

Chapter 1

Introduction to NV center and its common usage

The aim of this first chapter is to introduce the tools and concepts required for the next chapters. We will start

1.1 The NV center as a physical object

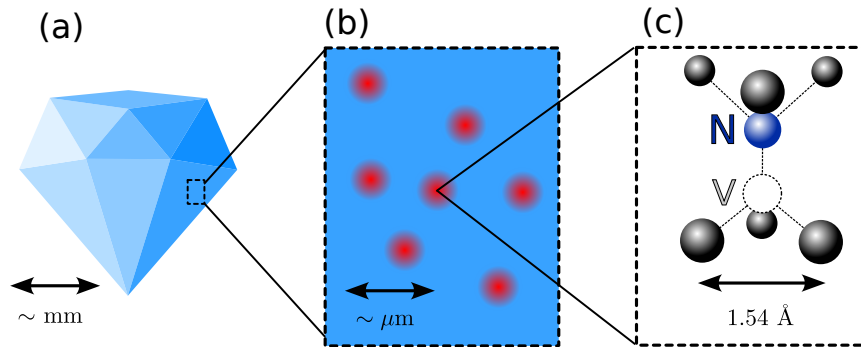


Figure 1.1: From the diamond to the NV center. a) Drawing of a bulk diamond. We consider a diamond to be “bulk” if it is bigger than a few $100 \mu\text{m}$. b) Drawing representing a fluorescence microscopy image of a diamond surface. The red fluorescent spots symbolize NV centers. c) Zoom-in on the crystalline structure of an NV center. Block dots represent carbon atoms

Refaire ce paragraphe te foutre le summary après la description de la figure. We will start this chapter by discussing the physical aspect of the NV center, and of its host material, the diamond. We will cover some of the basic properties of diamond and of its most common defects before addressing the creation process of both diamonds and NV centers.

Fig. 1.1 illustrates the various scales to consider in this study: we start

with a diamond which for lab purposes is generally no bigger than a few mm. If we zoom-in on the surface of some diamonds, we can find bright fluorescent spots corresponding to particular crystalline defects. Standard confocal microscopy is limited in its resolution to the $\sim \mu\text{m}$ range, but if we could zoom-in even further we would see the structure of the defect, illustrated here with the crystalline structure of an NV center.

1.1.1 Diamond overview

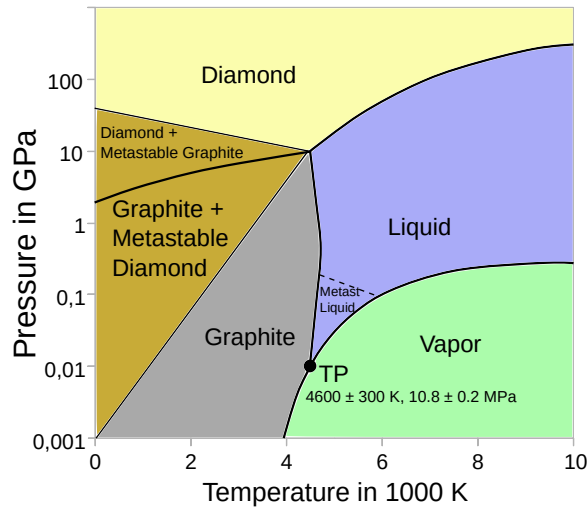


Figure 1.2: Pressure-temperature phase diagram of elemental carbon. From wikipedia, adapted from [1, 2].

Diamond is a remarkable material in many aspects, it is famous for having the highest hardness and thermal conductivity of any natural material, and for its high optical refractive index and optical dispersion which makes it an extremely valuable crystal in jewelry.

Diamond is also famous for being extremely rare in nature, even though its only constituent, carbon, is one of the most abundant element on the Earth surface. The reason is that diamond is not the most stable phase of carbon under atmospheric pressure and temperature. This honor goes to the graphite which is found abundantly in coal.

Fig. 1.2 shows the PT phase diagram of elemental carbon. We can see that diamond becomes the thermodynamically stable phase only for pressure above a few GPa, 10^4 times higher than atmospheric pressure. Even though diamond is unstable under ambient conditions, the extremely high energy activation needed to break the sp^3 bond between two carbon atoms means that the kinematics of the $C_{\text{diamond}} \rightarrow C_{\text{graphite}}$ transition is almost completely frozen. In many ways diamonds are more stable than graphite under ambient condition due to their relative chemical inertness.

Where the thermodynamic equilibrium really matters is for the crystallization process. The higher pressure needed to reach the diamond-stable region can only be found naturally deep under the earth crust, typically between 150 and 240 km below sea level [3], which explain their rarity. It also explains why, despite many previous efforts, diamonds were synthetically produced for the first time only in 1953 [4], more than 50 years after the first synthetic sapphires. To this day, artificial diamond synthesis remains an active field of research [5, 6].

Diamonds, either natural or artificial, are used in the lab and in industry for their extreme sturdiness, with applications ranging from abrasive to diamond anvil cells [7]. More recently, diamonds have been the object of optics and electronics applications. For both of these fields however, the focus is no longer solely on the diamond but also on the defects found inside it.

1.1.2 Point defects in diamond

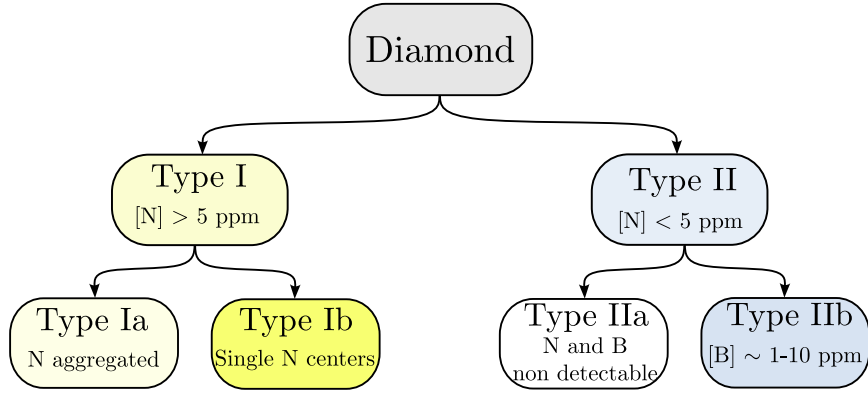


Figure 1.3: Traditional classification of diamonds, based on [3]

Diamond in its intrinsic form is an insulator with a bandgap of ~ 5.47 eV and is transparent from far infrared to deep UV. As any crystal however, diamond is prone to defects. We will concentrate here on 0D point-like defects and omit structural defects such as dislocations, even though those too can affect the optical properties of the diamond [8].

Point-like defects can be constituted by the absence of a carbon atom (“vacancies”), an interstitial defect between two carbon atoms or the substitution of a carbon atom with another atom. These impurities result in unpaired electron or holes localized around the impurity site. This localization causes discrete energy levels for the holes or the electrons, some of which will lie inside the diamond bandgap and will impact the crystal optical and electrical properties.

Defects with electronic transitions in the optical range are called “colored centers” as they are responsible for the coloring of the gems. H, He, Li, B,

N, O, Ne, P, Si, As, Ti, Cr, Ni, Co, Zn, Zr, Ag, W, Xe and Tl are known to form colored centers when introduced in diamond [5, 9], and each of these elements can form several defects. Nitrogen alone can form more than 50 different colored centers [10, 11].

Nitrogen, and to a lesser extent boron, are the most commonly found extrinsic elements in natural diamond. The traditional classification of diamond is presented in Fig. 1.3. It is based on the N and B concentration, with a threshold of a few ppm (part per million) for each species as this was the smaller amount easily detectable through IR absorption. Type Ia diamonds contain clustered N defects such as the B-center which is the N_4V defect. In contrast, type Ib diamond mostly contains C-center which are single substitutional N_s defects, also referred to as P1 centers in the spin community. Type IIb diamond contains B impurities which give them a blueish-grey color, and type IIa diamond contains no detectable impurities via IR absorption [11].

Nitrogen-vacancy centers are a rare occurrence in both natural diamonds and untreated synthetic diamonds, but we will see later that the much more common N_s defects can be converted in NV centers. When working with NV centers, the starting crystal is therefore often a type Ib if one wants to work with ensemble, or a type IIa if one wants to work with single NV centers.

The boron defects are mainly studied in the context of p-doped diamond semi-conductor: a concentration of $[B] \approx 1000$ ppm is needed to achieve a significant overlap between the impurity sites, which turns the diamond into a semi-metal [12]. Other defects of interest, generally not present naturally but introduced voluntarily, include P and S defects to create n-doped diamond [13] (still an active field of research), as well as group IV-vacancy defects (SiV , GeV , SnV , PbV) for quantum optics application [14].

The NV center however remains by far the most studied defect in diamond due to its unique spin properties which will be explained below.

1.1.3 Creation of synthetic diamond for optics and electronics applications

We will now focus on the creation process of the diamonds. Almost all diamonds used in optics or electronics experiments today are synthetic, due to the higher control of the growth process required for these applications. There are two main competing technologies for the growth of large ($\mu m \sim mm$) single crystal diamonds: High pressure high temperature growth (HPHT) and chemical vapor deposition growth (CVD). Both of these processes have their own specificities which we will detail below.

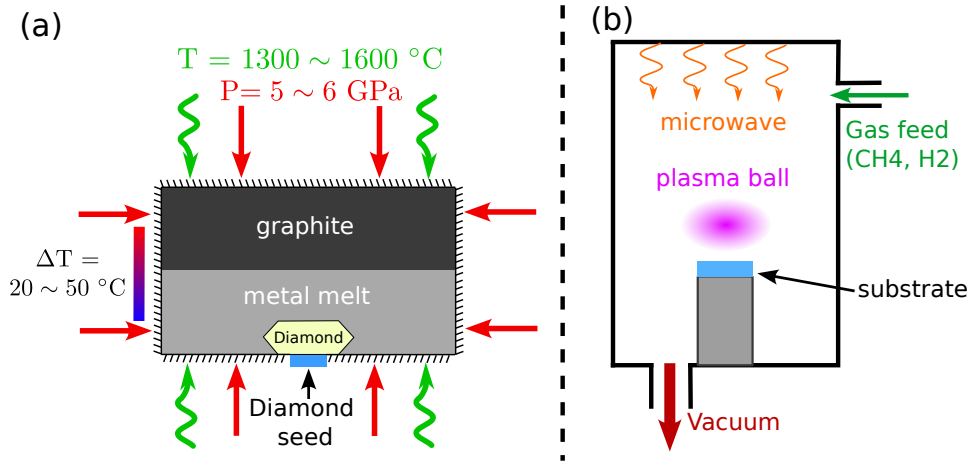


Figure 1.4: Schematics of HPHT (a) and CVD (b) growth process detailed in main text

HPHT growth

HPHT was the first route for synthetic diamonds, first developed in the 1950s [barnard2000diamond , 15]. It consists in reconstructing an environment where diamond is the thermodynamically stable phase of carbon, similarly to the growth process of natural diamonds.

Fig. 1.4-a) illustrates the apparatus of HPHT synthesis: a carbon source (graphite) and a solvent metal composed of transition metals (Fe, Ni, Co typically [16]) are put under 5 ~ 6 GPa pressure in a press and heated to temperatures ≥ 1300 °C. A diamond crystal seed is put in the metal catalyst and a temperature gradient insures that the carbon migrates from the graphite to the diamond.

The first synthesis of HPHT diamonds were all of type Ib due to unwanted nitrogen pollution in the metal melt. The first HPHT type IIa diamonds were produced in the late 90s by adding other elements to the metal melt (Ti, Al, Zr) which would react preferentially with nitrogen and prevent its incorporation in the diamond [17, 18].

CVD growth

CVD growth for diamond was first demonstrated convincingly in the 80s [19–21]. Unlike HPHT, CVD operates in a regime where diamond is not the thermodynamically stable phase. It relies therefore heavily on catalysts to stabilize the diamond phase versus the graphite one.

The main catalyst used is atomic hydrogen, which can both create the free radicals required to form the $C - C$ diamond bonds, and which etches sp^2 bonds (graphite) faster than it does sp^3 bonds (diamond) [22].

Fig. 1.4-b) illustrates the apparatus of a microwave plasma reactor: it consists in a modified vacuum chamber which acts as a microwave resonator. The microwave creates a plasma ball from the the gas introduced in the chamber (CH_4 and H_2 typically) with a plasma temperature $T \geq 3000^\circ\text{C}$ [11], enough to dissociate the H_2 gas in atomic hydrogen [23]. The plasma acts as the carbon source for the diamond growing on top of the substrate, and as the catalyst to favor the diamond phase. The substrate is kept at a temperature $800 \sim 1200^\circ\text{C}$ during the growth.

Other sources can be used to create the high temperature required for atomic hydrogen, such as a tungsten hot filament [24], electrical discharge (arcjet) [25] or even an oxygen-acetylene combustion flame [26].

The main sources of extrinsic impurities for CVD-grown diamond comes from the source gasses [23]. The commercial availability of source gases containing less than \sim ppm impurities made possible the growth of high purity type IIa CVD diamonds [27–29].

Both HPHT and CVD processes can produce diamonds of high quality for quantum optics or electronics application, each with their pros and cons. HPHT offers better scalability for thick crystals (\sim mm) and allows the incorporation of heavy atoms (Ge [30] , Sn [31]) which can be hard to incorporate from a gas phase. CVD on the other hand allows more versatility in the control of the impurities introduced in the crystal, including an isotopic control on both the impurities and the carbon itself. A particular advantage of CVD growth is the possibility of δ -doping where a specific defect is grown only within a very thin layer of the crystal, as low as 5 nm [32–34].

1.1.4 Optimizing NV center formation

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