

Quantum Chemical Studies of Growth Mechanisms of Ultrananocrystalline Diamond.

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Diamond films grown by the conventional plasma CVD methods from hydrogen/hydrocarbon mixtures typically have a microstructure with micron-size crystallites. The fraction of atoms in the grain boundaries relative to the bulk in the case of microcrystalline diamond is extremely small. In contrast, diamond films grown from hydrogen poor argon/fullerene or argon/methane microwave plasmas are characterized by a microstructure consisting of crystallites with an average size of 3-10 nm. The latter films are called ultrananocrystalline diamond (UNCD). Use of hydrogen-poor growth conditions produces uniform films with controlled grain size in a few nanometer range and with thicknesses up to several tens of microns. The growth mechanism for diamond films grown from hydrogen poor argon/fullerene or argon/methane microwave plasmas are significantly different than those in hydrogen rich plasma since the latter depends on hydrogen abstraction by the hydrogen present in the plasma. The carbon dimer has been proposed as the principal growth species in hydrogen poor plasmas used to grow diamond.

This paper will review our computational studies of C_2 growth mechanisms on diamond surfaces and implications for ultrananocrystalline thin film growth. These investigations have postulated reaction mechanisms with diamond growth occurring by insertion of C_2 into the C-H bonds of the hydrogen-terminated diamond surface or into π bonded carbon dimers on dehydrogenated diamond surfaces.

Quantum chemical calculations of C_2 addition to the diamond (110) surface showed that C_2 can add easily to the surface by inserting itself into first one C-H bond and then a second C-H bond producing an adsorbed ethylene-like structure. A second C_2 can then insert itself into two other C-H bonds to produce a surface with two adjacent ethylene-like groups. Formation of a C-C single bond between adjacent ethylene-like groups can produce a new layer on the diamond surface. This mechanism was found to have only very small reaction barriers and a large energy lowering. Quantum chemical calculations of the clean (100) surface indicates that it constitutes sites for both growth and re-nucleation. In contrast C_2 addition on the hydrogenated (100) surface was found to lead to growth. Because only a small fraction of the (100) surface sites are unhydrided, most C_2 insertion events likely lead to growth, with only a few leading to re-nucleation. This is likely to be sufficient to explain the small grain size observed in ultrananocrystalline diamond.

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