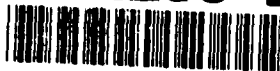


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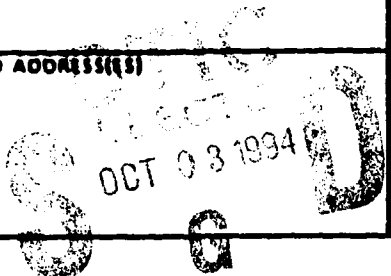
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1.0 Purpose of Research

The purpose of the research was to study the use of BeO and c-BN substrates for the pseudomorphic stabiliztion of diamond, and hence to their use as substrates for the epitaxial growth of diamond by chemical vapor deposition.

2.0 Overall Approach

A combined theoretical-experimental approach was used to explore the nature of diamond interfaces with BeO and c-BN. First principles electronic structure calculations were used to determine the adhesion, band-offsets, and other properties of the interfaces. Experimentally, we deposited diamond on BeO and c-BN and examined the interface with high resolution electron microscopy. A summary of the work done under the grant is given here. Details of the studies are given in a series of published papers that are listed in Section 6.0 of this report.

3.0 Rationale for Use of BeO

Heteroepitaxy of diamond continues to be one of the most challenging problems in diamond thin film technology. This is particularly true for the growth of films for electronic applications. Recently, heteroepitaxy of diamond was realized on single crystal c-BN substrates. The problem with c-BN, however, is that it has a competing layered hexagonal structure (analogous to graphite) that is the stable form at low pressures. The production of c-BN single crystals is thus difficult, perhaps as difficult as that of diamond itself.

It is generally believed that adhesion is an important factor in epitaxial growth. A simple picture of epitaxial growth based on energetic considerations suggests that two-dimensional layer growth is favored if the adhesion between film and substrate is larger than the adhesion of the film to itself (i.e., the free surface energy of the film). The fact that diamond has a very high surface energy may thus be one of the key difficulties in its epitaxial growth. It is plausible then that the key to the successful use of c-BN as a substrate for heteroepitaxy of diamond is the similarity in bonding or orbital hybridization



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Dear Sirs:

I have enclosed 12 copies of the Final Report on Grant N00014-89-J-1631 entitled, "Pseudomorphous Stabilization of Diamond on Non-diamond Substrates."

Sincerely yours,

John C. Angus
Professor of Engineering

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that, combined with the close lattice match, leads to a strong adhesion between diamond and c-BN.

We qualify the above remarks by cautioning that besides the energetic considerations, many factors, including substrate perfection, diffusion of growth species on the surface, and nucleation issues, may play important roles in the complex process of epitaxial growth. These are at present not well understood even for very well studied systems. The similarity in orbital hybridization between c-BN and diamond possibly plays a role even in these other considerations. Though the adhesion issue is only one of the factors involved, it is certainly worthwhile to consider. Furthermore, it is one that is addressable by theoretical calculations.

In this work, we consider the next best lattice-matched material to diamond with a tetrahedral coordination beyond c-BN: BeO. Although BeO is usually considered a typical ionic material, its structure is closely related to that of most semiconductors. It is the II-VI compound of the "carbon row" of the periodic table. After c-BN, the III-V semiconductor of this row, it thus appears to be the next best candidate for epitaxial growth of diamond. Another obvious candidate is SiC, the most closely related compound between the carbon row and the next row of the periodic table. We note, however, that SiC already has a 20% mismatch with the diamond lattice constant.

BeO is a wide band gap insulating material with the wurtzite structure. The latter differs from the zinc blende structure only in the stacking sequence of its double layers of cations and anions lying in the basal plane $\{0001\}$ as compared to that for the $\{111\}$ planes of zinc blende. The nearest neighbor positions are the same in the zinc blende and wurtzite structures. Its bond length differs from that of diamond by 7%. Epitaxial growth of semiconductors with similar mismatch is not uncommon: e.g., Si/Ge has a lattice mismatch of 4%, InAs/GaAs 8%, and SiC/Si 20%! Furthermore, the tetrahedrally coordinated structure of BeO is the stable form at low pressure. In particular, no competing layered hexagonal structure is known to exist in this material. In fact, it was shown theoretically that such a structure would not be stable.

4.0 Summary of Interface Calculations

4.1 Computational Methods

We use first-principles electronic structure calculations. Our computations thus yield results, not only on the energetics, but also on the electronic structure, which forms the basis for an understanding of the nature of the bonding. In particular, we discuss and band offset and the local densities of states near the interface.

The density functional method is used in the local density approximation (LDA) using the von Barth-Hedin parametrization of the exchange-correlation energy. This method reduces the many-body problem of strongly interacting electrons to a one-electron problem of independent electrons in an effective potential and provides a formalism for computing the total energy in the ground state as a function of the electron density. The density results from populating the one-electron levels according to Fermi-Dirac statistics. The band-structure method used to solve the effective one-electron Schrodinger equation is the linear muffin-tin orbital (LMTO) method in the atomic sphere approximation (ASA). So-called empty spheres are inserted in the tetrahedral interstices. This procedure removes the limitations of the ASA to close-packed structures, since the resulting packing of spheres is bcc. This procedure has been widely tested on semiconductors and is found to be quite accurate, at least for nondistorted structures. For the moderate distortions due to strain, the ASA is still expected to be fairly accurate. This is because the overlap of the spheres is not significantly changed from that in the unstrained case. Furthermore, we are not directly interested in the small energy differences due to the strain but rather in the bond energies.

We modeled the {110} interface between zincblende BeO and diamond because this is the simplest interface exhibiting compensated Be-C and O-C bonds. The real interface structure at wurtzite BeO/diamond interfaces is not known but is expected to exhibit this compensation for charge neutrality reasons.

The interface is modeled by means of the supercell approach. That is, an artificial system is considered in which the interface is repeated periodically. We used a

superlattice of five layers of each material. This size has been found to be adequate in previous calculations for diamond/c-BN to obtain bulk-like properties for the central layers of each half of the cell and to represent isolated interfaces. Since the {110} plane is a symmetry plane of both crystal structures, the two interfaces per cell are equivalent. Thus, the energy cost of the boundary can be obtained directly by subtraction of the energy of the appropriate number of layers of the bulk systems from the energy of the supercell. In this case, the energy of diamond strained biaxially in the {110} plane is used for the bulk since we do not wish to include the strain energy of the diamond film, which depends on the film thickness, in the definition of the interface energy. Since small energy differences are computed as a difference between two large energies, care must be taken in adequately converging the Brillouin zone summations. The best results are ensured by taking equivalent sets of k-points for the bulk or by repeating the bulk calculations in a supercell geometry equivalent to the interface system.

The adhesion energy normalized per interface unit area of the separated surfaces is given by

$$2W_a = \gamma_s(A) + \gamma_s(B) - \gamma_i(AB),$$

where γ_s is the surface energy and γ_i the interface energy. The factor two is introduced by normalizing with respect to the area of the separated surfaces rather than to the area of the interface after the two have been joined. This has the consequence that the adhesion energy for a solid to itself equals its surface energy. In principle, one could calculate the surface energies by a supercell approach, similar to the one used for the interface. The vacuum region separating the material parts of the supercell would be represented by empty spheres. However, the potential and charge density near a free surface deviate too strongly from spherical symmetry to be described within the ASA. On the other hand, a simple estimate of the surface energy can be obtained from a bond breaking model. In order to produce a {110} surface one needs to break exactly one bond and this corresponds to a quarter of the cohesive energy per bulk unit cell (i.e., per pair of atoms).

Of course, this gives only a rather crude estimate, but it is sufficiently accurate for our present purpose. Note that here we are mainly interested in a qualitative discussion of the nature of the bonding and in comparing BeO to c-BN as a substrate for diamond growth.

4.2 Results of Interface Calculations

(i) The bonding with diamond is better for c-BN than for BeO. On the other hand, c-BN is not readily available because of the competing layered hexagonal phase, which is similar in structure to graphite. Also, the band-offset is found to be of type II, with the conduction band of c-BN below that of diamond.

(ii) BeO has the wurtzite structure, which is tetrahedrally bonded as is diamond. We find that the 7% lattice mismatch and the differences between the wurtzite and diamond layer stacking should not be a major problem for the adhesion with diamond. The resulting strain effects in the diamond film were investigated. Our calculations indicate the presence of strong electronic bonds between C in diamond and Be and O atoms in BeO. Their spectral signatures in the densities of states were identified. Furthermore, our calculation indicates that the heterojunction band-offset is of type I. That is, the large bandgap (of BeO) encloses the smaller gap (of diamond). The type I offset is desirable for diamond-semiconductor/BeO-insulator structures. We note that the valence band offset is very large (of order 3 eV), which is interesting for device applications with p-type diamond.

(iii) Complementary to the work on BeO and c-BN, we have also studied the bonding between diamond and Cu along the {111} interface. Because of the different types of bonding in these materials, in particular the difficulty of the Cu3d orbitals to form strong bonds with C dangling bonds, and the lower surface energy of Cu, we find a much weaker adhesion in this case. The hole Schottky barrier was found to be nearly zero for an ideal interface with Cu in on-top-positions on the unreconstructed C {111} surface. This is due to pinning of the Fermi energy by an interface state close to the valence band maximum.

(iv) In connection with c-BN/diamond interfaces, we have investigated the properties of mixed crystals of diamond and c-BN. The latter are found to be thermodynamically unstable towards phase separation up to the melting temperature. Since phase separation requires large mass transport, it may, however, be inhibited, and metastable growth of these mixed crystals is thus conceivable. The remarkable property of these mixed crystals, is that up to 75% of c-BN concentration, the alloys have band gaps which are lower than that of diamond. This behavior is related to the fact that the valence band maximum in these materials is C-like and the conduction band minimum is BN-like, which in turn is related to the unusual type-II line-up mentioned above.

(v) We also studied BeCN_2 , a hypothetical material that was predicted by our calculations to have a 3% mismatch with diamond and which could thus form an interesting buffer layer between BeO and diamond. Related materials BeSiN_2 , MgCN_2 and MgSiN_2 were also studied.

5.0 Summary of Experimental Program

5.1 Deposition Methods

Hot-filament-assisted chemical-vapor deposition (HFCVD) is one of the most popular methods to grow diamond because of its simplicity, low cost, and ease of scaling up to large surfaces. However, metal contamination from the filament has been detected within the deposited film and in the interfacial layers. Much of this contamination comes from the initial heating up of the filament at the beginning of the deposition, perhaps from volatile metal oxides such as WO_x . To reduce contamination, we use a movable molybdenum shutter that can be placed between the filament and the substrate during start-up. Secondary-ion-mass spectroscopy (SIMS) was used to detect W contamination within a continuous diamond film grown on a scratched silicon wafer. No W contamination was detected either in the bulk of the film or at the interface between the silicon substrate and the film.

Prior to start-up, the molybdenum shutter was placed between the filaments and substrate. A flow of 100 sccm of H_2 at 20 Torr was started and the temperature of four filaments connected in series was raised to approximately $2000^\circ C$. The temperature of the substrate holder during this procedure was approximately $500^\circ C$. Since the shutter was between the filaments and the substrate, the substrate surface was exposed primarily to molecular hydrogen, which cleans the surface of nitrogen, water, hydrocarbons, and other atmospheric contamination adsorbed by the surface. After 10 min a flow of 0.5 sccm of CH_4 was started. The shutter was removed 5 min later and the distance between the substrate holder and the filaments reduced from 22 to 5 mm. The sample temperature was estimated by a thermocouple at one side of, and at the same level as, the sample. The measured temperature was $850^\circ C$. The substrate holder was rotated at $\frac{1}{3}$ rpm to ensure deposition uniformity.

5.2 Electron Microscopy

Single crystals of $\langle 0001 \rangle$ and $\langle 11\bar{2}0 \rangle$ -oriented BeO were provided by Brush Wellman, Inc. After verification of their orientation by x-ray Laue reflection, the samples were cut into pieces convenient for plan-view and cross-sectional transmission electron microscopy (TEM).

The single-crystal $\langle 0001 \rangle$ -oriented sample, was cut into small pieces ($2 \times 2 \times 2 \text{ mm}^3$). The (0001) basal plane was selected for diamond deposition instead of the $(000\bar{1})$ oxygen-terminated plane, because it is expected to be more resistant to attack in an atomic hydrogen environment. We determined the polarity of the crystal using the pyroelectric effect. The samples were polished with 4000 grade SiC paper and cleaned ultrasonically in isopropanol.

After 8 h deposition, some of these samples were used to prepare $\langle 11\bar{2}0 \rangle$ cross-sectional specimens for conventional and high-resolution TEM, using a standard technique. The (0001) surfaces, partially covered with diamond particles, were bonded facing each other with epoxy resin. The interface region where the two surfaces were

joined was mechanically thinned perpendicular to one of the $\langle 11\bar{2}0 \rangle$ direction to a thickness of 100 μm . Finally, ion milling from both sides with 5 kV Ar^+ produced a hole at the center of the specimen where the two faces were joined. The two intersections between the edge of the hole and the bonded (0001) surfaces were available for TEM observation.

In the case of the $\langle 11\bar{2}0 \rangle$ -oriented single-crystal BeO, plan-view TEM specimens were prepared prior to diamond deposition. Several $3 \times 3 \text{ mm}^2$ sections were cut from the original $\langle 11\bar{2}0 \rangle$ -oriented sample. The substrates were then mechanically thinned, dimpled, and ion milled as described above to obtain the $\langle 11\bar{2}0 \rangle$ plan-view samples. This procedure produced a sample with a $\langle 11\bar{2}0 \rangle$ surface that was sufficiently thin to permit transmission electron microscopy. At this stage the samples were introduced to the CVD reactor. The deposition conditions were the same as those used for the (0001)_{BeO} substrates; only the deposition time was shorter (4 h) in order to study the initial stages of nucleation.

After deposition, the samples were examined by conventional TEM in a Philips CM20 scanning transmission electron microscope (STEM) operated at 200 kV. High-resolution transmission electron microscopy (HRTEM) was performed in a JEOL 4000EX operated at 400 kV (point-to-point resolution of $\sim 0.18 \text{ nm}$ at Scherzer defocus). Micro-Raman spectroscopy was performed with a Dilor XY modular Raman spectrometer, which has a spatial resolution of approximately 1 μm .

5.3 Diamond Deposition on BeO

The conclusions can be summarized as follows:

(i) Diamond particles were grown heteroepitaxially on the basal plane of BeO with an epitaxial relationship $\{111\}_{\text{diamond}} \parallel \{0001\}_{\text{BeO}}$. Since large crystals of BeO can be grown, this material is a potential substrate for growing diamond single crystals, or highly oriented diamond films.

(ii) A high resolution transmission electron microscope (HRTEM) image and selected area diffraction (SAD) patterns of the diamond/BeO interface show that, under

the conditions utilized, no interfacial phases form during the deposition of diamond on BeO.

(iii) No epitaxial relationship has been found when diamond is grown on $(11\bar{2}0)_{\text{BeO}}$.

(iv) Small particles of Be_2C have been found when diamond is grown on the $(11\bar{2}0)$ prism plane of BeO.

(v) The selected area diffraction pattern of diamond grown on the $(11\bar{2}0)$ prism plane of BeO shows the presence of weak spots that can be assigned to either the forbidden $\frac{1}{3}$ (422) spots of cubic diamond, or the $10\bar{1}0$ diffraction spots of hexagonal diamond.

5.4 Diamond Deposition on c-BN

The results of this work can be summarized as follows:

(i) Thick ($\sim 10\mu\text{m}$) continuous diamond films with linear dimensions of approximately $300\mu\text{m} \times 300\mu\text{m}$ were grown on the $\{111\}_{\text{B}}$ faces of single-crystal c-BN. Cross-sectional selected area diffraction (SAD) and high resolution transmission electron microscopy (HRTEM) of the diamond/c-BN interface show that the diamond film has a parallel orientation relation with respect to the substrate.

(ii) Diamond growth on $\{111\}_{\text{B}}$ proceeds by formation and growth of isolated three-dimensional nuclei. Each island has the same orientation relationship with respect to the substrate. Thus, the continuous film resulting from the coalescence of the islands is monocrystalline.

(iii) Numerous microtwins are formed during growth of diamond on $\{111\}_{\text{B}}$ faces. Interactions of these microtwins form higher order twin boundaries.

(iv) The interface produced by HFCVD growth is atomically sharp. Under the conditions utilized, no interfacial phases form during the deposition of diamond on c-BN.

(v) The small lattice mismatch (1.4%) between diamond and c-BN is accommodated by misfit dislocations. The projected Burgers vector of one such

dislocation along the $[1\bar{1}0]$ directions was determined to be $a/4[11\bar{2}]$. Hence, it is likely that the actual Burgers vector is $a/2[01\bar{1}]$, inclined at 60° with respect to $[1\bar{1}0]$, as this is a lattice dislocation in diamond.

(vi) Evidence of epitaxial growth of diamond on $\{100\}$ faces of c-BN was obtained by SEM observations. Under the experimental conditions utilized, diamond does not grow epitaxially on $\{111\}_N$ faces; evidence of epitaxy on the $\{111\}$ faces has been observed only around microscopic defects (e.g., cracks). It appears that diamond has nucleated and grown heteroepitaxially on the side walls of the microcrack.

(vii) The present results show that, with appropriate shuttering to avoid metal contamination, hot-filament methods can be used for heteroepitaxial growth of diamond.

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