



A review of diamond synthesis by CVD processes

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ABSTRACT

Diamond has some of the most extreme mechanical, physical and chemical properties of all materials. Within the last 50 years, a wide variety of manufacturing methods have been developed to deposit diamond layers under various conditions. The most common process for diamond growth is the chemical vapor deposition (CVD). Starting from the first publications until the latest results today, a range of different developments can be seen. Comparing the basic conditions and the process parameters of the CVD techniques, the technical limitations are shown. Processes with increased pressure, flow rate and applied power are the general tendency.

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1. Introduction

The range of industrial used tools reaches from single bulk material, coated and treated systems to multilayer devices. Depending on the

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requirement of the system, different material compositions can be chosen. Because of its extreme properties, diamond is one of the most versatile usable materials for coated systems. Almost all diamond properties are in a higher or lower limit of possible desirable behavior. Diamond is for example the hardest known material and at the same time it has the lowest coefficient of thermal expansion. Other advantages are attributes like being chemically inert, highly wear-resistant, highly thermally conductive, electrically insulate and broadly optically-transparent from the ultraviolet (UV) to the far infrared (IR) [107].

Diamond consists of carbon atoms, which are bonded over tetrahedral sp^3 hybrid orbitals in a face centered cubic (fcc) crystal system. Furthermore, each primitive (Bravais) cell consists of two carbon atoms. The structure can be seen, as two face-centered cubic lattices interpenetrating along the body diagonal ($1/4 \ 1/4 \ 1/4$) of the cubic unit cell [84].

The industrial use of diamond began with the first synthesis by “General Electrics” in 1955 [14]. High pressure and high temperature (HPHT) surrounding conditions were generated, which were similar to the conditions for natural diamond growth. The conversion of carbon depended on the fact, that diamond is the densest allotrope form of carbon. With this technique, monocrystalline diamonds with high purity can grow up to several millimeters. Most of these diamonds are used for grinding and cutting tools. Nevertheless, there are also strong disadvantages like the highly expensive equipment and the limited size of the diamonds.

Since the middle of the 1950s, the interest in diamond increased with the possibility of growing carbon by using a wide variety of chemical vapor deposition (CVD) techniques. These techniques allow the deposition of four different types of carbon: amorphous carbon with sp^2 -bonded atoms (a-C), tetrahedral bonded amorphous carbon (ta-C), polycrystalline and monocrystalline diamonds [3].

This review focuses on the various deposition techniques by using CVD for poly- and monocrystalline diamond growth and on the basic energy transfer concepts. Special attention is given to the different energy supply, associated temperature and density distribution. The review concludes with a comparison of process parameters, which are measured for all types of CVD apparatuses.

2. Applications of diamond coatings

Due to the notable properties, diamond coatings find use on a variety of applications including, as semiconductor, as an optical component, as heat sink and as wear-resistant coating.

The advantages of semiconductor are the wide band gap, the very high electric breakdown and the thermal conductivity. For the applications diamond can be doped by boron, which results in a p-type semiconductor with a bandgap about 0.37 eV from the valence band maximum [76]. The phosphorus doping can result in an n-type semiconductor and a donor level of 0.6 eV from the conduction band minimum [32]. Without doping the wide bandgap at 300 K of 5.5 eV from diamond is used for photodetectors. These photodetectors are interesting for investigation of inflammation and explosion dynamic because of the sensitivity in the range of 185 to 250 nm [36]. One advantage is the transmission of near-UV (300–400 nm), visible and IR radiation, so that diamond can be used as solar-blind UV photodetectors, even on a daylight background.

The features of hardness, highest bulk modulus, lowest compressibility, high wear resistance and a low friction coefficient against a wide range of materials are used for diamond coatings onto cuttings tools. MMCs, aluminum–silicon alloys and Co-cemented tungsten carbide tools are used [2] as substrates. But Co-cemented tungsten carbide (WC–Co) is commonly considered the most suitable substrate to receive a diamond layer for tooling applications [81]. However, the major drawback is a very good solvent (0.2–0.3 wt.%) of carbon into cobalt (Co) and the resulting poor adhesion which is the main technical limit for diamond-coated tools [19]. Besides, the presence of

metallic cobalt suppresses the diamond nucleation through catalyzing the formation of graphite. Because of these facts, the Co binder is removing from the substrate surface by using Murakami reagent and acid etching. This can result in an optimally conditioned substrate surface for diamond coating [23].

The thermal, mechanical and optical properties of diamond are used in optical windows, especially for high-power IR lasers and airborne IR sensor systems. The diamond windows combine withstand again high power irradiation, high temperatures and aerodynamic load [112].

“The physical properties of CVD diamond can differ significantly from their single-crystalline counterparts due to intentionally or unintentionally added impurities, grain boundaries and other extended defects. For any industrial application precise knowledge of the relevant material is necessary” [112]. Therefore, this paper makes no statement about the quality of diamond films, it only gives a brief summary of the produced layers in each chapter.

3. The chemical vapor deposition process

As its name implies, chemical vapour deposition (CVD) involves chemical reaction inside a gas-phase as well as deposition onto a substrate surface. An early work which deals with chemical processes that is important for the diamond generation had been published in 1993 by J. E. Butler et al. [15]. However, the processes have been developed since this time. The process procedure with the whole range of selectable process parameters is shown in Fig. 1. The sketch illustrates the various direct and indirect adjustable parameters. The first group shows the different selectable process gases which can be used for CVD. The second group reflects a selection of energy sources for the activation of the chemical process, followed by ensuring parameters. Below that, there is the substrate with the growing diamond layer.

However, in most cases a mixture of hydrogen and methane is used for diamond growth. It is generally accepted that atomic hydrogen (or oxygen) is the most critical component in the gas phase mixture and methane or other hydrocarbon molecules are only needed for the supply of carbon atoms. The primary function of hydrogen (or oxygen) is to terminate the dangling carbon bonds on the surface of the diamond layer or diamond nucleus. Beyond this, the hydrogen atoms can cleave the neutral hydrocarbons and create reactive radicals such as CH_2 . This excited hydrocarbon can bond on this exposed carbon and form trigonal sp^2 (a-C) graphite or tetrahedral sp^3 (ta-C) bonded carbon [5]. Another purpose of hydrogen is to prevent the growth of graphite. This is possible due to the fact, that atomic

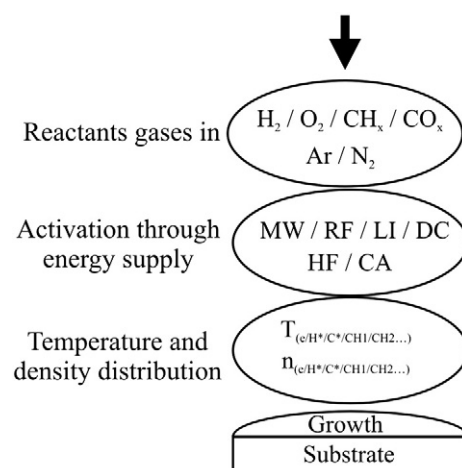


Fig. 1. Schematic diagram of the mechanism from CVD processes for diamond growth.

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