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Spectroscopic identification of Lab-grown diamonds

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Lab grown diamonds are identical to natural diamonds in terms of their mechanical, thermal and general optical properties. However, diamond growth conditions deep inside the earth are different from those in modern machinery, and therefore some difference do exist. The recognition of these differences, and therefore the identification of diamonds as lab-grown, relies on careful spectroscopic observation of minute changes in their crystal structure. The spectroscopic methodologies used for this purpose include, among others, Fluorescence , Photoluminescence and Raman measurements. In all these methods, a laser is used to excite some impurity lines (typically various color centers) within the diamond band-gap, and the light emission from these color centers is then used for spectroscopic characterization of the source, and information can be derived as to the type of diamond being examined. These color centers are local changes in the diamond crystal, involving vacancies (a missing carbon atom), or an impurity atom (such as nitrogen, silicon, etc.) found in the crystal, and very often a combination of both an impurity and a vacancy in close proximity to each other.

The ability to identify diamonds as lab-grown is, therefore, based on two major prerequisites:

- The availability of a large data-base with information on both natural and lab-grown diamonds
- The spectroscopic ability to measure and resolve features characteristic to each type.

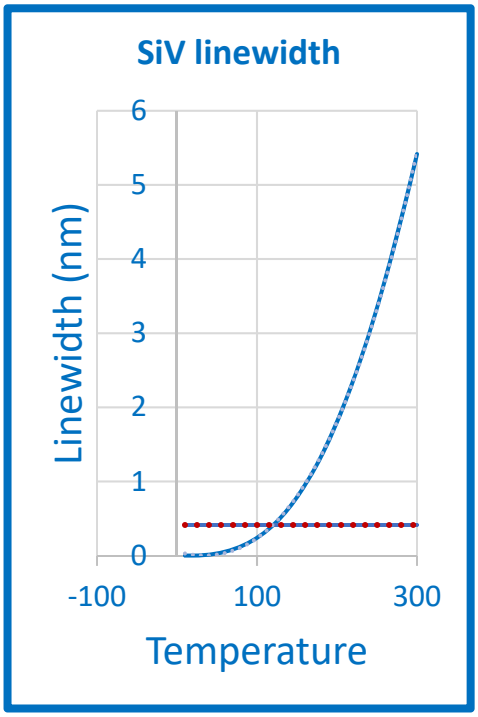
Detailed spectroscopic information is necessary in order to identify specific features resulting from the CVD process of the growth of the diamonds. Moreover, growth methods constantly evolve, addressing various issues so that the spectroscopic signature also changes with time, in particular after HPHT heat treatment or other annealing processing. Thus, the data base available to the testing laboratory is a critical element in its ability to reliably identify the lab-grown diamonds.

The spectroscopic measurement suffers from a major obstacle due to the small concentration of the color centers to be detected. Thus, like in many other similar configurations, it is difficult to separate the contribution from the specific transition one is interested in from the background signal. For efficient measurement, the background signal has to be reduced, and this is best done by performing the measurement at low temperature. A typical telltale signature of lab-grown diamonds includes, for example, the silicon-vacancy (SiV) Photoluminescence peaks at 736.6 and 736.9 nm, which originated from silicon impurities hardly ever found in natural diamonds. However, in any measurement there is a strong background PL signal at these frequencies coming from the main diamond crystal, and it is this background that should be controlled. This situation is known and is common to many other spectroscopic measurements such as Raman.

It is well known and understood that the probability of an excited state to be populated, be in in a crystal, liquid or gas, is determined by its energy and the temperature via the Boltzman factor, $P(E_i) \propto \exp[-(E_i / k_B T)]$, $P(E_i) \propto \exp-(E_i / k_B T)$ where E_i is the energy, k_B is the Boltzman

constant and T is the temperature. In order to estimate realistic situations, note that at room temperature (300K) $k_BT = 200cm^{-1}$, and the above expression indicates that any state with energy of a few hundred cm^{-1} will be significantly populated at room temperature and will contribute to the background signal. As an illustration, consider a typical local crystal phonon excitation at 300 cm^{-1}, at room temperature this state will be populated with a non-negligible probability of $\exp[-(300/200)] = 0.22$, and will therefore contribute to any optical measurement involving it. At a lower temperature of liquid nitrogen (77K), on the other hand, the relevant Boltzman factor reduces to $k_BT = 50cm^{-1}$, and as a consequence, the population of the same state reduces to $\exp[-(300/50)] = 0.002$, namely a factor of 100 lower (!), virtually eliminating its contribution to optical observations.

The temperature dependence of the SiV color center was measured and analyzed in a recent publication [*Nicolas, L., et al., Diamond nano-pyramids with narrow linewidth SiV centers for quantum technologies. Aip Advances, 2018.* ***8****(6)*]. The Zero Phonon linewidth (ZPL) of the 736nm PL doublet was measured at various temperatures, and its linewidth $\Delta\lambda$ was found to be well described by a polynomial $\Delta\lambda \approx 2.447*10^{-7}T^3 - 4.9*10^{-13}T^5$ where T is the temperature (K) and the width is given in nm (figure 3a in that paper). The extracted polynomial fit to the linewidth is plotted in the figure, where a horizontal line was added for $\Delta\lambda = 0.4$ nm which is the doublet (actually quadruplet) splitting of this SiV PL line.



From the figure one can see that the SiV linewidth reaches the value of 0.4nm at around 120K, which means that in order to see the splitting, the temperature must be significantly lower than 120K. The temperature of 77K, achieved by cooling the diamond to liquid nitrogen temperatures, satisfies this condition.

A similar analysis applies to the linewidths of other color centers typical of lab-grown diamonds, and it is therefore clear that without cooling to liquid nitrogen temperatures (or lower) it is quite impossible to resolve the relevant lines.

In conclusion, , in order to spectroscopically identify a lab-grown diamond unambiguously, it is necessary to cool it down to low temperatures (<100K), which in practical terms means cooling it down to liquid nitrogen temperatures.

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