Electronic supplementary information (ESI)

n-Type Phosphorus-Doped Nanocrystalline Diamond: Electrochemical and In-situ Raman Spectroelectrochemical Study

Zuzana Vlčková Živcová [a,*] , Otakar Frank [a], Sien Drijkoningen [b], Ken Haenen [b,c], Vincent Mortet [d,e] and Ladislav Kavan [a]

[a] *Department of Electrochemical Materials, J. Heyrovsky Institute of Physical Chemistry of the AS CR, v.v.i., Dolejškova 3, 182 23, Prague 8, Czech Republic*

[b] *Institute for Materials Research (IMO), Hasselt University, Wetenschapspark 1, B-3590 Diepenbeek, Belgium*

[c] *IMOMEC, IMEC vzw, Wetenschapspark 1, B-3590 Diepenbeek, Belgium*

[d] *Institute of Physics of the AS CR, v.v.i., Na Slovance 2, 182 21, Prague 8, Czech Republic*

[e] *Czech Technical University in Prague, Faculty of Biomedical Engineering, Sítná 3105, 272 01 Kladno, Czech Republic*

* Corresponding author. E-mail: zuzana.vlckova@jh-inst.cas.cz. Phone: +420 26605 3446

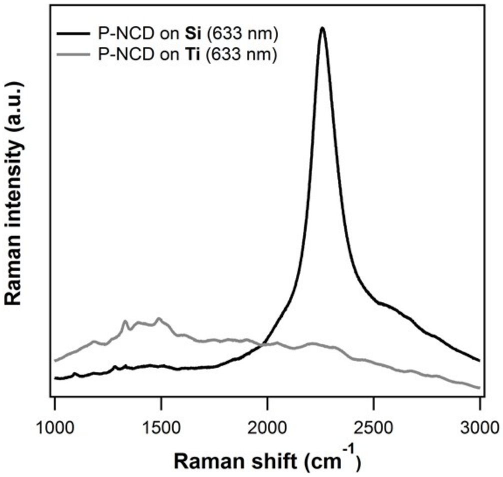

Fig. S1 Raman spectra of the phosphorus doped nanocrystalline diamond (P-NCD) deposited on Si substrate (black line) and Ti substrate (grey line) excited by 633 nm laser radiation. The spectra are offset for clarity, but the intensity scale is the same.

We monitored the possible in-situ Raman spectroelectrochemical changes of the photoluminescence peak at 2258 cm^{-1} (1.68 eV; for the 633 nm laser excitation) which corresponds to the presence of silicon in the P-NCD film. As could be expected from the origin of this band from the region close to the Si substrate, i.e. far away from the possible influence of the electrolyte ions, this Raman peak exhibited no changes with the applied potential (see Figure S2).

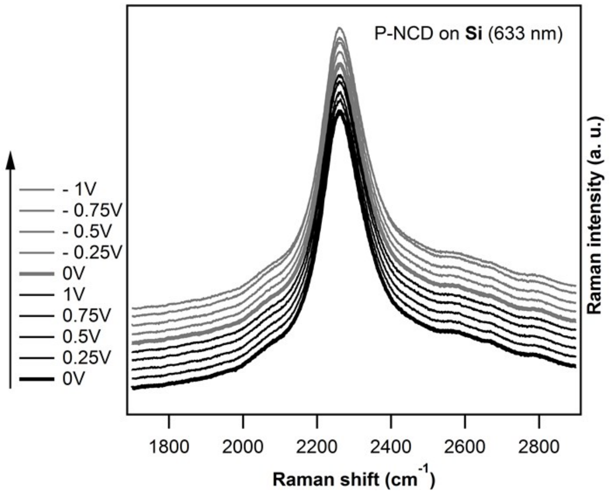

Fig. S2 In-situ Raman spectroelectrochemical data (at 633 nm excitation) of the Si-supported nanocrystalline phosphorus doped diamond (P-NCD) measured at cathodic (gray line) and anodic (black line) potentials. The spectra are offset for clarity, but the intensity scale is identical for all spectra. The supporting electrolyte was aqueous 0.5 M H_2SO_4. The electrode potentials are given versus the Ag/AgCl reference electrode. The measurement direction was from bottom to top.

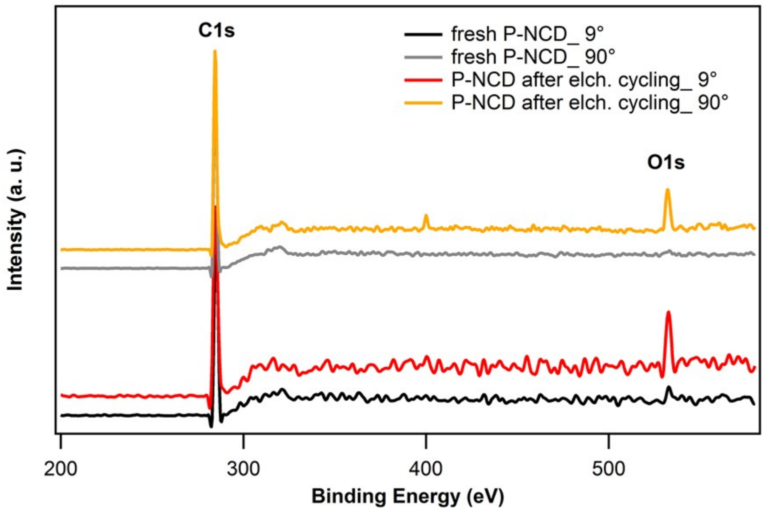

Fig. S3 XPS spectra of phosphorus doped nanocrystalline diamond films (P-NCD) with as-grown fresh surface (gray and black line) and of the P-NCD surface (yellow and red line) after 12 electrochemical cycles at large anodic (2.5 V vs. Ag/AgCl)/cathodic (-2.5 V vs. Ag/AgCl) electrochemical potentials obtained at different emission angles (9°and 90°). All spectra were normalized to the C1s peak intensity.

Tab. S1 Surface elemental XPS analysis at different emission angles (9°and 90°) on the phosphorus doped nanocrystalline diamond films (P-NCD) with as-grown fresh surface and of the P-NCD surface after 12 electrochemical cycles at large anodic (2.5 V vs. Ag/AgCl)/cathodic (-2.5 V vs. Ag/AgCl) potentials. The binding energy of C1s corresponds to the position of an envelope of several overlapping lines. For their deconvolution see Fig. S4. The sulfur impurity in electrochemically treated samples comes obviously from the used electrolyte solution. The same samples contain also nitrogen impurity which origin is unknown. The electrochemically treated samples exhibit significant enrichment of the surface by oxygen-containing species.

emission angle	sample	line	binding energy (eV)	Concentration (At %)
9°	**fresh P-NCD**	**C 1s**	285.2	97.7
		O1s	532.8	2.3
	P-NCD after elchem.cycling	**C 1s**	284.8	87.6
		O1s	532.4	9.3
		N1s	400.8	2.4
		S2p	168.4	0.7
90°	**fresh P-NCD**	**C 1s**	284.8	98.7
		O1s	533.2	1.3
	P-NCD after elchem.cycling	**C 1s**	284.4	89.6
		O1s	532.4	7.3
		N1s	400.0	2.8
		S2p	168.8	0.3

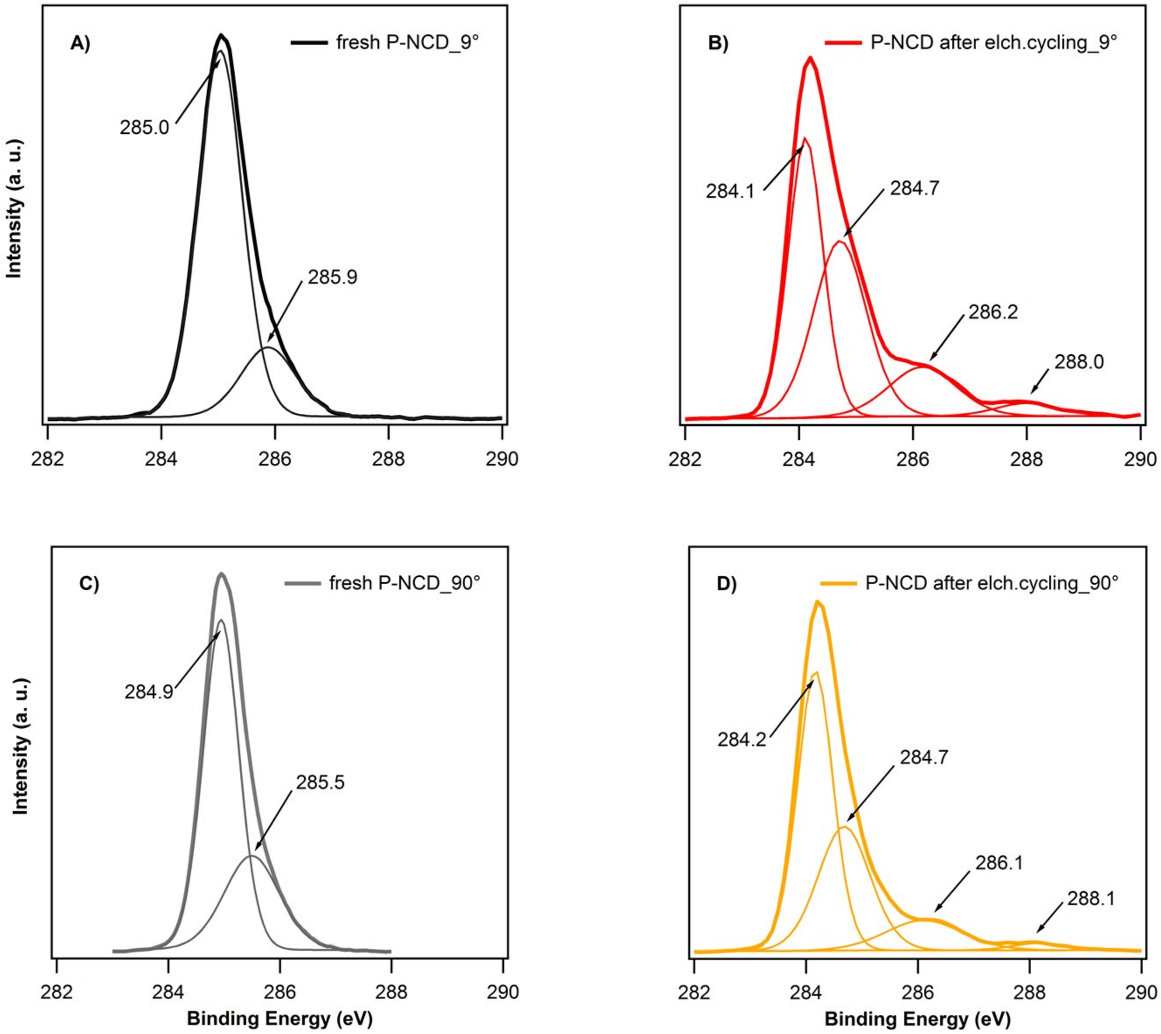

Fig. S4 Detailed XPS spectra in the region of C1s for the phosphorus doped nanocrystalline diamond film (P-NCD) with as-grown fresh surface (left) and of the P-NCD surface (right) after 12 electrochemical cycles at large anodic (2.5 V vs. Ag/AgCl)/cathodic (-2.5 V vs. Ag/AgCl) potentials obtained at different emission angles; A, B) – 9°and C, D) – 90°. The electrochemically treated samples exhibit significant enrichment of the surface by oxygen-containing species which are assigned to C-O (ca. 286 eV) and C=O (ca. 288 eV). We do not assign the splitting of the main line (near 285 eV), because various species, like C-H, sp^2-C and sp^3-C are assumed to be present here, and the corresponding changes in chemical shifts are too small to be clearly distinguished.

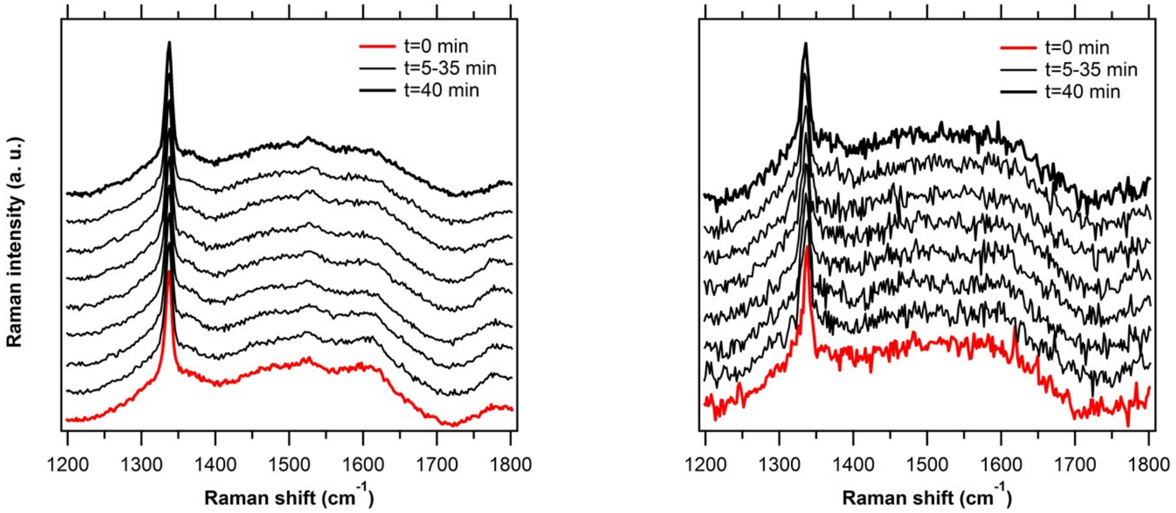

Fig. S5 Raman spectra of the phosphorus doped nanocrystalline diamond (P-NCD) deposited on Si substrate continuously irradiated by the 488 nm laser for 40 minutes (Raman spectra acquired each 5 minutes) in air (left) or in aqueous electrolyte solution 0.5M H_2SO_4 (right). The spectra are offset for clarity, but the intensity scale is the same.

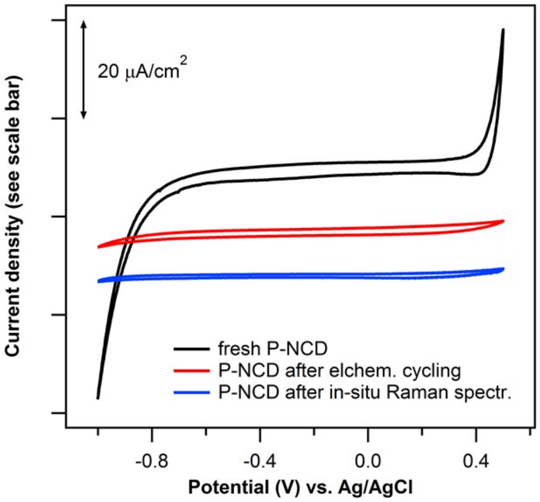

Fig. S6 Cyclic voltammograms of phosphorus doped nanocrystalline diamond (fresh P-NCD electrode – black line, P-NCD electrode after electrochemical cycling – red line, and P-NCD electrode after in-situ Raman spectroelectrochemistry – blue line). Electrolyte solution; aqueous 0.5M H_2SO_4. Scan rate; 100 mV/s. The main changes occur between the pristine sample (black line) and then after electrochemical treatment in dark (red line) – see also the main text. Subsequent changes upon simultaneous electrochemistry and laser irradiation are negligible (blue curve).