

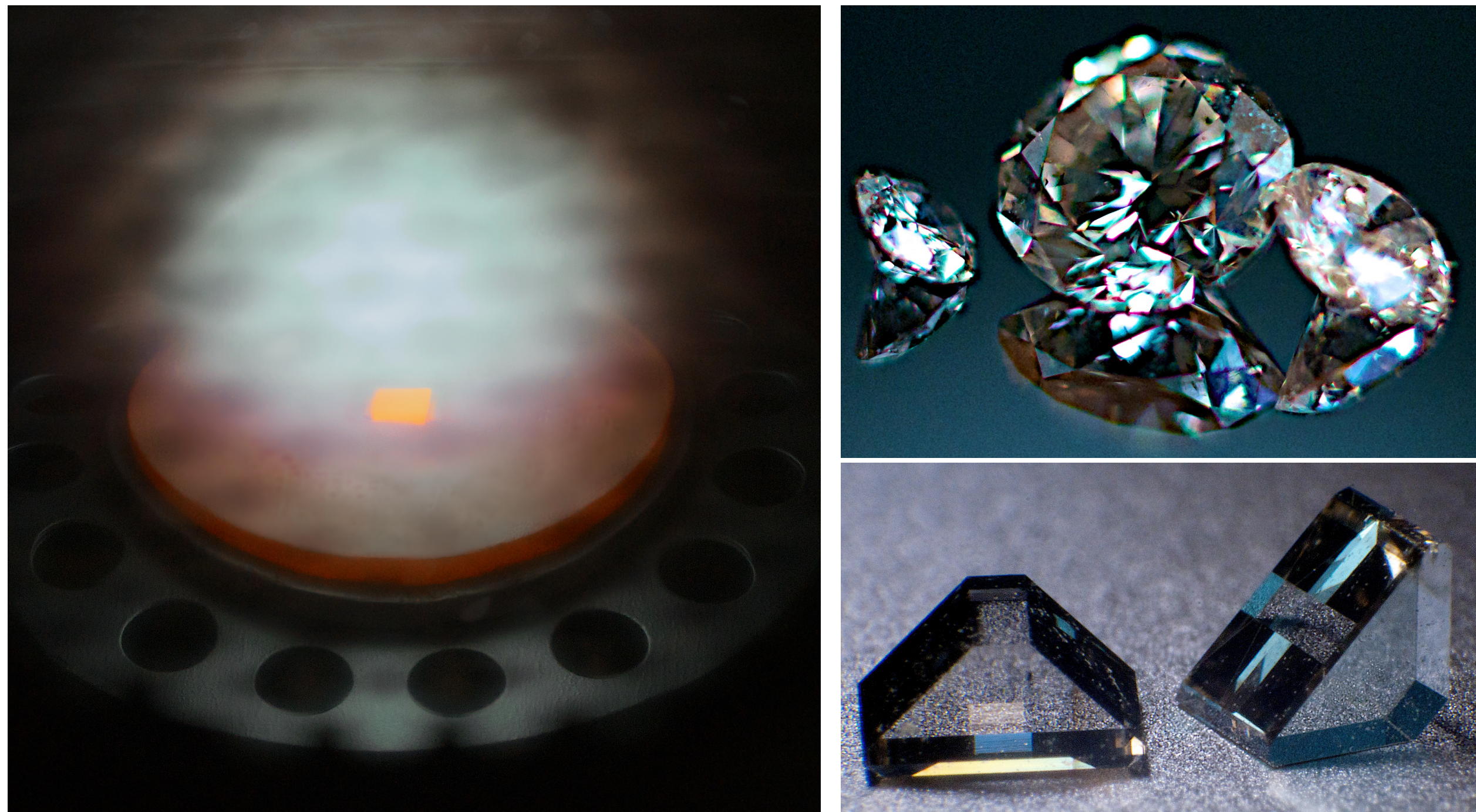
Quality and internal stress of single crystalline diamond synthesized by microwave plasma assisted chemical vapor deposition

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Abstract

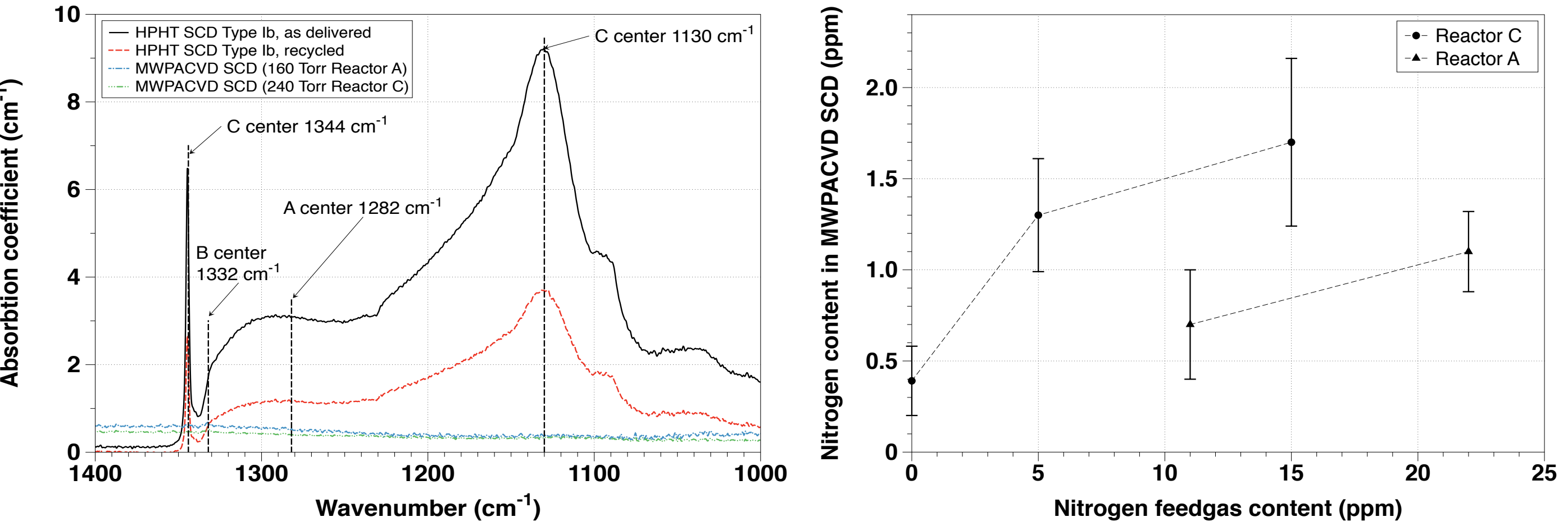
This poster discusses the quality and internal stresses in single crystal diamond (SCD) plates that were produced by homoepitaxial microwave plasma assisted chemical vapor deposition (MWPACVD). Nitrogen concentrations, stress levels and stress distributions in the synthesized crystals were evaluated and also compared with data obtained from type Ib seed crystals produced by high pressure high temperature (HPHT) synthesis. Infrared absorption spectral analysis yielded a nitrogen defect concentration of 230 ppm in as delivered HPHT seed crystals while from a growth process recycled seed crystals had half that amount. MWPACVD grown crystals have much lower nitrogen concentrations depending on the amount of nitrogen added to the process feedgas. The lowest measured concentration was 400 ppb. Despite the much higher nitrogen concentration in the HPHT seed crystals, the average stress levels in the MWPACVD grown crystals (80 MPa) are about twice that of the HPHT crystals (40 MPa). MWPACVD diamonds grown at 240 Torr of process pressure show about 20 % lower stress levels compared to samples grown at 160 Torr. The First order Raman peak shows FWHM values of 1.6 cm⁻¹ proving the high crystalline quality making the material useful for optical applications such as attenuated total reflectance (ATR) crystals.



Single Crystal Diamond Growth

3.5 x 3.5 mm² type Ib HPHT diamonds, acquired from a commercial vendor, with (100) surface orientation were used as seed crystals. Homoepitaxial MWPACVD single crystal diamond growth was performed in two reactor setups: (a) a newer version of the microwave cavity plasma reactor (MCPR) operating at 160 Torr and (b) a newly designed reactor operating at 240 Torr. Both reactors operate with a 2.45 GHz microwave excitation frequency and the input feed gases were hydrogen, 5 – 9 % methane with 0 – 22 ppm of nitrogen in the gas phase. The growth temperature was in the region of 1000 – 1200°C. The growth times were up to 120 hours. The resulting bulk CVD crystals were almost colorless after laser cutting and polishing.

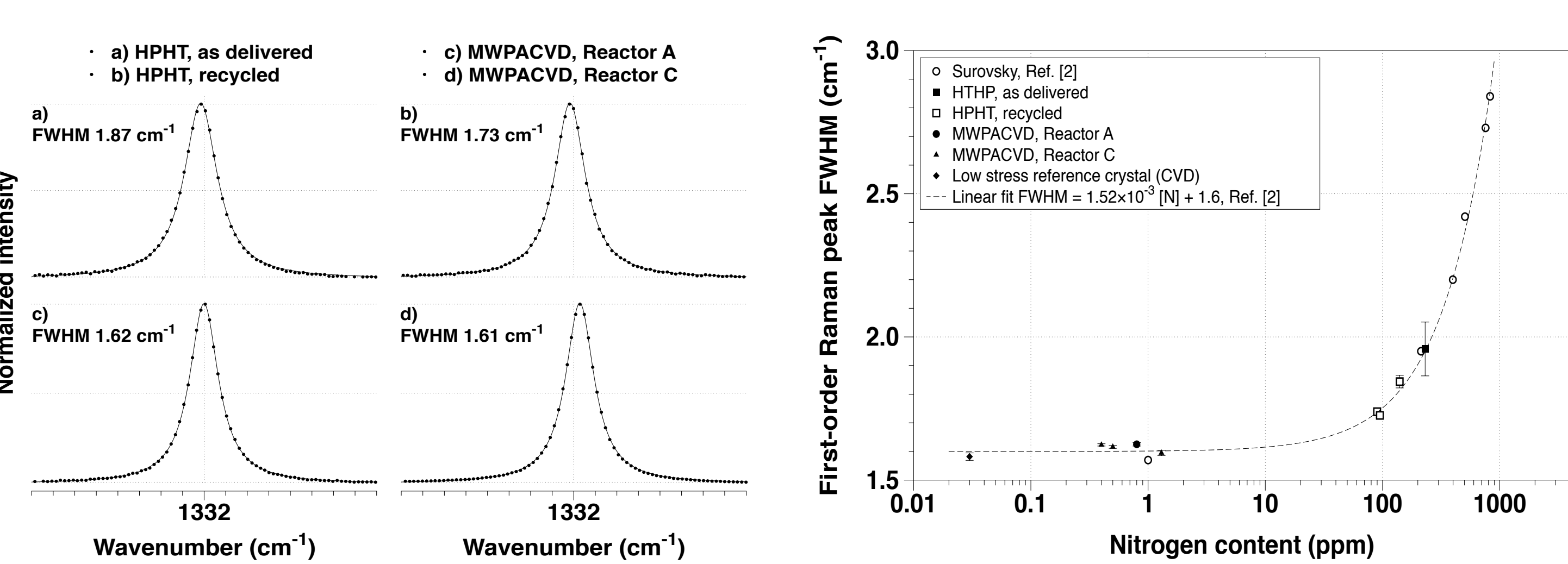
Nitrogen Impurities



The FTIR spectra show additional absorption bands for HPHT crystals between 1000-1400 cm⁻¹. These can be attributed to nitrogen related crystallographic defects (C-center) in the diamond lattice. From the peak heights we determined that an as delivered HPHT crystal's nitrogen content is about 230 ppm [1]. When such a crystal was used as a seed plate in a homoepitaxial MWPACVD experiment its nitrogen content reduced to about 95 ppm of nitrogen. These data were also in agreement with SIMS measurements.

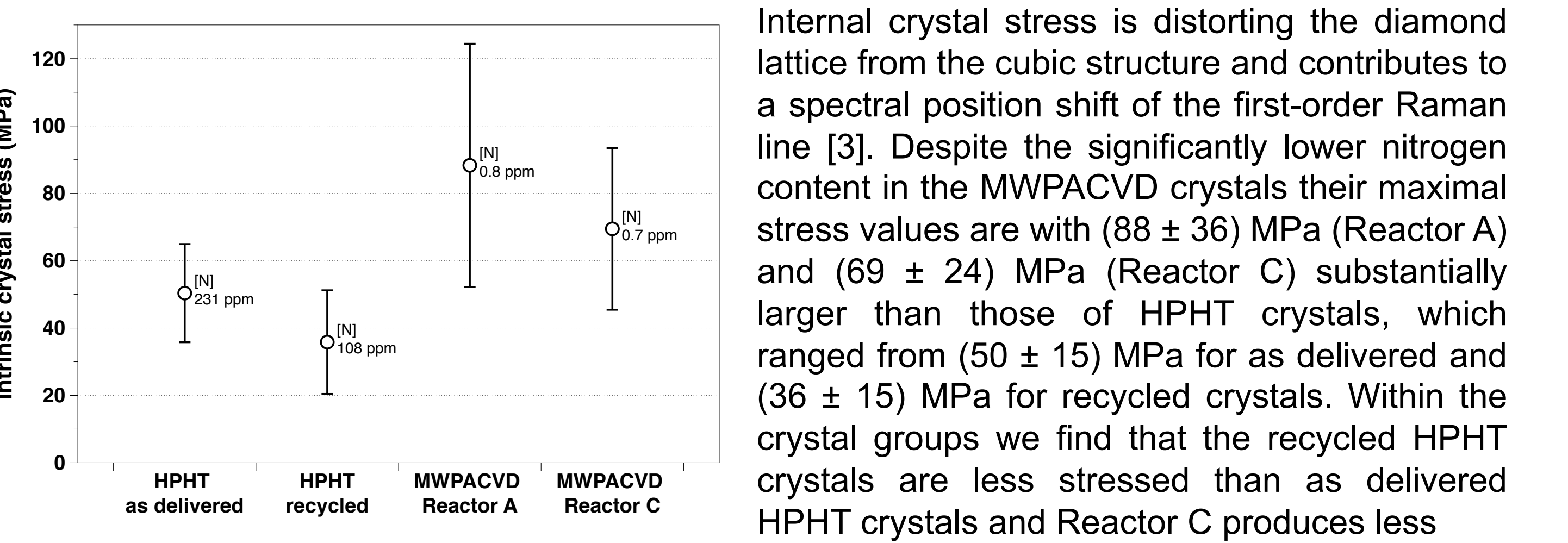
The presence of nitrogen in the gas phase during SCD synthesis also leads to nitrogen incorporation into the MWPACVD grown crystals. The nitrogen content in in-house MWPACVD synthesized SCD crystals ranged between 0.4-1.3 ppm and is at least ten times less than the nitrogen content in the gas phase.

Crystal Quality Analysis



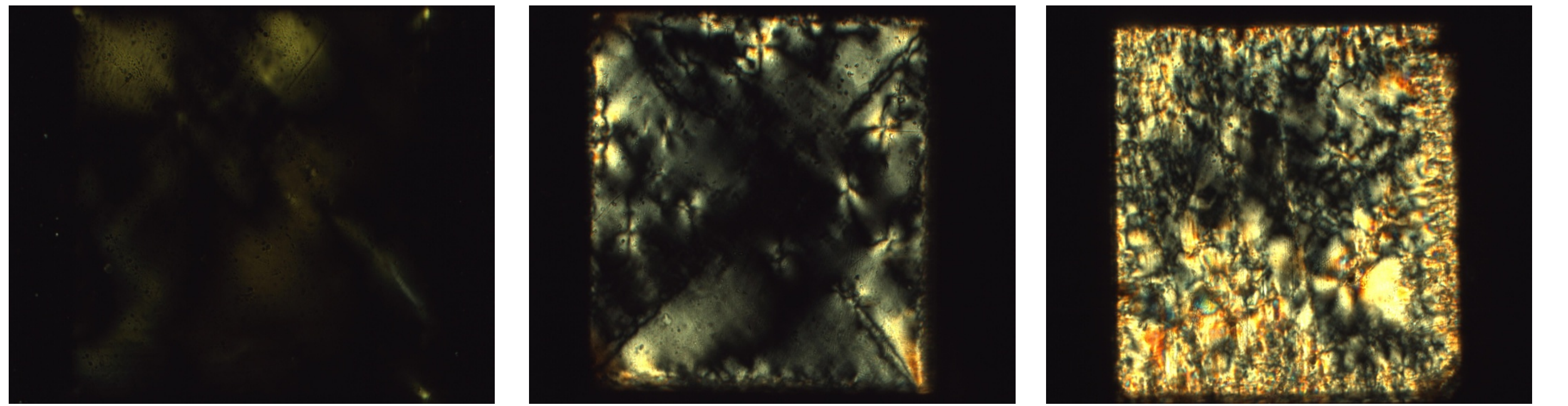
The shape, spectral width (FWHM) and spectral position of the optical phonon line in the Raman spectrum at 1332 cm⁻¹ is traditionally used to judge the perfection or quality of a diamond sample. The FWHM values for as delivered HPHT crystals reduce from (1.83 ± 0.03) cm⁻¹ to (1.72 ± 0.01) cm⁻¹ for recycled HPHT crystals. Reactor A and C MWPACVD synthesized crystals have spectral widths of (1.62 ± 0.01) cm⁻¹ and (1.59 ± 0.01) cm⁻¹ respectively. For comparison, the first-order Raman peak of the low-birefringence reference crystal yielded Lorentzian profile with an FWHM value of (1.58 ± 0.01) cm⁻¹. Based on these data we conclude that the range of measured FWHM values is mainly a function of the nitrogen content. Comparing our FWHM data with others published in the literature supports this conclusion [2]. Considering the statistical variation of or data we find a good match with the linear relationship. Subsequently the first-order Raman peak FWHM of high quality SCD allows to estimate the nitrogen concentration but does not yield statistically relevant additional information on crystal quality differences among the samples.

Internal Crystal Stress



stressed crystals than Reactor A. The data indicate that the nitrogen content in these samples is not the main stress-inducing factor. However, within a group of samples, i.e. HPHT versus CVD grown material, the stress is smaller in the samples with less nitrogen.

To obtain more detailed information on the spatial distribution we performed birefringence imaging. The as delivered HPHT crystals show (left) a cloverleaf shaped birefringence intensity pattern. These patterns are associated with (011) growth directions formed during the HPHT process [4]. The reduced intensity indicates an overall reduction of the stress level in the recycled HPHT crystals similar to the trend observed with the Raman shift method. For the MWPACVD grown crystals the birefringence patterns are unique to each sample. Most MWPACVD samples show more randomized stress distributions of higher intensity.



References

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