Chapter 14
Spectroscopic Discrimination Between Natural and Nonnatural Diamond

Nonnatural diamonds are, of course, all diamonds from HPHT or CVD synthesis. Of increasing interest are diamonds, which were originally natural, but have been artificially changed in their properties.

The first question is: Are there spectroscopic properties, which are observed exclusively either in natural or in nonnatural diamond?

The answer for synthetic diamond is: Yes. Now, the second question concerns the spectroscopic method: Preferable is a simple apparatus, which can finally be developed into a handheld version. The apparatus should also accept raw or multifacetted diamonds, in contrast to the polished parallel plates, generally used in spectrometers.

Indeed, the method named "diamond view" perfectly meets these requirements (see Sect. 14.1).

14.1 Existing Methods

Researchers (Paul Spear et al.) at the discrimination laboratory of De Beers in London have presented the "diamond view" method [Pen00]. A bright blue luminescence is observed (after excitation with hard ultraviolet light) in synthetic diamonds. Very characteristic is a phosphorescence for 3–5 s after the UV light is switched off. In natural diamonds the phosphorescence is totally absent, and the blue luminescence is also absent or very weak [Shi92].

No satisfactory physical explanation for the phenomenon can be given at present. Initially, it was proposed, the difference should arise from the different growth planes of diamond. These are dominant octahedral in natural and dominant cubic in synthetic diamonds. This explanation turned out to be insufficient, after purely octahedral synthetic diamonds were grown [Pen00]. The phenomenon originates rather from the significantly different growth history. The natural diamonds have a growth time of many years and experience annealing conditions during millions of years. In contrast, the synthetic diamonds are grown within several days.

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14.2 Alternate Methods

(a) Synthetics: For the future is may be necessary to develop alternate methods, replacing the very efficient "diamond view" method, which is the best spectroscopic choice at present, but can possibly be ruled out by novel synthesis methods.

One existing alternate method is the search for growth features, which are characteristic for synthetic diamonds. Here again, these features could be avoided in the future with refined technology.

It is promising to look for spectral features, which occur *exclusively* in *natural* diamonds. The (V_1H_1) center can serve as an example. It is a common defect in natural diamonds, but is absent in synthetic diamonds. There are two *sharp* absorption lines arising from C–H stretch (0.3852 eV) and bend (0.1742 eV) vibrations (see Table 9.3.1). Using a tunable laser, the absorption ratio measured at the line and in the neighborhood should provide high sensitivity.

In Table 14.2, additional lines are listed, which after present knowledge should be exclusive to natural diamond. Broad bands are omitted, because their identification is more difficult than for sharp lines.

(b) Fancy Colors: The artificial coloring of diamond by radiation damage and annealing has been discussed in detail in [Col97]. More recent results on the recognition of HPHT treatments of diamond will be published in a forthcoming book [Zai10].

Table 14.2 Lines (probably) exclusively observed in natural diamond

Label	Energy (meV)	Defect	Name	Comment
NA0058	57.65	?		Fig. 3.7, [Fer96]
NA0174a	174.2	$^*(V_1H_1)^\circ$		Natural C–H bend
NA0182a	182.2	$^*(V_1N_1H_1)^\circ$		Natural N–H bend
NA0174b	385.2	$^*(V_1H_1)^\circ$		Natural C–H stretch
NA0182b	401.2	$^*(V_1N_1H_1)^\circ$		Natural N–H stretch
NL1264	1.264	?		
NL1328	1.328	?		
NL1360	1.360	?		
NA1500	1.500	?	**N1**	
NL1559	1.559	?		
NL1946	1.946	?		NBD
NL2001	2.001	?		
NL2024	2.024	?		
NL2082	2.082	?		NBD
NL2088	2.088	?		NBD
NL2099	2.099	?		
NL2134	2.134	?		
NL2157	2.157	?		NBD, related to NL2082?
NL2167	2.167	?		NBD, related to NL2082?
NL2175	2.175	?		NBD, related to NL2082?

(continued)

Table 14.2 (continued)

Label	Energy (eV)	Defect	Name	Comment
NA2202	2.202	?		NBD
NL2205	2.205	?		NBD
NL2391	2.391	?		NBD
NA2596	2.596	?	**N2**	
NA2615	2.615	?		NBD
NA2767	2.767	?		NGD
NA2792	2.792	?		NGD
NA3593	3.593	?		
NA3877	3.877	?		
NA4191	4.191	?	**N8**	
NA4468	4.468	?		
NA4646	4.646	?		
NL4986	4.986	?	**N** line	
NA4990	4.990	?	**N10**	
NL4999	4.999	?	**M** line	
NL5037	5.037	?	**L** line	
NL5092	5.092	?	**K** line	

? unknown defect