Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

In situ doping of epitaxial diamond with germanium by microwave plasma CVD in GeH_4-CH_4-H_2 mixtures with optical emission spectroscopy monitoring

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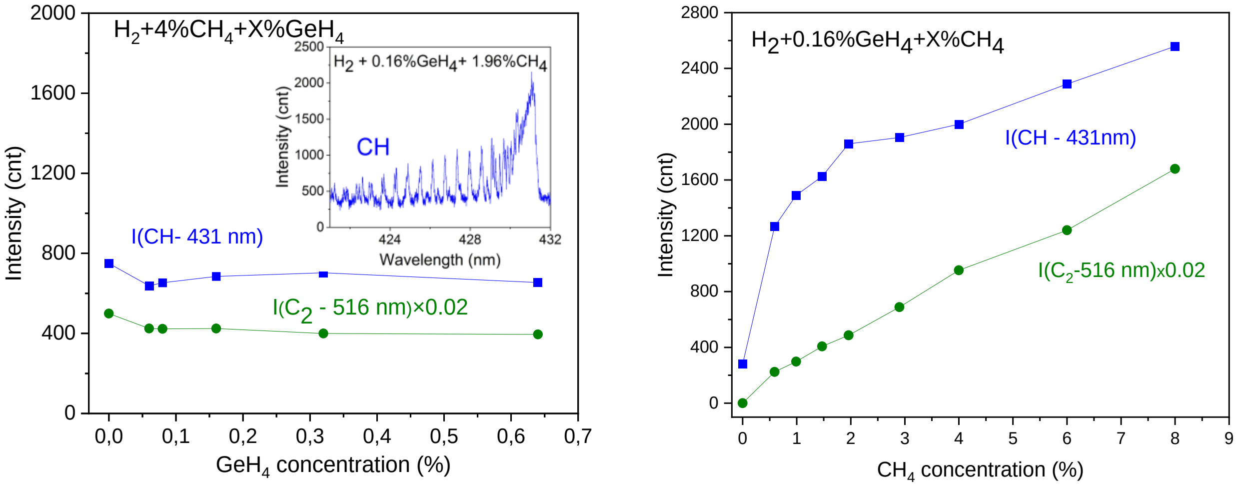
SUPPLIMENTARY INFORMATION

1. Dynamics of CH band intensity with CH_4 and GeH_4 addition in the GeH_4-CH_4-H_2 plasma



(a) **(b)**

Fig. S1. Comparison of intensity variations for CH band (head line at5 λ=431 nm) and C_2 band (λ=516 nm) with addition of GeH_4 in H_2 – 4%CH_4 plasma. Pressure 100 Torr, MW power 2.5 kW (a). Evolutions for CH band (431 nm) and C_2 band (516 nm) with addition of CH_4 in H_2 – 0.16%GeH_4 plasma. Pressure 100 Torr, MW power 3.0 kW (b).

2. Excitation temperature T_{exc} for H_2+4%CH_4+GeH_4 plasma

The T_{exc} was estimated from the Boltzmann plot for relative intensities of the Balmer series lines (Figure S2a). It was assumed that the population density of excited hydrogen atoms follows the Boltzmann law [S1,S2]:

$$\ln(I_{ij}\lambda/g_jA_{ij}) = (-E_i/k_BT_{exc}) + C \qquad (1)$$

where I_{ij} is relative intensity of the emission line corresponding to transition between the energy levels *i* ang *j*, λ_{ij} its wavelength, g_i is the degeneracy or statistical weight of the emitting upper level *i* of the transition, *Aij* is the transition probability for spontaneous radiative emission from the level *i* to the lower level *j*, E_i is the excitation energy of level *i*, and *C* is a constant. The constants g_i and *Aij* (*j*=2) are tabulated in Ref. [S3]. The excitation temperature was determined by plotting $\ln(I_{ij}\lambda/g_jA_{ij})$ as a function of the upper level energy E_i, the slope of which is equal to $-1/k_BT_{exc}$. The intensities of Balmer series lines were corrected for spectral sensitivity of spectrometer-detector system by preliminary calibration of spectrometer with using light-measuring wide-range incandescent lamp SIRSh 6-40. We found increasing trends both with GeH_4 and CH_4 addition (Figure S2b).

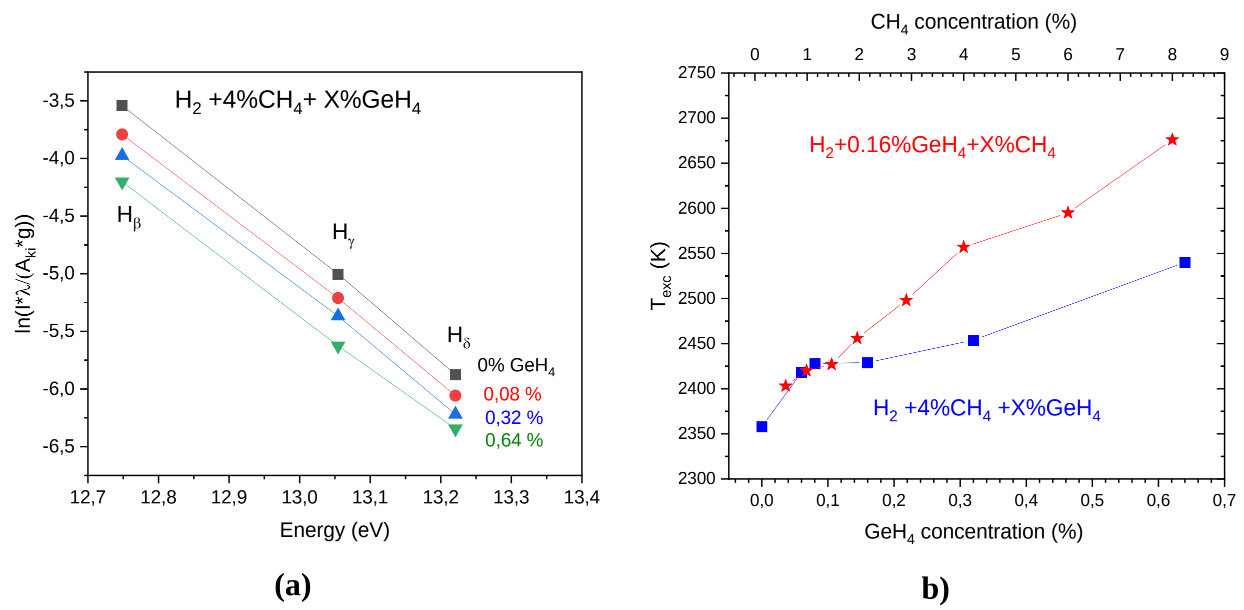


Fig. S2. (a) Boltzmann plot for H_β, H_γ and H_δ line intensities of Balmer series for H_2+4%CH_4+GeH_4 plasma with GeH_4 concentrations of 0% (squares), 0.06% (circles) and 0.32% (triangles up) and 0.64% (triangles down). (b). Excitation temperature T_{exc} as function of CH_4 concentration (stars) and of GeH_4 concentration (squares). Pressure 100 Torr, MW power 2.5 kW.

3. Polishing of epitaxial diamond film. Evaluation of thickness of the removed layer

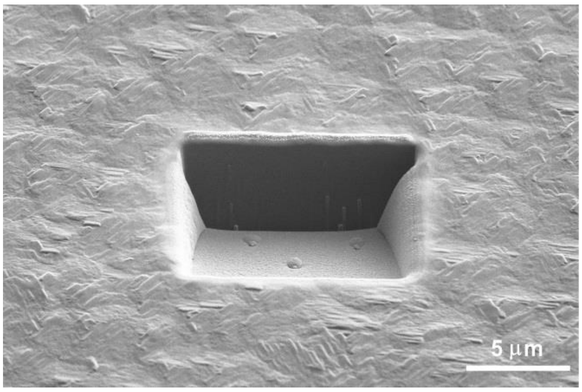


Fig. S3. SEM image of a pit produced on the as-grown surface by focused ion beam milling to serve a reference point for evaluation of the thickness of the removed layer upon polishing. The pit lateral size is 6×8 μm^2 and the maximum depth of 5 The bottom of the pit is inclined.

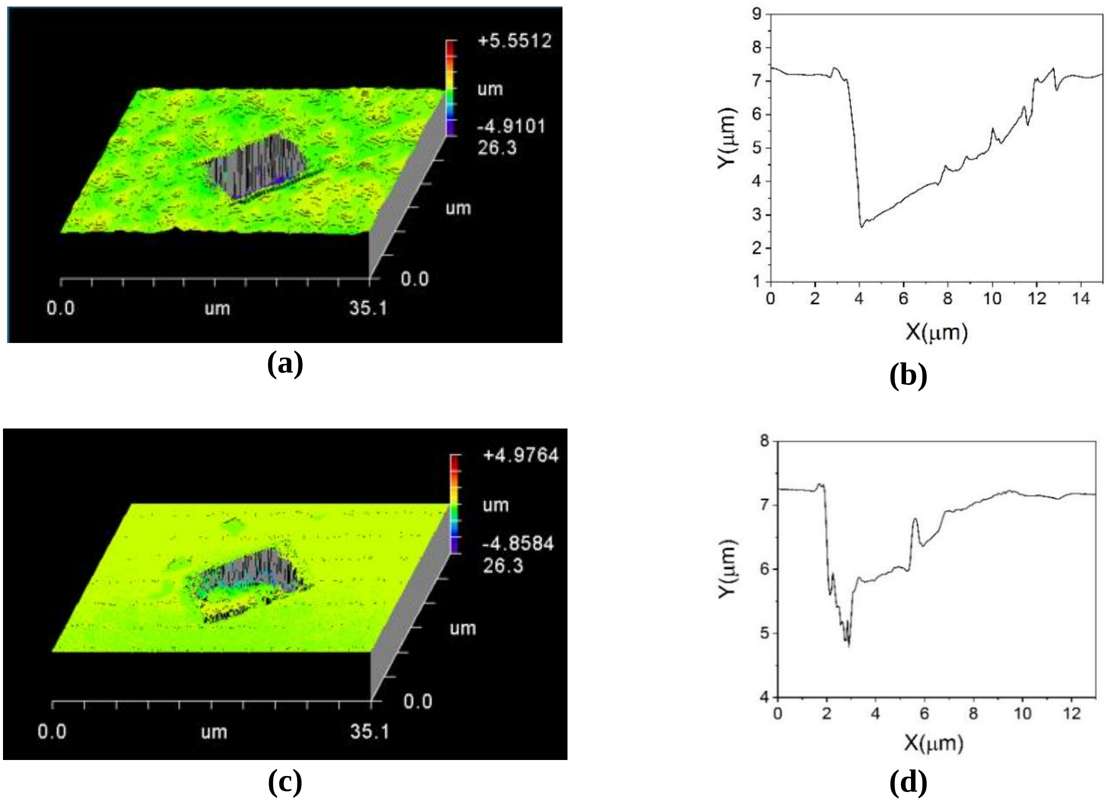


Fig. S4. Optical profilometer (ZYGO NewView5000) images of surface relief of as-grown (111) oriented sample (a,b) and after polishing and cleaning in ultrasonic bath (c,d). A pit with lateral size of 6×8 μm and maximum depth of 5 μm produced on as-grown surface by focused ion beam milling served a reference point to evaluated the thickness of the removed layer. The bottom of the pit is inclined. The image area is 35 × 26 μm^2. The profiles on the right panel are traced across the pit. The change in the pit depth after the polishing indicates the thickness of the removed layer of ≈ 2 μm.

4. PL spectra for (111) Ge-doped film at low temperatures

The ZPL GeV width remained almost the same at temperatures decreasing from 308 to 77K (Fig. S5), that is ascribed to significant stress in the film. In contrast, SiV ZPL reduced in width (FWHM) and increased in intensity by a factor of five at 77K.

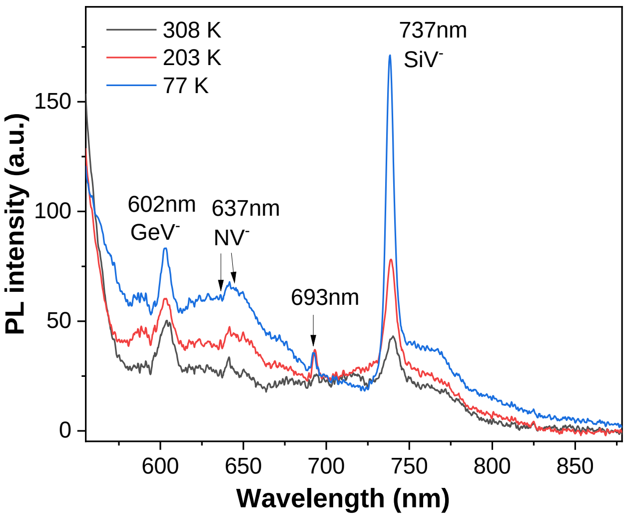


Fig. S5. PL spectra of Ge-doped (111) diamond film at temperatures of 308, 203 and 77K. The spectra are vertically shifted for clarity. The peak at 693 nm is not identified. The PL excitation wavelength is 450 nm. The GeV peak does not narrow at low-T because of high stress induced broadening.

5. PL spectrum of epitaxial film on (100) substrate

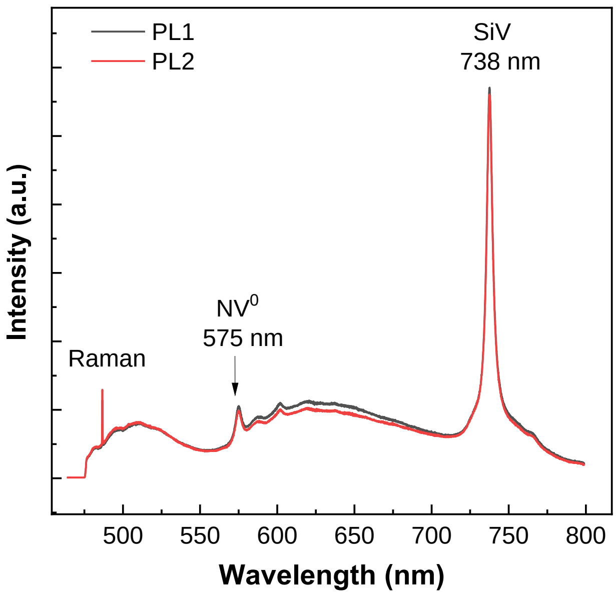


Fig. S6. Photoluminescence spectrum at R.T for epitaxial film on (100) substrate. The process parameters, including GeH_4 concentration in gas mixture, were identical to those for the film on the (111) substrate. The spectra are taken in two arbitrary chosen locations, PL1 and PL2, on the film surface. The PL excitation wavelength λ =473 nm. Besides Raman peak, two other features are NV^0 ZPL at 575 nm with a phonon band at longer wavelengths, and SiV^- ZPL at 738 nm, while no GeV peak near 602 nm is observed.

6. PL spectra for epitaxial film grown with reduced germane concentration (0.28% GeH_4) on (111) oriented substrate

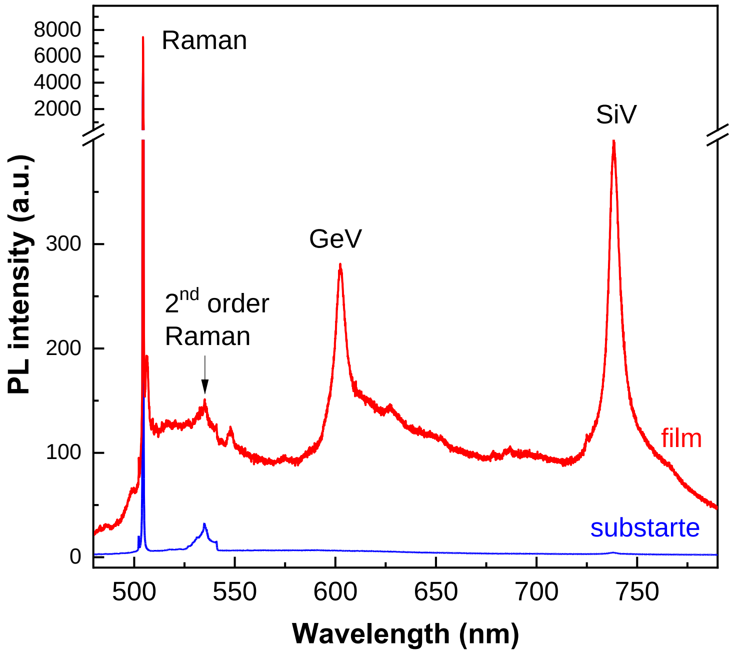


Fig. S7. PL spectra at room temperature for Ge-doped diamond film with thickness of 3.5 μm (top spectrum), and for the (111) oriented substrate (bottom spectrum). The film is grown at reduced germane concentration of 0.28% GeH_4. Excitation wavelength of 457 nm. No features associated with NV PL are seen.

7. Photoluminescence spectra deconvolution for annealed (111) oriented film

The PL spectrum measured at room temperature for the Ge-doped sample (0.8% GeH_4) annealed in vacuum at 1400°C for 1 h was deconvoluted to 9 individual peaks, including GeV ZPL (Fig. S8). The deconvolution was performed for the spectrum converted to energy scale (in eV). All the deconvolution components were fit with Gaussian profiles. The fit accuracy is high, with the Residual Sum of Squares of as small as 4×10^{-4}.

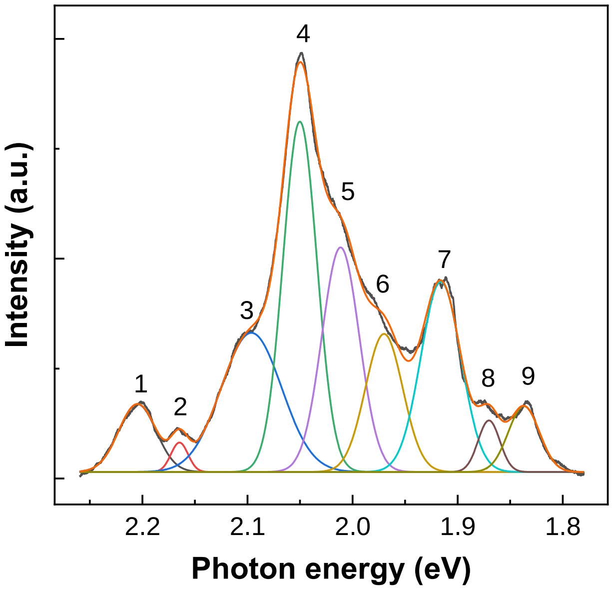


Fig. S8. Deconvolution of the PL spectrum measured at room temperature (black color) and synthesized spectrum (red color) for the 111) oriented Ge-doped sample annealed in vacuum at 1400°C for 1 h. Nine individual peaks, including GeV ZPL are fit with Gaussian profiles. The components are numerated consequently from left to right. See Table S1 for the fit details.

Table S1. Position and width (FWHM) of components of PL spectrum deconvolution for (111) oriented Ge-doped sample annealed in vacuum at 1400°C.

Peak #	Peak position (eV/nm)	Peak width (eV/nm)	Assignment	Ref
1	2.205/562.4	0.036/11.6	divacancy and a foreign atom	[S4]
2	2.165/572.8	0.016/ 3.9	not identified	
3	2.096/591.5	0.057/18.5	divacancy and a foreign atom	[S4]
4	2.050/604.8	0.032/8.8	GeV ZPL	[S5]
5	2.011/616.5	0.036/10.1	GeV LVM*	[S6,S7]
6	1.970/629.4	0.036/10.1	GeV phonon band	[S7]
7	1.916/647.2	0.038/9.3	divacancy and a foreign atom	[S4]
8	1.870/663.0	0.021/10.0	not identified	
9	1.8370/675.0	0.0230/10.5	divacancy and a foreign atom	[S4]

*Local vibration mode with Ge atom

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