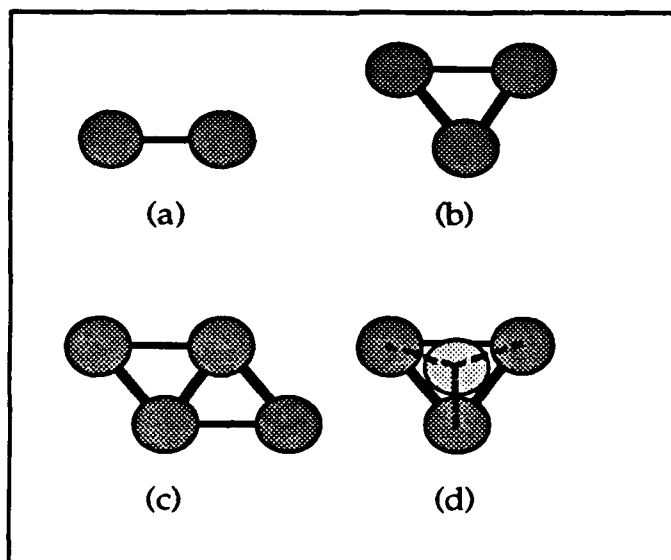


Figure 2. Clusters of atoms on a hexagonally closed packed plane: (a) two, (b) three, (c) four 2-D, and (d) four 3-D atom clusters.

For example, if there are 2 atoms on the substrate (figure 2-a) which have a single bond to each other and one bond each to the substrate, the binding energy for that 2-atom cluster would be $E_2 = 2E_a + E_b$. For 3 atoms on the surface (figure 2-b), the cluster would still be planar and the binding energy would equal $3E_a + 3E_b$. A cluster of 4 atoms may either be planar (figure 2-c) or three dimensional (figure 2-d), depending upon the respective binding energies for each case. The binding energies for these two cases may be calculated as follows;

$$E_4 = 4E_a + 5E_b \quad (2-D), \quad (3)$$

$$\text{and } E_4 = 3E_a + 6E_b \quad (3-D). \quad (4)$$

If $E_{i(2-D)} > E_{i(3-D)}$ then the 2-dimensional cluster configuration should be more energetically favorable.

So based on the above formulation, one may calculate the most favorable cluster configuration as a function of cluster size, i , and thus be able to determine the expected growth mode for a given condensate/substrate system. For the above example of a 4-atom cluster, the relationship; $E_a \geq E_b$ should be sufficient to promote 2-D growth. For slightly larger clusters ($i \geq 6$) E_a must be $\geq 2E_b$ for 2-D growth to be favored, which is similar to the condition predicted for small clusters by the capillarity model⁹.

The above discussion covers only the simplest of models. Second nearest neighbor interactions, bond relaxation and distortion, and atom vibrations were not considered. Others have performed more elaborate calculations of the structure and stability of small clusters of atoms of various sizes¹¹⁻¹³. Allpress and Sanders¹¹, and Hoare and Pal¹³ in particular, have performed calculations on the stability of multiply twinned particle clusters.

To apply the atomistic binding energy calculations to small clusters of diamond, one must simply utilize the correct covalent bonding configurations. The following results and discussion will be based on diamond growth under typical CVD conditions. All carbon bonding will be assumed to be sp^3 in nature. It will also be assumed that both substrate and diamond cluster surface bonds will be hydrogen terminated (as expected due to the atomic hydrogen growth environment for most CVD), and strain energy due to interfacial lattice misfit is negligible (i.e. assume growth on a closely lattice matched substrate). Simple cluster binding energies will be calculated under these conditions for diamond growth on a (100) surface.

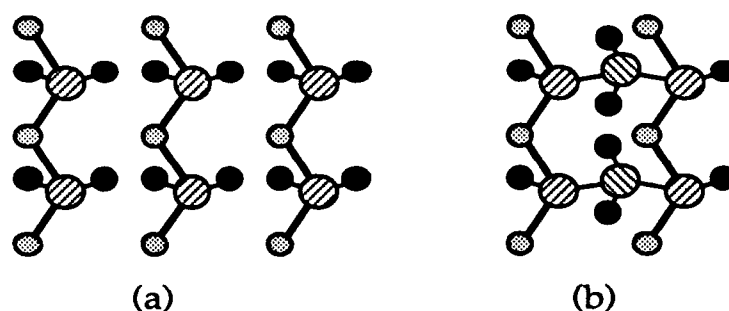
Consider first, a single carbon atom on the (100) surface that is hydrogen terminated with two hydrogens attached to every substrate atom. Since it was stipulated that all carbon atoms will be sp^3 bonded, there should be two bonds attached to the substrate atoms, and two that are hydrogen terminated for each surface carbon atom. The binding energy for this single carbon-atom cluster will be;

$$E_1 = 2E_a - 2E_{S-H} + 2E_{C-H} . \quad (5)$$

Where E_{C-H} and E_a are the bond strengths of a C-H bond and a C-substrate bond respectively. E_{S-H} represents the bond strength of a substrate-hydrogen bond. The quantity $2(E_a - E_{S-H})$ therefore represents the energy required to remove two hydrogens atoms from the substrate surface and replace them with a single carbon atom. Now consider a six atom cluster of 2-D (figure 3-a) and 3-D (figure 3-b) configurations. The corresponding binding energies for these two clusters are calculated to be;

$$E_{6(2-D)} = 12(E_a - E_{S-H}) + 12E_{C-H} , \quad (6)$$

$$\text{and } E_{6(3-D)} = 8(E_a - E_{S-H}) + 4E_{C-C} + 8E_{C-H} . \quad (7)$$



- Carbon(bottom layer)
- Carbon(top layer)
- Hydrogen
- Substrate Atom

Figure 3. Diamond cluster of six atoms on (100) plane in (a) 2-D and (b) 3-D configurations.

Since the C-H bond is stronger than a single C-C bond (100 vs 85 kcal/mol at R.T.), when one substitutes these numbers into the previous equations, it is evident that the binding energy of the 2-D cluster will always be higher than that of the 3-D cluster, for $(E_a - E_{S-H}) \geq 0$. The 2-D growth mode may still be favored for $(E_a - E_{S-H}) < 0$ if the following inequality is maintained;

$$(E_a - E_{S-H}) + (E_{C-C} - E_{C-H}) > 0. \quad (8)$$

In other words if equation (8) holds true, 2-D growth is expected on any lattice matched substrate to which the diamond can bond when the film is hydrogen terminated. The hydrogen termination therefore appears to lower the surface energy of the diamond nuclei enough to promote layered growth. If one continues to increase the size of the cluster ($i \gg 6$), calculations show that layered growth should continue to dominate. A similar formulation for growth on a (111) surface yields a similar result where;

$$E_{6(2-D)} = 6(E_a - E_{S-H}) + 18E_{C-H}, \quad (9)$$

$$\text{and } E_{6(3-D)} = 4(E_a - E_{S-H}) + 6E_{C-C} + 8E_{C-H} . \quad (10)$$

Obtaining a triply hydrided (111) diamond surface such as this in reality may be difficult, though, due to steric hindrances between hydrogens. Even though the data above suggest strongly that layered growth should be favored under the given conditions, in reality, it is not observed except in homoepitaxial growth. The possible explanations for this are discussed below.

The above example is that of an ideal experiment. The following non-idealities may enhance 3-D growth and thus explain why layered growth has not yet been obtained on non-diamond substrates. First, it was assumed that the interfacial strain and/or misfit relaxation energy was negligible. Strain and misfit dislocations at the interface will increase the interfacial energy, and therefore decrease the binding energy of the cluster. This implies that a new atom being added to the cluster would prefer to go to second or higher levels and thereby avoid the added interfacial strain associated with an atom addition onto the surface level. By making it more energetically favorable for atoms to join to the upper layers of the cluster, 3-D growth becomes more likely.

The second assumption, that all surface carbon bonds are both tetrahedrally coordinated and hydrogen terminated, may also be in error thus resulting in a lower binding energy for the 2-D cluster. The fact that the C-H bond is stronger than the C-C bond effectively stabilizes the 2-D configuration by maximizing the number of C-H bonds in the cluster. Tsuno and coworkers have shown, via STM analysis, that the surface of homoepitaxial diamond films grown at higher surface temperatures (≥ 800 °C) are in a mono-hydride configuration^{14, 15}. Films grown at 600 °C, however, appeared to be in an

ideal di-hydride arrangement. In the case of a mono-hydride diamond cluster, the binding energy of a 2-D cluster would be greatly reduced due to the removal of half of the C-H bonds. If one assumes that the now unsatisfied bonds on the mono-hydride surface reconstruct and form distorted σ -bonds (or dimer chains) with neighboring carbon atoms as suggested by Tsuno et al.^{14, 15} and Hamza et al.¹⁶ (figure 4a & b), then the binding energy for this configuration of a 6-atom cluster may be calculated as follows;

$$E_6 = 12(E_a - E_{S-H}) + 6E_{C-H} + 3E_{\sigma} \quad (2-D, \text{ mono-hydride}), \quad (11)$$

and $E_6 = 8(E_a - E_{S-H}) + 6E_{C-H} + 4E_{C-C} + E_{\sigma} \quad (3-D, \text{ mono-hydride}). \quad (12)$

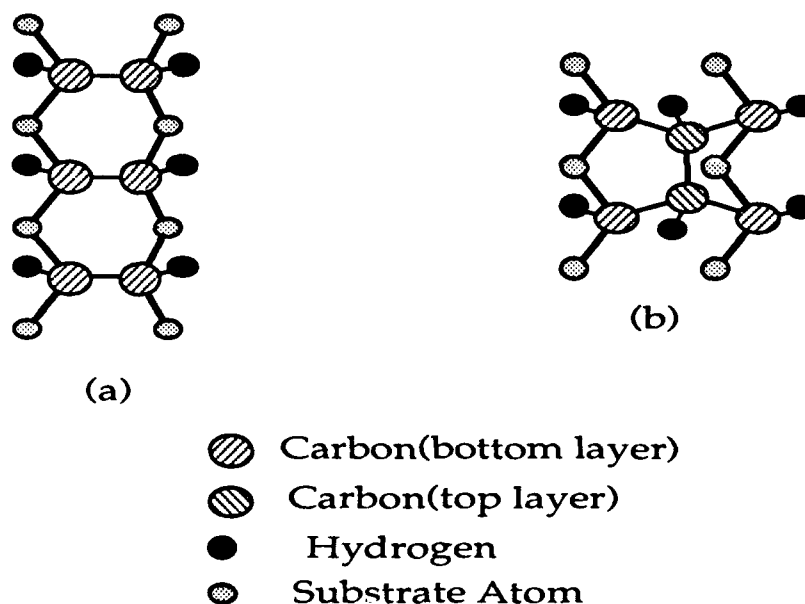


Figure 4. Reconstructed mono-hydride configuration of a six atom cluster in (a) 2-D and (b) 3-D configurations.

It is evident from figures 4-a & b that the σ -bonds associated with the reconstruction are slightly distorted. This implies that E_{σ} will be less than E_{C-C} because of this distortion. So if one assumes that $E_{\sigma} < 85 \text{ kcal/mol}$ and

substitutes this and the other bond energies into the above equations the resulting decrease in cluster binding energies due to the de-hydrogenation and corresponding reconstruction will be;

≥ 345 kcal/mol for the 2-D cluster,

and ≥ 115 kcal/mol for the 3-D cluster.

From these calculations, it is clear that when de-hydrogenation occurs, the binding energy of a 2-D cluster is decreased by significantly more than that of a 3-D cluster thus suggesting that the mono-hydride terminated case will favor 3-D growth more so than the di-hydride case. It is impossible to determine the exact cluster binding energies without proper knowledge of the interfacial quantity ($E_a - E_{S-H}$), however based on the above equations for a mono-hydride surface, 3-D growth will be favored if $(E_a - E_{S-H}) \leq 60$ kcal/mol. Thus suggesting that island growth is highly favored under growth conditions where the diamond surface is only mono-hydrided. Since the di-hydride case is more promising for potential 2-D growth, the low temperature homoepitaxial experiments performed by Tsuno et al.^{14, 15}, in which di-hydride surfaces were observed on films grown at 600 °C, suggest that layered growth should be more favored at lower temperatures assuming surface mobilities are kept sufficiently high.

By using an atomistic approach it was possible to determine the most stable growth mode for diamond deposited by chemical vapor deposition by maximizing the binding energy for a cluster of a given size. During typical CVD conditions, it was found that the diamond surface free energy may be greatly reduced by full hydrogenation of the diamond surface, thus improving the chances for 2-D growth. However, interfacial strain, misfit energy, and incomplete hydrogenation during deposition are believed to

create strong driving forces towards 3-D growth by increasing both the interfacial and surface free energy and thus decreasing the binding energy of a 2-D cluster. These are the most probable explanations for why 2-D growth on non-diamond substrates has not yet been achieved. By obtaining near complete hydrogenation of the diamond surface during growth, possibly through lower deposition temperatures, as well as decreasing the interfacial energy, the chances for layered growth of diamond are expected to be improved.

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II. Schottky Barrier Height and Negative Electron Affinity of Titanium on (111) Diamond *

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Abstract

Titanium was deposited on a natural type IIb diamond surface with a (111) orientation. The titanium-diamond interface was studied with UV photo emission spectroscopy, using 21.2eV light. Prior to deposition the diamond was chemically cleaned, and a sharp (0.5eV FWHM) peak was observed at the position of the conduction band, indicating a negative electron affinity surface. After a subsequent argon plasma clean this peak disappeared, while the spectrum shifted 0.5 eV towards higher energies. Upon sub-monolayer titanium deposition the spectrum shifted 0.5 eV down, while the negative electron affinity peak reappeared. Further titanium depositions caused this titanium induced negative electron affinity peak to be attenuated, indicating that the emission originated from the interface. By determining the relative positions of the diamond valence band edge and the titanium Fermi level, the Schottky barrier height of titanium on diamond (111) was measured and found to be 1.0 ± 0.2 eV. A model for the observed titanium induced negative electron affinity is proposed, based on the Schottky barrier height of titanium on diamond, and the work function of titanium.

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I Introduction

Continuing advances in the CVD growth of doped diamond thin films offer the possibility of diamond semiconductor devices. As a result, diamond-metal interfaces and their properties as electrical contacts have received recent attention, and both ohmic and rectifying contacts to both natural diamond and CVD grown diamond have been reported [1-6]. To fully understand the rectifying contact it is necessary to determine the Schottky barrier characteristics. Current-voltage measurements of the rectifying contacts typically show a high ideality factor and cannot be used for an accurate Schottky barrier determination [7]. Photoemission, however, has been successfully used to measure the Schottky barrier height of Al and Au on diamond [8].

Previous current-voltage measurements have demonstrated that titanium, deposited at room temperatures, forms a rectifying contact to p-type diamond. Upon annealing to $>400^{\circ}\text{C}$ the current-voltage characteristics become ohmic.[6]. It has been suggested that this transformation is due to the formation of a titanium carbide [2]. In a previous study we have shown that titanium carbide formation does indeed occur in the same temperature range in which titanium contacts are found to change from rectifying to ohmic [9]. In this paper we report a UV photoemission study of thin titanium layers deposited on a diamond (111) surface. From the measurements the Schottky barrier height of titanium on p-type diamond (111) is determined.

It has been shown that the onset of photoemission from the chemically cleaned diamond (111) surface occurs at bandgap energy radiation, indicating a negative electron affinity surface [10]. Photoemission spectra of negative electron affinity surfaces generally show a sharp peak at the low energy end of the spectrum. This peak is attributed to emission of electrons that are quasi-thermalized to the bottom of the conduction band of the semiconductor [11], and it has also been observed on chemically cleaned diamond (111) surfaces [12, 13]. There is evidence that this negative electron affinity effect on these diamond (111) surfaces is related to a hydrogen termination [14,15]. In our experiment the diamond (111) surface was cleaned in an argon plasma and the negative electron affinity peak disappeared. We have found that in the photoemission spectra of the titanium covered diamond a similar sharp peak appeared, suggesting a titanium

induced negative electron affinity. A model, based on the observed Schottky barrier height and the work function of titanium, is proposed to explain this effect.

II Experimental

The diamond substrate used in this study was a $3 \times 3 \times 0.5 \text{ mm}^3$ IIb (p-type) natural diamond with a (111) surface orientation and a $1.6 \text{ } \Omega\text{-cm}$ resistivity. The substrate was polished with $0.25 \text{ } \mu\text{m}$ diamond grit and cleaned in a chromic acid solution before loading. Once in vacuum the diamond was further cleaned in a remote, RF induced, argon plasma, while the sample was heated to 350°C . Titanium was evaporated by resistively heating a titanium filament, and spectra were taken at increasing thicknesses. The thickness of the deposited films was monitored with a crystal rate monitor. The photoemission was excited with 21.21 eV He(I) radiation, and the data presented here was obtained with an angle resolved ultraviolet photoemission spectroscopy (ARUPS) system, which included a 50 mm radius hemispherical analyzer with an angular resolution of 2° . A bias voltage of 0.5V to 0.75 V was applied to the sample during the measurements to overcome the work function of the analyzer. The bias voltage allowed the collection of the low energy electrons, which show the negative electron affinity effect.

III Results and Discussion

A. Schottky Barrier Height Measurement

The Schottky barrier height of a metal on a p-type semiconductor is defined as the difference between the valence band edge of the semiconductor and the Fermi level of the metal at the interface. Photoemission spectroscopy is commonly used to determine Schottky barrier heights by measuring energy shifts of core levels as a function of metal coverage. These measurements then need to be corrected for chemical shifts and photo voltaic effects. The latter effect can be prominent in low temperature situations and for wide bandgap materials such as diamond [16].

Since photo voltaic effects cause a uniform shift in the spectra, however, the relative positions of the Fermi level and the valence band edge remain unchanged. Therefore, by

determining the valence band edge and the Fermi level position from one spectrum in which both can be located, the Schottky barrier height can be directly determined and no corrections need to be made for photo voltaic effects.

The determination of the Schottky barrier height from UV photoemission, relies on the fact that features of both the metal and the underlying semiconductor are visible in one spectrum. Experiments are therefore limited to thin metal films with a thickness on the order of the mean free path of the electrons ($\sim 5\text{\AA}$). Even at metal coverages less than the mean free path, it is not always possible to determine the position of the valence band edge accurately from the spectra, since emission from the metal d-band obscures the relatively weak semiconductor valence band emission. In those cases, a more accurate determination can be made, by relating the valence band edge to a feature in the diamond spectra that does remain visible at higher metal coverages. It is in this analysis assumed that shifts in the diamond features are uniform so that relative positions are maintained. In our experiment the valence band edge was determined from the spectrum of the argon plasma cleaned diamond and related to a stronger emission feature at lower energies, labeled B, in Figure 1. Although this diamond feature was attenuated upon metal coverage, it remained much more visible than the valence band edge. In order to determine the valence band edge from the position of peak B, their relative positions should not change upon titanium deposition. Since the relative positions of feature B and the valence band edge did not change after the first metal depositions in which both were visible, we do not expect this to occur at the higher metal thicknesses.

The location of the valence band edge was determined by extrapolating the spectrum to zero, as illustrated in Figure 2. The valence band edge was found to be 8.2 eV above feature B. After the first titanium deposition the diamond spectrum shifted 0.5 eV towards lower energies, indicating a change in the pinning position of the Fermi level in the gap. No Fermi level emission due to the titanium could be discerned, however, at this coverage. Upon further titanium deposition, emission from the d-bands of titanium became pronounced, and the Fermi level could be clearly discerned. The position of the valence band edge, however, became more difficult to

locate. Based on the position of feature B, no further shifts in the diamond spectrum were observed. This indicates that the Fermi level was pinned, and the Schottky barrier height established, after the first titanium deposition. The Fermi level was found to be 9.2 eV above feature B. Since the valence band edge was 8.2 eV above B this results in a Schottky barrier height for titanium on p-type diamond (111) of 1.0 ± 0.2 eV. Reported values for the Schottky barrier height of titanium on CVD grown diamond films range from $0.9(+0.5/-0.2)$ eV [9] to 1.3 eV [17].

B. Metal Induced Negative Electron Affinity

The diamond (111) surface showed a sharp peak (0.5 eV FWHM) at low energies, after chemical cleaning. This peak is labeled A in Figure 2. The position of this peak coincides with the position of the conduction band edge [18], which is indicative of a negative electron affinity surface. However, after exposure to the argon plasma this peak disappeared, while the spectrum shifted 0.5 eV towards higher energies. We attribute this peak to a hydrogen passivation of the surface which is removed by the argon plasma [14,15].

After the first titanium dose a sharp peak, similar to the one found on the chemically cleaned diamond (111) surface, develops at the low energy end of the spectrum. In the same spectrum a 0.5 eV shift towards lower energies is observed. For increasing titanium coverages the peak is attenuated, and no further shifts in the diamond features are observed. We attribute this peak to a titanium induced negative electron affinity. This would be due to a lowering of the work function by the titanium, as illustrated in Figure 3. Before the titanium deposition the Fermi level at the surface is 0.5 eV above the valence band edge. The vacuum level was determined from the low energy cutoff point of the emission, and is found to be about 5.5 eV above the valence band edge. Using a value of 5.45 eV for the bandgap of diamond we find therefore the vacuum level to be ~ 0.05 eV above the conduction band edge; electrons that are quasi-thermalized to the bottom of the conduction band are therefore unable to escape the surface. After the first sub-monolayer of titanium is deposited, the Fermi level is pinned at 1.0 eV above the valence band edge, which is the

Schottky barrier height described in the previous section. The effective work function of the surface is now determined by the work function of the titanium. Using the value of 4.33 eV for the work function of bulk titanium [19] we find that the vacuum level of the surface is now located 0.2 eV below the conduction band edge and quasi-thermalized electrons can escape, causing the sharp peak in the spectrum. The fact that this peak is due to the interface of the diamond and the titanium, can be deduced from the attenuation of the peak as a function of coverage. Note that in this model the Schottky barrier height plays an important role in determining the position of the vacuum energy level. This is different from the Schottky-Mott model where the Schottky barrier height is determined by aligning the vacuum levels of the metal and the semiconductor.

IV Conclusions

From the UV photoemission spectroscopy measurements presented here, a Schottky barrier height of 1.0 ± 0.2 eV was found for the titanium-diamond (111) interface. It was found that the Schottky barrier height was established for sub-monolayer titanium coverages. Upon titanium deposition a sharp (0.5 eV FWHM) peak developed at the position of the conduction band edge. This is indicative of a negative electron affinity surface. Negative electron affinity surfaces are commonly obtained on III-V semiconductors by depositing a thin layer of a low work function material such as cesium or cesium-oxide. This study shows that it is possible to obtain a negative electron affinity on diamond (111) by depositing a sub-monolayer of a titanium, and suggests the possibility of inducing a negative electron affinity on diamond using other transition metals. A model for the observed negative electron affinity was presented, based on the Schottky barrier height of the diamond-metal interface, and the work function of the metal.

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18. The energy of valence band edge emission $E_{v'} = E_v + h\nu$, and $E_c = E_v + E_g$. The energy position of E_c is therefore $E_c = E_{v'} + E_g - h\nu$. The energy gap $E_g = 5.45$ eV and the energy of the exciting He(I) radiation $h\nu = 21.21$ eV, resulting in an energy position of the conduction edge emission 15.76 eV below the valence band emission.
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Figures

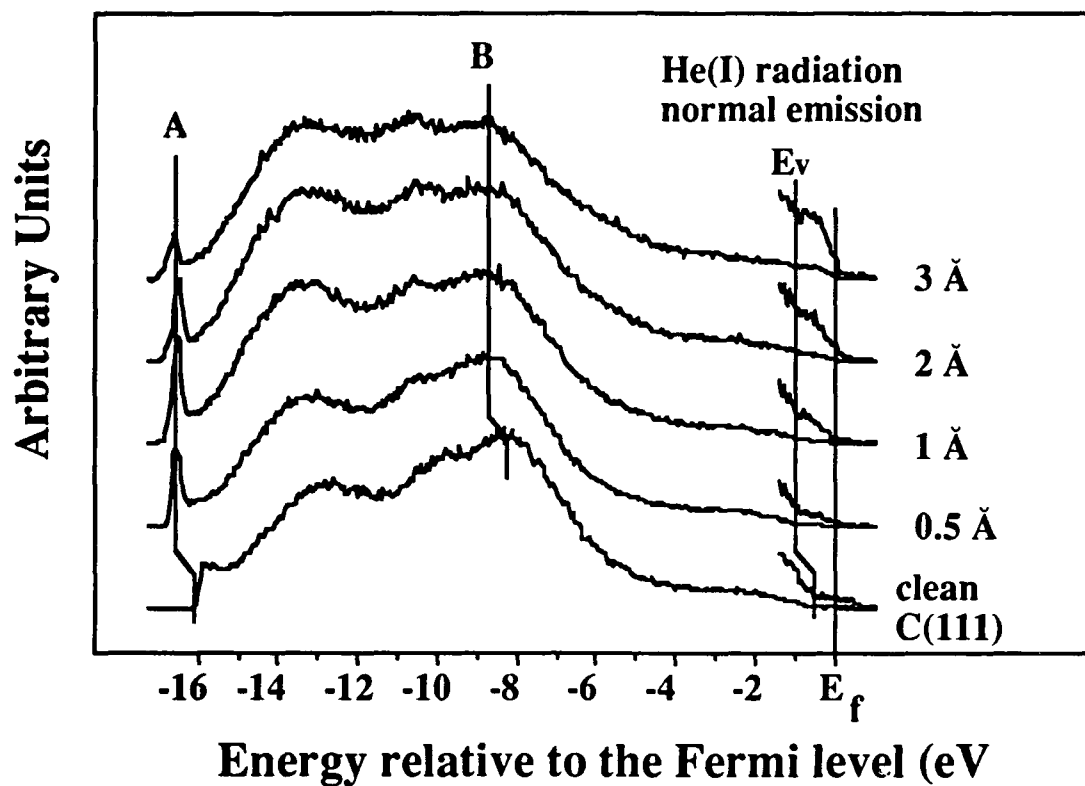


Figure 1. ARUPS spectra of titanium on diamond (111) for increasing titanium thicknesses. After the first deposition the spectrum moves 0.5 eV toward lower energies and a sharp peak (A), indicative of a negative electron affinity, develops at the low energy cutoff. For increasing titanium thicknesses a Fermi level edge (E_f) develops, while at the same time the position of the valence band edge (E_v) becomes harder to locate. Since the position of E_v relative to peak B is known from the clean surface E_v can be determined indirectly from the position of peak B for higher coverages. The Schottky barrier height is the energy difference between E_v and E_f

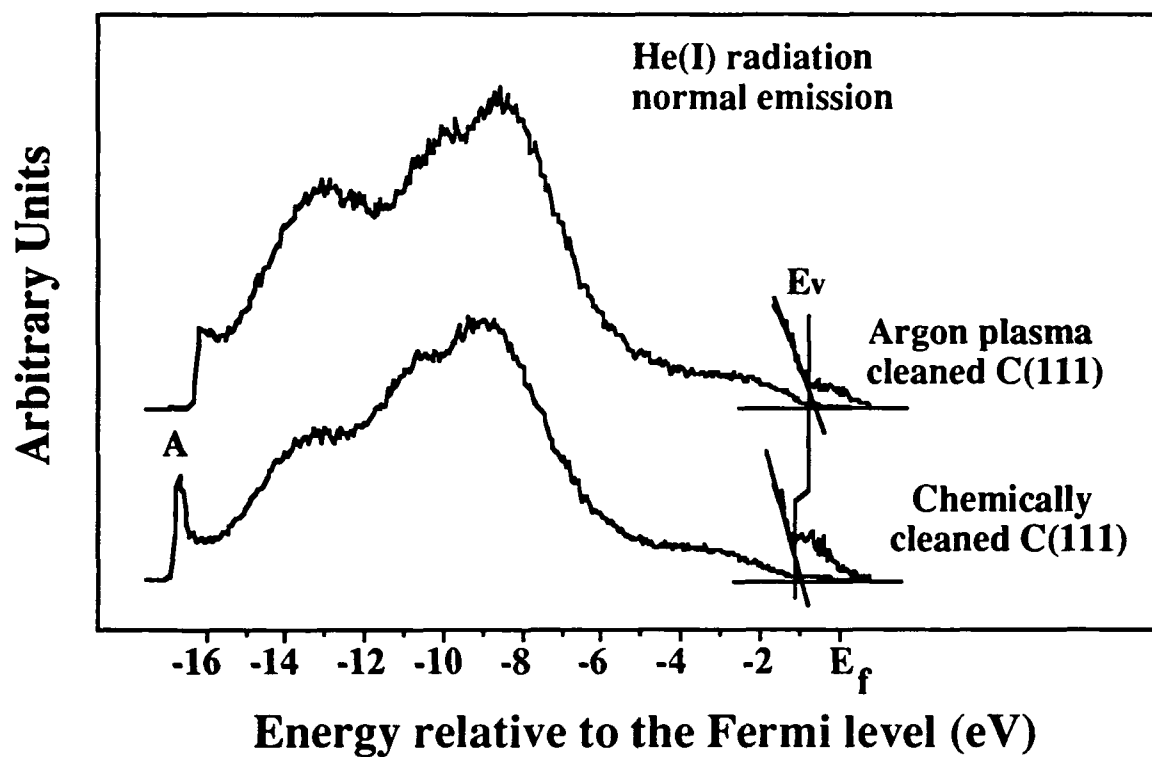


Figure 2. ARUPS spectra of diamond (111) before and after argon plasma cleaning. The spectrum shifts by 0.5 eV towards higher energies while the negative electron affinity peak (A) is significantly reduced after the argon plasma cleaning. The latter effect is attributed to the removal of hydrogen from the surface. The valence band edge is determined by linearly extrapolating the onset of emission down to zero.

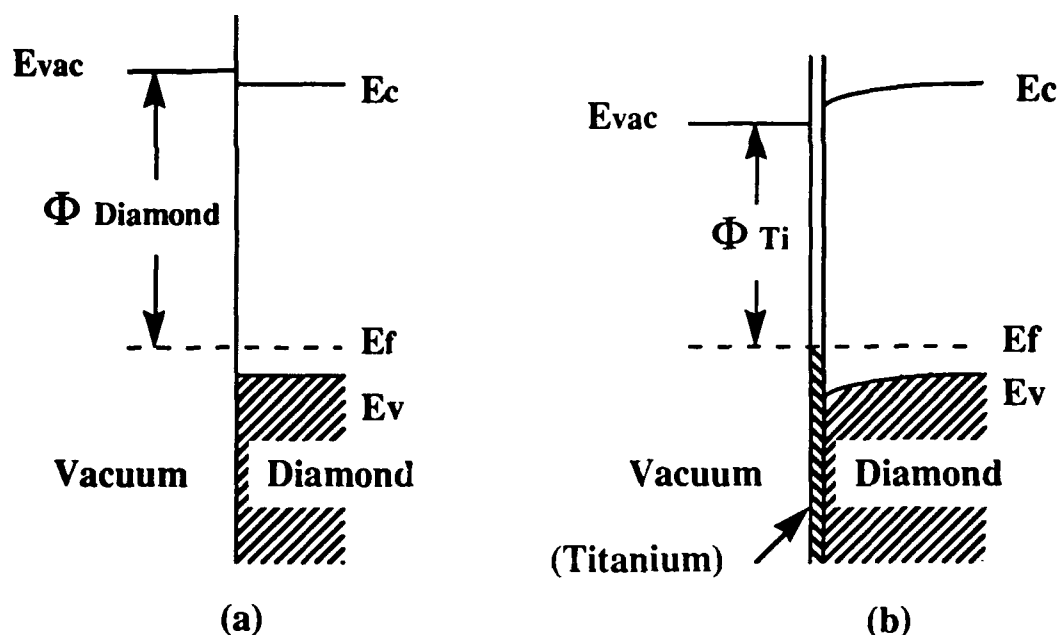


Figure 3. Model for the titanium induced negative electron affinity of diamond. In (a) the argon plasma cleaned surface has a work function large enough to bring the vacuum level slightly above the conduction band of the diamond, whereas the work function of the titanium in (b) lowers the effective work function of the surface enough to put the conduction band minimum above the vacuum level. Notice the effect of the Schottky barrier height, a higher Schottky barrier could bring the vacuum level below the conduction band, resulting in a positive electron affinity.

III. Modeling of Microwave MESFET Electronic Devices Fabricated from Semiconducting Diamond Thin Films

Abstract

The microwave performance of p-type diamond MESFETs is under investigation. A detailed, theoretical model for the device that includes all known physical phenomena of significance is being developed. The model is based upon a full two-dimensional formulation of the appropriate semiconductor device equations. The equations are solved using numerical simulation procedures. Of particular interest in the model formulation is the development of a complete and accurate description of the semiconductor surface between the gate and drain electrodes. Accurate inclusion of the surface effects requires the development of models for both surface conduction and channel breakdown. The initial formulation of the model is complete and some test simulations of an ultra short gate length MESFET have been performed.

A. Introduction

The operation of p-type diamond MESFET's is under investigation. It has been observed that these devices are limited in possible applied drain bias by a gate leakage problem. The gate leakage prevents the application of sufficient drain bias to saturate the current flow in the channel. The inability to achieve full channel current saturation limits the gain that can be achieved with the device.

Generally, device breakdown is assumed to be due to semiconductor material breakdown. This is certainly true for well designed diodes. However, for field-effect transistors it is possible to have device breakdown occur that is dominated by surface effects. This can occur essentially in parallel with material breakdown. If the surface phenomenon occurs at a lower potential, the surface breakdown mechanism will dominate and can prevent the material from developing its full potential. We believe that this, in fact, occurs and limits the performance so far reported for diamond field-effect transistors.

We have formulated a breakdown mechanism for MESFET's that explains the gate leakage and breakdown phenomena observed in experiments. The gate leakage and breakdown mechanisms are based upon electron tunneling from the gate metal to the surface of the semiconductor between the gate and drain electrodes. The electrons accumulate on the semiconductor surface, where they are free to flow to the drain contact, thereby creating the gate leakage. This mechanism occurs at lower drain potential than the avalanche breakdown mechanism.

A model that can accurately predict this behavior has not been previously reported and is under development on this program. The model is based upon finite difference numerical

solution techniques. Accurate description of the gate tunnel leakage and surface conduction is the primary goal of this model. Once the model is complete, it will serve as the basis for investigations directed towards limiting the surface leakage so that channel current saturation can be achieved.

B. Investigation Procedure

The surface of the MESFET is a complex physical system where a periodic lattice of diamond atoms terminate into either free space or another material such as gate metals, other semiconductors, or passivating (i.e., insulating) materials. Typical numerical or analytic models for MESFET's neglect surface effects and only include the first order bulk transport properties in the formulation. MESFET models vary in complexity and level of sophistication, but consistent with most MESFET models is a lack of proper characterization and modelling of the surface. First order physics describes MESFET operation in terms of particle conservation equations and particle flux equations which have field, diffusion, and sometimes thermal components. Poisson's equation completes the set by relating the particle and fixed charges within the device to potential. This fluid model of transport is an incomplete description and must be modified to take into account electric field or energy dependent carrier mobilities, generation and recombination mechanisms, thermal effects, and other transport mechanisms such as tunneling and trap-to-trap hopping. Many of these effects have been included in previous models, but typically only one effect is investigated at a time. Thus, although many of the previous phenomena have been examined before in terms of the effects on MESFET RF or dc performance, combining all these phenomena in one complete model where the effects can occur simultaneously has not been reported. Such a model is necessary to adequately describe the performance of realistic devices and this model is the subject of the modeling effort.

C. Results

The NCSU MESFET model under development incorporates all dominant physical effects simultaneously. Effects such as electric field or energy dependent carrier mobilities, generation and recombination mechanisms, and thermal effects are being included in the formulation. A detailed description of the semiconductor surface is under development. The semiconductor surface is reactive due to unsatisfied bonds at the surface, which can adsorb contaminants. Any foreign species on the surface, combined with bond realignment and surface relaxation, causes a high density of surface trap formations. One method thought to prevent or reduce the formation of the traps is to grow a surface material on the channel semiconductor that will satisfy the bonding requirements and continue the semiconductor lattice into the insulating surface layer. A model that describes the surface physics and especially the conduction phenomena is under development.

The physical MESFET model is developed from standard semiconductor physics describing conservation of charge, flux, and forces. The model is a full two-dimensional simulation. The model has a user defined grid generator. The user customizes the grid density within the MESFET. The grid generator then wraps a grid around the internal boundaries of the MESFET and conforms to the recessed or stepped regions and contacts. Application of bias and driving potentials results in terminal currents, thereby allowing device performance to be simulated. The two-dimensional formulation allows detailed investigations of device physics to be investigated.

An initial formulation of the model is complete. The I-V characteristics determined by the model for an ultra small MESFET operating under high frequency are shown in Fig. 1. The MESFET has a gate length of $0.1\text{ }\mu\text{m}$ and the interelectrode spacing is also $0.1\text{ }\mu\text{m}$. The drain voltage was ramped from zero to 20 v in 150 psec for a fixed gate voltage. To generate the I-V data the gate voltage was varied from zero to -6 v. As indicated in Fig. 1, the device cannot be pinched off, which is typical of MESFET's with small gate lengths. The breakdown characteristics shown in Fig. 1 were calculated assuming avalanche ionization in the conducting channel. Inclusion of the avalanche mechanism is important to the model development, but is not sufficient to completely describe the breakdown phenomenon. The surface breakdown mechanism will be added in the near future.

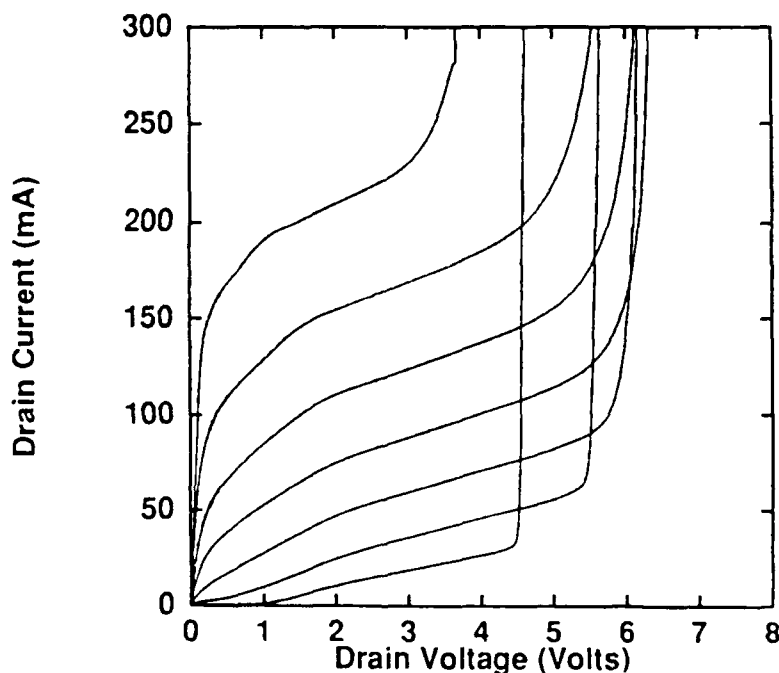


Fig. 1. Transient I-V characteristics for a short gate MESFET, including avalanche breakdown.

The detailed physical operation of the device can be investigated by plotting various parameters of interest. For example, the internal potential, hole charge density, electron charge density, and electric field are shown as a function of position within the device in Figs. 2-5. These figures reveal the importance of holes in the breakdown process as the gate voltage decreases towards zero. This result is in agreement with recent simulations of breakdown in GaAs MESFET's.

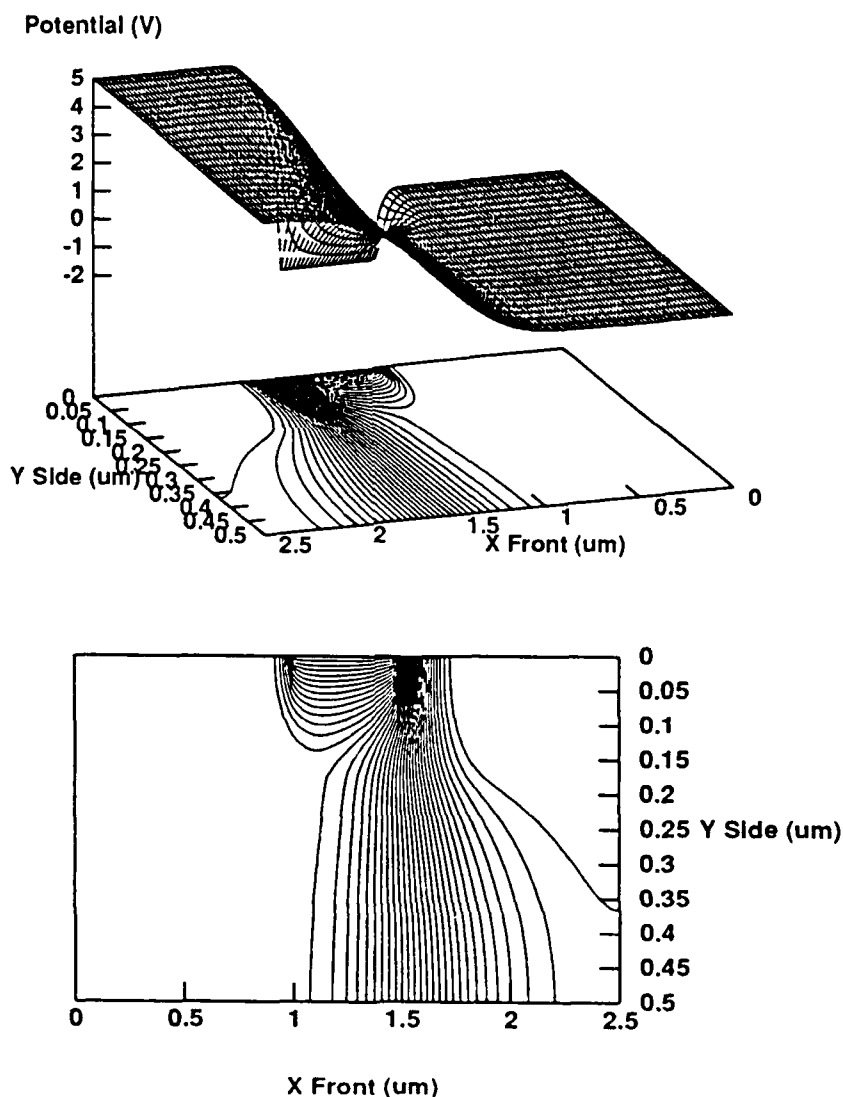


Fig. 2. Electric field contours within a short gate MESFET.

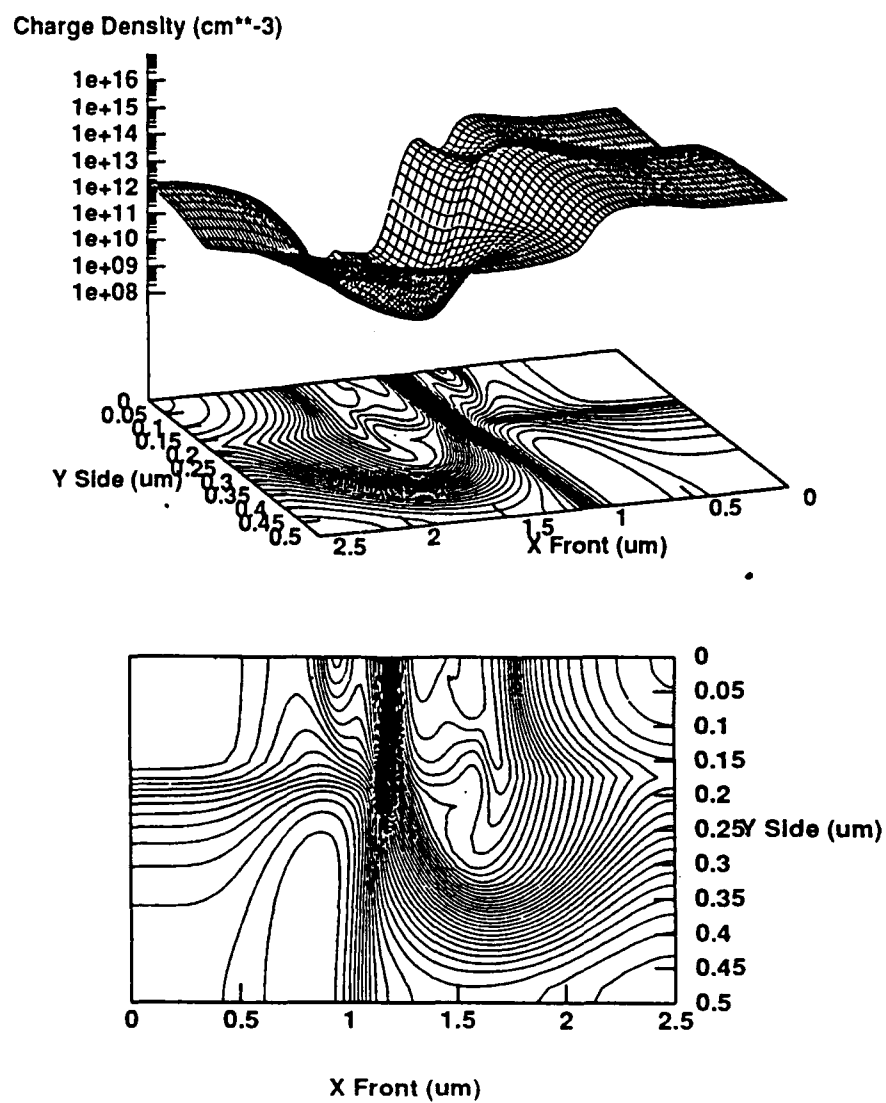


Fig. 3. Electron charge density contours within a short gate MESFET.

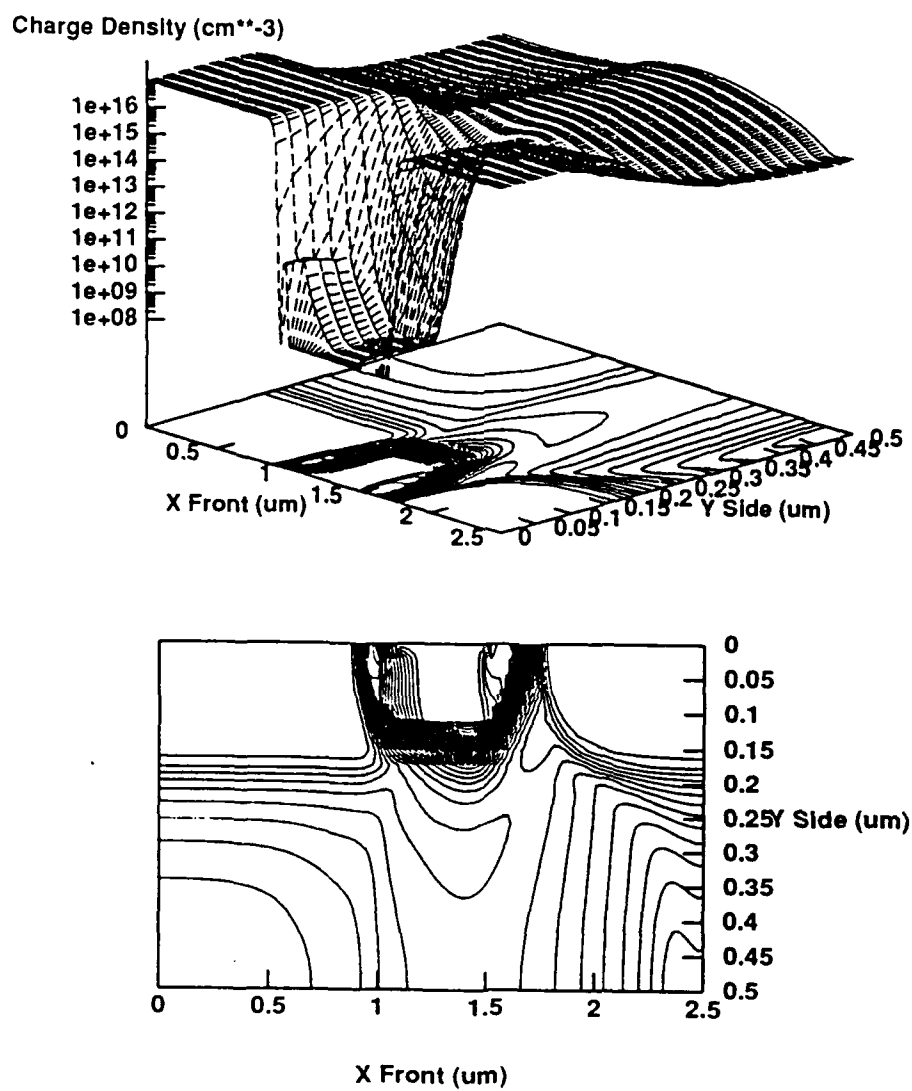


Fig. 4. Hole charge density contours within a short gate MESFET.

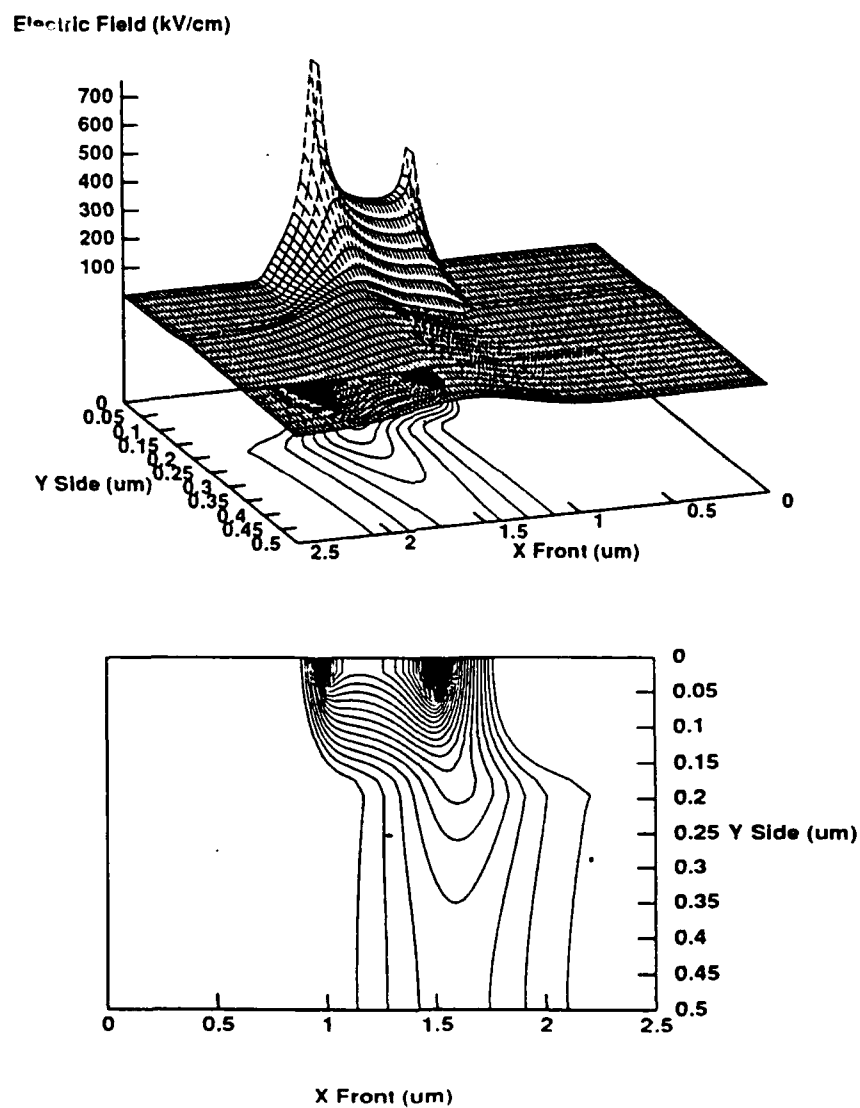


Fig. 5. Internal potential contours within a short gate MESFET.

D. Conclusions

The operation of a p-type diamond MESFET is under investigation. The investigation is directed towards the development of a physical model for the device. The model is being formulated to include all physical phenomena known to be of significance to device operation. Of particular interest is an accurate simulation of gate breakdown, including both gate tunneling and avalanche breakdown. A comprehensive model that includes the desired features has not been reported.

An initial formulation for the model has been completed and some test simulations performed. The initial investigations successfully predict the dc operation of an ultra short gate length MESFET operating under pulse bias conditions.

E. Future Research Plans and Goals

The model will be modified to include more phenomena. In particular, the surface algorithms will be developed and introduced into the simulator. The initial formulation will concentrate upon an electron hopping mechanism in which charge conduction occurs by trap-to-trap transfer. Continuum mechanics can be applied to particles in the surface energy bands due to the high density of states in these bands. The stochastic transfer of particles to adjacent states appears at the macroscopic level to be continuous, with the effect of the lattice being combined into the effective mass of the particle. Therefore, the particle behaves as if it has an effective mass which is related to the curvature of the appropriate energy band. Charge packets propagate and disperse in a Gaussian shape. The packet moves in time if there is an applied field, and simultaneously disperses due to mutual repulsion of the carriers in the packet. Transport in a disordered medium is markedly different from an ordered semiconductor. The full nature of this will be investigated.