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Why is iridium the best substrate for single crystal diamond growth?

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The synthesis of heteroepitaxial monocrystalline diamond films has been of technological and scientific interest for several decades. Using chemical vapor deposition techniques, polycrystalline diamond has been successfully grown on many substrates. However, iridium emerges in providing highly oriented films, significantly better than any other transition metals. In the present work we propose an *ab initio* density functional study of the interaction of diamond with different substrates used experimentally. The origin of iridium's specific behavior is investigated. The kinetics of carbon atoms in the substrate lattice is found to play a key role, determining the nucleation mechanisms and hence the quality of the final diamond film. © *2005 American Institute of Physics*.
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The growth of large single crystals of diamond has been an experimental goal for several decades. Diamond has many interesting features, first, its unsurpassed hardness, used in many applications for cutting tools, coatings, and tribology. In electronics, the growth of diamond films has attracted experimental attention due to other properties. Diamond conducts heat more than 10 times better than silicon (which would allow microchips to be cooled more efficiently), has higher carrier mobilities, and is very resistant to radiation damage, thanks to its large band gap.

Recently, methods of synthesis based on chemical vapor deposition (CVD) techniques have become popular because they use low temperatures and pressures. In this way diamond crystallites of up to a few hundred μm can be synthesized.[1] For applications in electronics, diamond is used as the semiconducting medium. In order to benefit from the optimal mechanical, thermal, and electronic properties of diamond, the films must be as monocrystalline as possible.

The choice of the substrate is primordial in determining the properties of the film: the lattice mismatch with the substrate, its chemical reactivity with the CVD precursor (namely its tendency to form stable carbides), and the solubility of carbon in the substrate will all influence the way diamond is nucleated and grown. Typical substrates for diamond CVD are silicon, β-SiC, and transition metals. Over the past five years, several studies have shown that iridium (100) is an exceptional substrate for diamond growth.[2] The crystallinity of the films is an order of magnitude better than for other substrates (Si,[3] Pt,[4] Pd,[4] Ni,[5] or Re[6]).

The fact that iridium stands out so strongly calls for an explanation. In the following, we present *ab initio* density functional theory (DFT) calculations of the interactions between diamond and different substrates used experimentally. We differentiate the systems based on their interface energies and especially the dissolution energies of carbon atoms in the bulk metal lattices. We further characterize the carbon–iridium interaction by studying the migration energies of carbon in bulk Ir. Based on these results we explain the uniqueness of Ir, and propose a growth model for diamond on Ir(100).

The *ab initio* calculations are performed with the ABINIT package,[7] which contains a standard implementation of DFT using a plane-wave basis set[8] and norm-conserving pseudopotentials.[9] The generalized gradient approximation[10] is used to approximate the exchange-correlation energy. A plane-wave kinetic-energy cutoff of 40 Ha is used throughout. Structural relaxations are performed with a tolerance on forces of 5×10^{-5} Ha/Bohr (2.6×10^{-3} eV/Å) and on stresses of 5×10^{-7} Ha/Bohr.[3]

Using this technique, iridium, platinum, silicon, and rhenium are compared as substrates for diamond growth. Silicon is a popular and economical choice, platinum is very close to iridium in crystal structure and chemical nature, and finally rhenium shows interesting features experimentally,[6] as it can absorb much more carbon than Ir.

Several different types of models are also considered. First, supercells containing alternating layers of metal and diamond, in order to calculate their interface energy. For Ir, Pt, and Si, the (100) orientation of diamond and the metal are matched [for Si the cubic diamond cell is doubled and the Ir (100) direction is aligned with the Si (110)]. In the case of hexagonal rhenium, the orientations are (111) for diamond and (0001) for Re. The lattice parameter mismatch produces lattice strain, so we calculate the interface energy with respect to strained diamond (all atomic positions and lattice parameters perpendicular to the surface are relaxed). The values of the strain are 7.8%(Ir), 9.7%(Re), 10.2%(Pt), and 7.9%(Si). The Brillouin zone was sampled with a $6\times6\times3$ mesh of k points, using the cold-smearing scheme[11] and a smearing width of 0.01 Ha.

Second, single atoms of carbon are placed in supercells of bulk metal. The full system is allowed to relax (cell and atomic positions), for several sizes of supercell. For the cubic cases, k-point meshes of $8\times8\times8$ (one unit cell) and $4\times4\times4$ (two or eight unit cells) points were used. For Re $6\times6\times4, 3\times3\times4$, and $3\times3\times2$ meshes were chosen, for one, four, and eight unit cells, respectively.

We calculate the interface energy of diamond with the various metal substrates using a supercell containing three to five layers of metal and four or five of diamond, as in Fig. 1.

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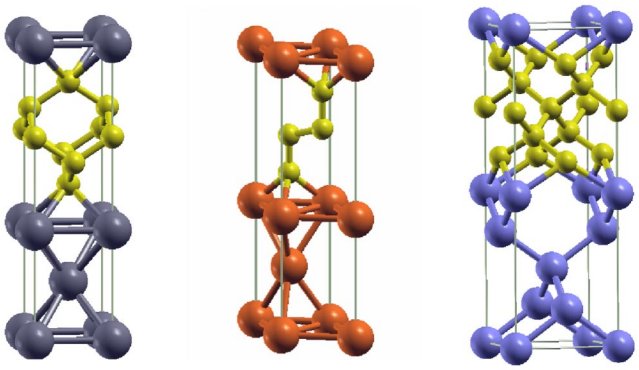

FIG. 1. Supercell structures for diamond interfaces with Ir,Pt (left) Re (middle), and Si (right). Small spheres are C (yellow online).

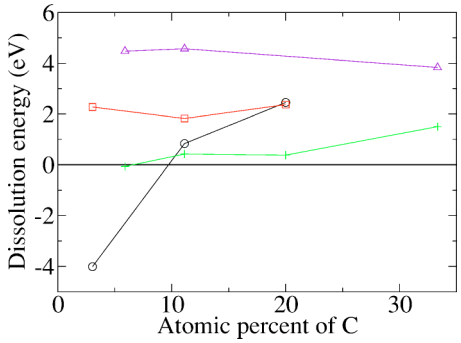

FIG. 2. Dissolution energies of interstitial carbon in different metal substrates; (○)=Ir, (+)=Re, (□)=Pt, (△)=Si. Dissolution in Ir is very favorable at low concentration and remains possible in Re up to much higher concentrations.

For silicon ten layers of Si were used (thicker than in Fig. 1). In these configurations, the interface energy is calculated from the difference in energy between the supercell and the individual bulk materials (metal and strained diamond). The in-plane lattice parameter is fixed to that of the metal, to simulate the presence of a thick substrate.

The interface energies obtained are 0.42, 0.38, 0.04, 0.36 eV/Å^2 for Ir, Pt, Re, and Si, respectively. The energies per unit area are very close, except that of rhenium, which is significantly lower. This behavior of Re is consistent with a general tendency of transition metals to create carbides if the *d* shell is less than half filled,[12,13] but may be simply due to the diamond presenting its (111) face instead of (100). Surprisingly, iridium does not present a better interface than platinum or silicon. This leads us to the conclusion that kinetic effects dominate the CVD process. Finally, let us recall that these energies do not contain the contribution of diamond strain, and are idealized. In practice the stability of a macroscopic interface will depend on other factors: the thicker the film, the greater the force which will detach the diamond, as happens with rhenium,[6] unless the interface strain can be relaxed with dislocations and defects.

In CVD diamond growth it is not clear which species are the most important. C, C^+, C^-, C_2, CH, CH_2, CH_3, C_2H_2, and others may be present.[1] The most successful CVD growth techniques for diamond require that, in a first nucleation phase, a bias voltage be applied to the plasma (Bias-Enhanced Nucleation BEN[2,14]). Carbon atoms can then implant themselves into the surface. *Post hoc* analysis of the samples shows that a varying amount of carbon finally stays inside the metal lattice, depending on the substrate and on the process details.

In order to understand the dynamics of the implantation and nucleation process, we consider a supercell of metal with an additional carbon atom. The atom is either in an interstitial position or in substitution in the lattice. We calculate the difference in energy for the lattice with and without a carbon atom. In this way we can determine the behavior of carbon atoms in the bulk or near the metal surface: if the energy difference is positive and sufficiently high to overcome barriers to diffusion, then the carbon will be expelled to the surface.

For the fcc metals, there is only one natural interstitial site, the octahedral site. For silicon, one tetrahedral site is occupied by a silicon atom, so the only site left is the other tetrahedral one. For rhenium the site at $(1/3, 2/3, 1/4)$ is the most stable.

Calculations were performed with interstitial and substitutional carbon for various concentrations between 0% and 50%.[15] The resulting interstitial dissolution energies are shown in Fig. 2.

The most striking feature in the case of interstitial carbon is the behavior in iridium for low concentrations, where the inclusion of carbon is very favorable. For larger concentrations (15%), however, carbon quickly becomes unstable in the lattice. Rhenium has a very different behavior, as carbon is only slightly unstable in the lattice, and stays so up to a much higher concentration of 20% or even 30%. Substitutional carbon is uniformly less stable than interstitial, except for very high concentrations, close to 50%, where carbide formation is evident for Si, and to a lesser extent, Re. The differences between Re, Ir, and Pt follow the broad tendency of carbon interacting more strongly with less filled *d*-shell transition metals. Ir is the limiting case of the first non-carbide-forming 5*d* metal.[12]

In order to complete our study of carbon in iridium, we estimate the diffusion barrier of C in bulk iridium in the following way: the energy of a $2\times2\times2$ fcc supercell of bulk Ir is calculated, with a carbon atom in different positions. First in the octahedral and tetrahedral sites, then in the center of a face of an octahedron. Atomic positions are relaxed. In the last case the Ir is constrained in the octahedron face.

The octahedral site is the most stable, at 0.84 eV, followed by the tetrahedral one at 2.17 eV. The real barrier to migration lies in the octahedron face the atom must squeeze through to pass into the tetrahedron. The face site is at 3.26 eV (a maximum value). The barrier should be compared to the dissolution energy for a carbon atom in bulk Ir above. From this point of view we see that above a concentration of 15–20 at. % in carbon, the migration of the atoms becomes possible, and they will segregate to the surface.

At this stage it has become evident what the difference is between the substrate metals, and we can suggest a scenario for the CVD nucleation and growth of diamond. Iridium happily accepts carbon at the beginning of the CVD process. Employing BEN further increases the quantity of carbon beyond equilibrium, and once the concentration goes above 10% the carbon is expelled to the surface. The large quantity of carbon present allows nucleation and growth to proceed. There is much speculation on the precise effect of using BEN,[1] and many results suggest that the induced changes in surface morphology give many nucleation sites, and/or that carbon clusters are needed as seeds, and are created during

BEN. Both of these phenomena would be enhanced for Ir, due to the very rapid transition from carbon-absorbing to carbon-expelling regimes. BEN also increases etching but this is not taken into account in our study, and is probably less substrate specific.

In Re, carbon can also be incorporated, though not spontaneously. However, it is retained inside the lattice up to much greater concentrations. For the other substrates, little carbon is allowed into the lattice, and all nucleation must occur using only the carbon present at the surface.

We note that the carbon concentrations considered here concern only the last few nm of metal. Our calculations remain "equilibrium" estimations, and must be taken with the appropriate grain of salt, but nevertheless demonstrate clearly the uniqueness of Ir.

In conclusion, we have demonstrated the chemical specificity of the interaction between carbon and iridium. Interface and dissolution energies were calculated for a number of representative substrates used in CVD diamond growth. The differing behavior of iridium was shown: carbon dissolution in bulk Ir is highly favorable for low concentrations, but increasing the concentration beyond 15 at. % makes the system unstable. Si and Pt do not dissolve carbon easily. Rhenium can also dissolve carbon, but does so up to much higher concentrations. Only Ir, therefore, expels sufficient amounts of carbon to its surface sufficiently fast for efficient diamond nucleation and growth. The concentration of carbon must nevertheless be pushed beyond the thermodynamical equilibrium using BEN. The migration of carbon atoms in bulk Ir is shown to be possible once the concentration is higher than 15%.

Exploiting the model proposed here for diamond nucleation will require a finer understanding of the dynamics of the carbon migration processes. In particular in order to determine more precisely the critical conditions which favor carbon segregation at the right moment during nucleation. The position of iridium as a borderline case suggests experimenting with ruthenium and copper, the corresponding 4*d* and 3*d* elements. Finding a silicon-based, or otherwise less expensive, substrate which presents a dissolution versus concentration curve similar to Ir would open the way to large scale industrial applications of diamond transistor technology.

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[15] These numbers should not be directly compared to equilibrium concentrations of carbon in metal. The latter are governed by equilibria between different phases, and carbon can cluster at grain boundaries and defects, which increases the effective local concentration. Our calculation shows a difference in affinities and behaviors as a function of concentration.