

Michael Sternberg, *The Atomic Structure of Diamond Surfaces and Interfaces*.
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137 pages, 41 figures, 24 tables.

Abstract

This thesis investigates several theoretical issues on the growth and structure of diamond films produced by chemical vapour deposition. The work is divided into two major parts, the first being methodological in character, and the second devoted to applications.

After an overview on electronic structure theory certain aspects of the density-functional-based tight-binding method (DFTB) are examined, primarily its connection to the underlying density functionals. A review of the approximations taken in various implementations of this scheme over the years is given as well. In the present work this method is extended to a linear scaling ($O(N)$) formulation. The first part concludes with test results and a general assessment.

In part two, the standard DFTB method is applied to several problems of interest in the context of diamond materials. First, an overview of the properties of diamond bulk and surfaces is given. Energy and geometry data set the stage for the subsequent calculations and serve as performance benchmarks. The remaining chapters address questions related to the relatively new class of ultrananocrystalline diamond (UNCD) thin films grown primarily from C_2 species. A complete mechanism for the growth of a diamond (110) monolayer is established by investigating total energies and adsorption barriers on an initially clean surface, followed by chain growth and coalescence, and finishing with the filling of surface vacancies. The mechanism is qualitatively different from conventional methyl-based diamond growth. A stabilisation of the diamond phase over graphite due to C_2 was observed in the absence of hydrogen.

The internal structure of UNCD films is investigated by considering high-angle high-energy (100) twist grain boundaries. They differ significantly from those in microcrystalline diamond, where low-angle and tilt grain boundaries, as well as stacking faults and twins prevail. First, the structure of pure grain boundaries is established, followed by an investigation of the effects of impurities. The grain boundaries are confirmed to be very narrow, essentially spanning only two atomic monolayers. The atomic structure is characterised by threefold coordinated atoms which amount to about 50% of all interface atoms and introduce electronic levels into the diamond band gap. The electrical conductivity observed in the films is attributed to carbon π -states in the grain boundary regions. It is found that nitrogen impurities are energetically easier to incorporate into the grain boundaries than into the grain bulk and that nitrogen promotes threefold coordination of carbon atoms in the grain boundary. A shift in the Fermi energy towards the conduction band at larger nitrogen concentrations was noticed. These mechanisms support experimental evidence on enhanced electrical conductivity due to nitrogen. In contrast, hydrogen saturates dangling bonds and so lowers the film conductivity.

Keywords

diamond, surfaces, grain boundaries, growth, conductivity, density functional theory, tight-binding, linear scaling, $O(N)$

PACS

71.15.Dx Computational methodology
61.43.Bn Structural modeling: serial-addition models, computer simulation
61.72.Mm Grain and twin boundaries
68.35.-p Solid surfaces and solid-solid interfaces: Structure and energetics
81.15.Aa Theory and models of film growth