

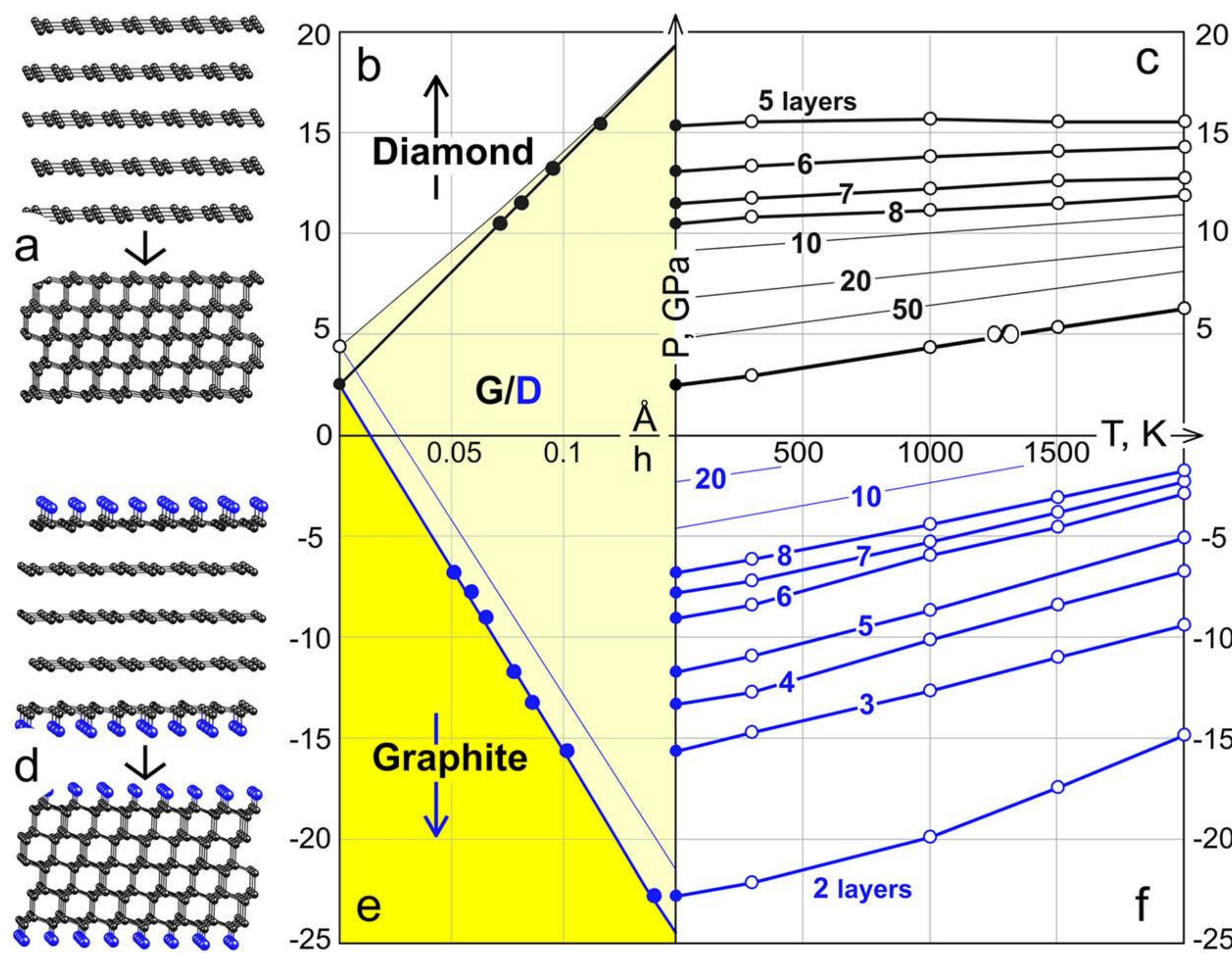
From multi-layered graphene to diamond film of nanometer thickness. Chemically induced phase transformation

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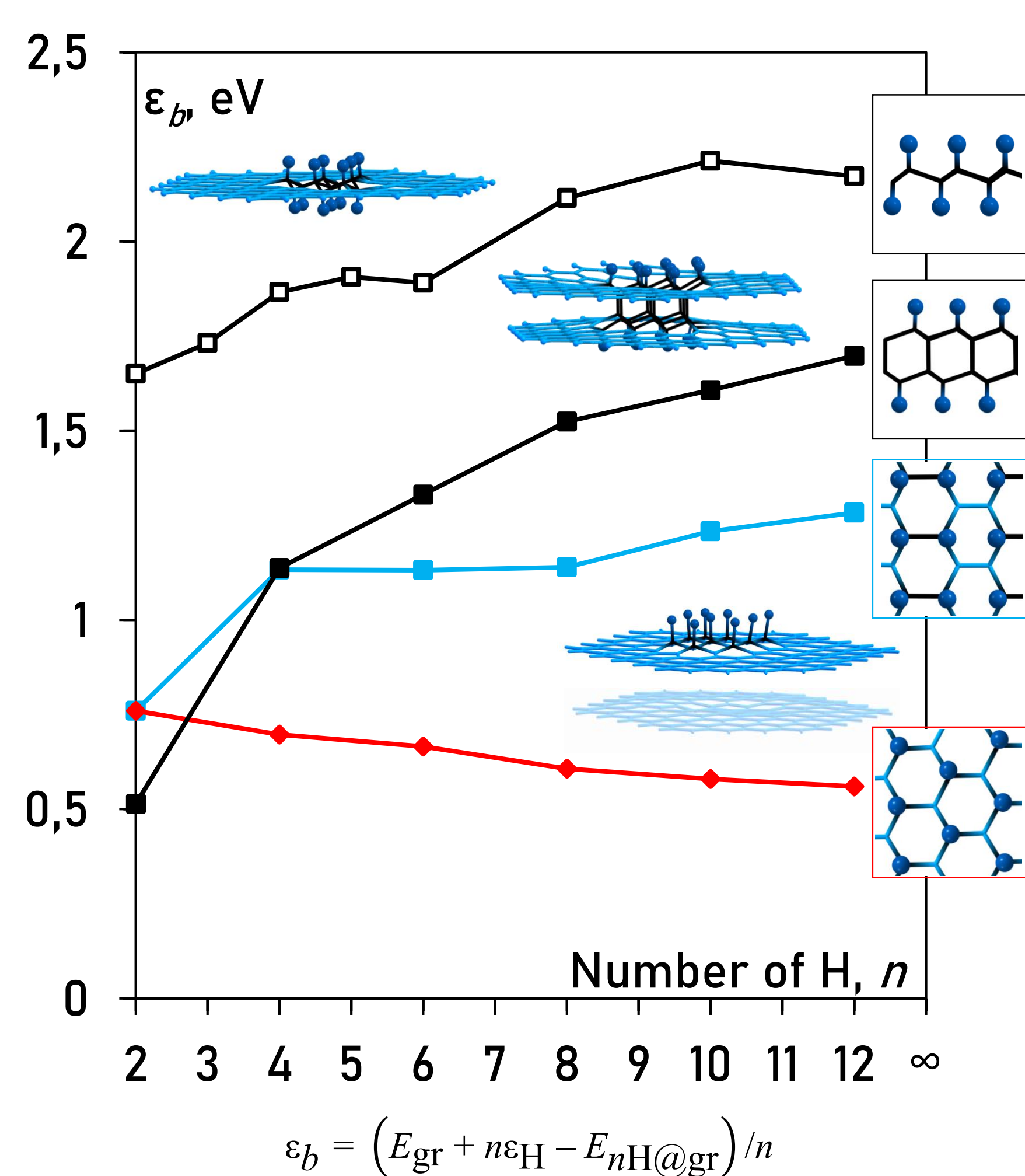
Thermodynamical approach

It is previously shown [2] that the total chemical adsorption (of atomic H or F) on the multilayer graphene surface facilitates the formation of diamond films: pressure of phase transition is reduced and formally turns negative, this becomes "chemically induced" phase transition.



A lot of questions remain unanswered like "why formation of diamond nanofilm was observed in experiment only for the case of bilayer films?", "what the mechanism of phase transition from graphene to diamane?", "what the final structure of the resulted diamond film and how it depends on the external conditions?". All of them require extension of the somewhere oversimplified theory and take into account a new phase nucleation process, describe the "reaction path" and nucleation barrier.

"Nano-thermodynamical" approach

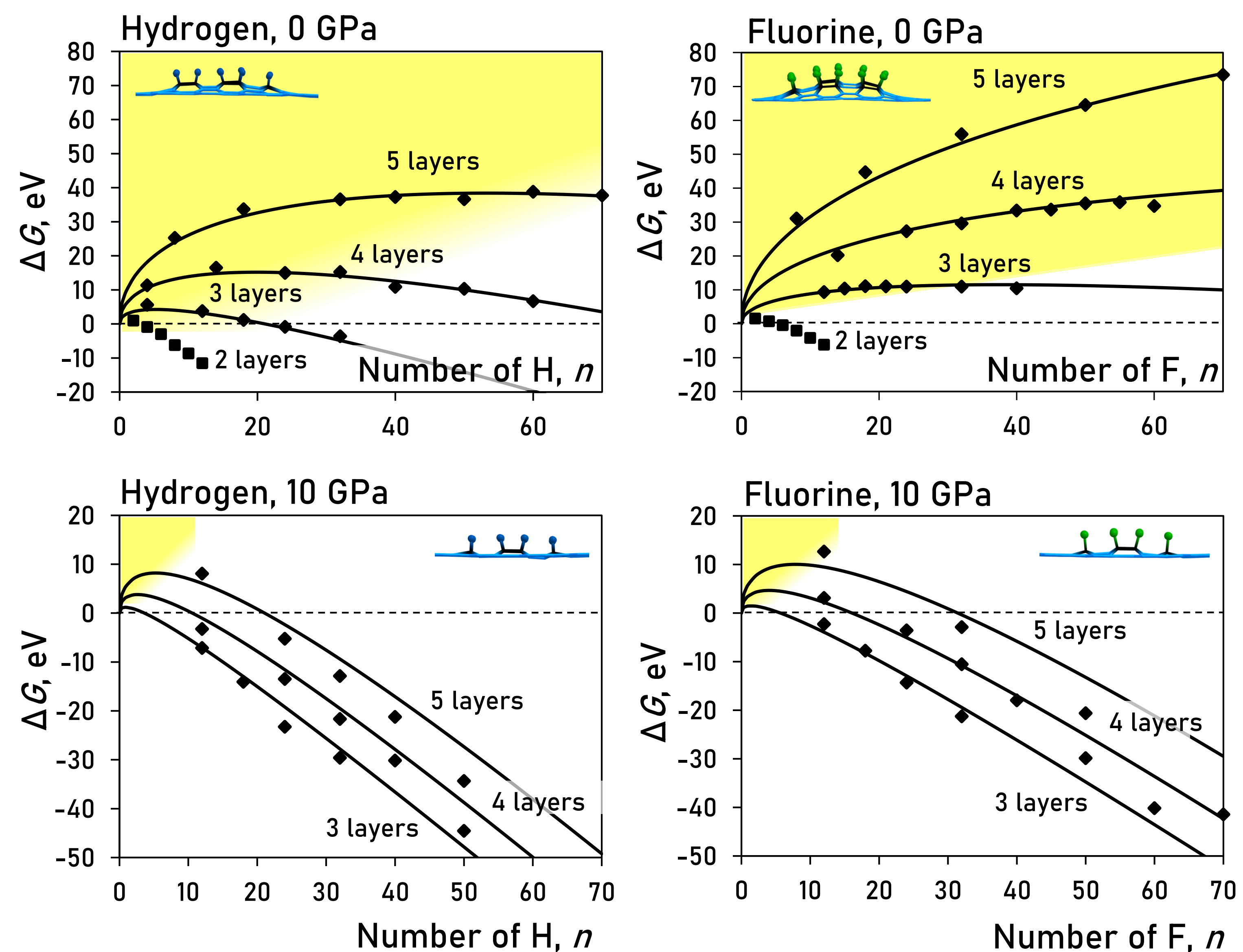


Atomistic picture reveals that the chemically induced phase transition occurs in specifically different ways for the single-, bi- and multilayer graphene cases. For the film of more than two layers the opposite surfaces do not "communicate" easily, so the hydrogenation starts from each one side without immediate bonding to underneath layers. The conformation of semi-hydrogenated single layer (which imitates the hydrogenated multilayer graphene without bounded layers) is not chair- but boat-type. Such FLG forms a new type of diamond film, hexagonal diamond, lonsdaleite (only if graphene stacking is AA').

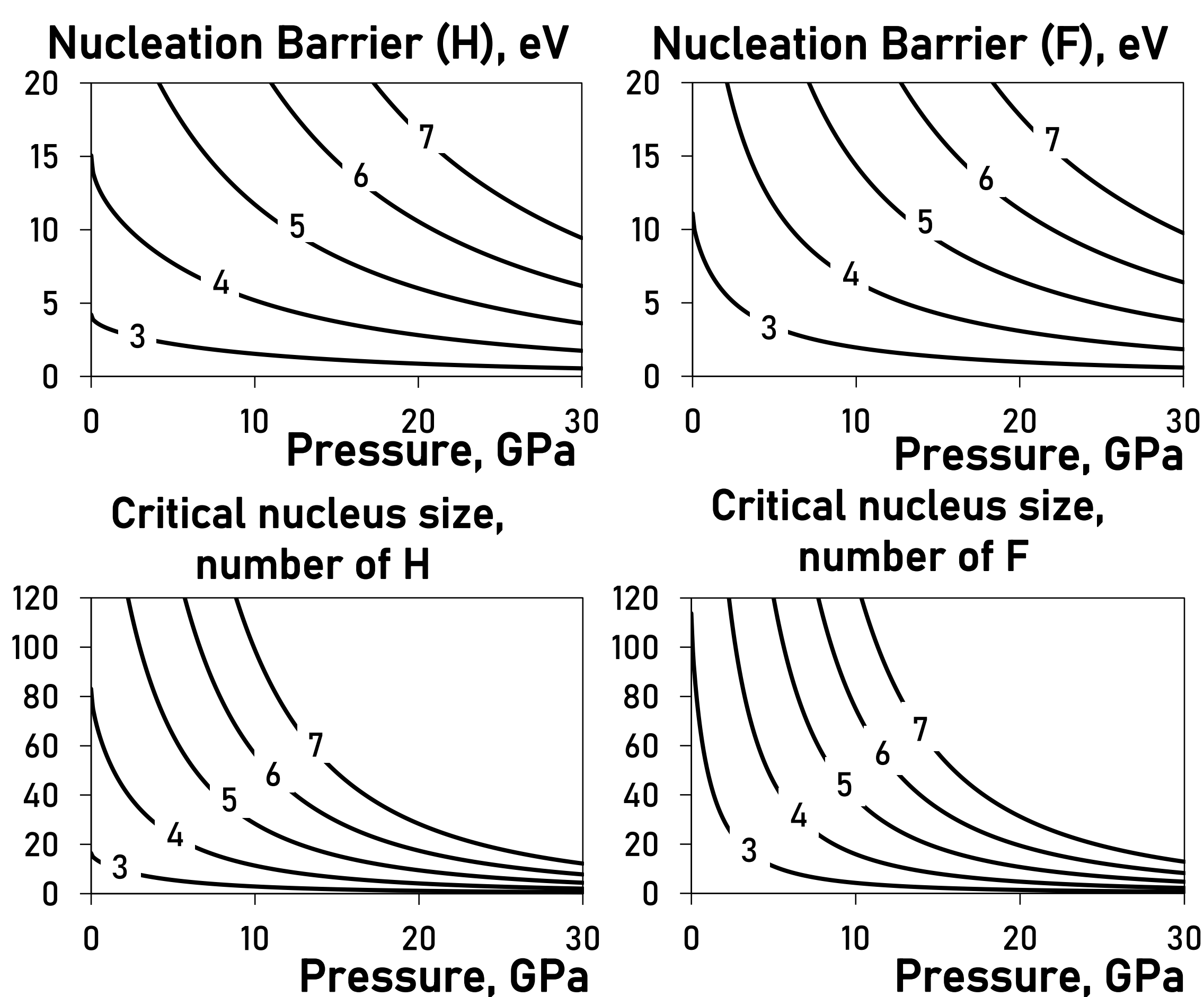
The nucleation barrier of the diamond phase formation can be determined by tracking the Gibbs free energy as a function of nucleus size, n . For FLG with n chemisorbed chemical species on both surfaces, the ΔG is between the sp^3 -diamond state of chemically bonded interior and the all sp^2 -graphene layers

$$\Delta G = \Delta E^{bulk}(N-2)n + \Delta E^{surf}_n + \gamma + p\Delta V,$$

The surface-chemical term ΔE^{surf} and pressure-driven terms are negative, representing the general trend of phase transition induced by surface chemisorption and external pressure. The uphill, positive terms all scale as $\sim N$ or even $\sim N^2$, and for large number of layers, ΔE^{bulk} term (phase-change energy, $\sim N$) and costly mismatch strain overcome the surface chemistry gains and thus prohibit the nucleation. For thicker FLG, both critical size of sp^3 -cluster and nucleation barrier increase rapidly.



The nucleation barriers for fluorination process are surprisingly higher than for the hydrogenation. Moreover, for the chlorine case simulations reveal that the ordered boat-conformation on the surface is entirely unstable. This is apparently due to the atomic radii of adatoms crowded in the compact cluster and causing more initial buckling of the surface layer



Combining pressure and chemistry allows to form diamane of more than two layers. While at $p = 0$, the barrier for F-case is much higher, with increasing pressure it falls faster and reaches that for H. If p suppresses the surface buckling, the behavior of fluorinated and hydrogenated films become similar [3].

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