# Basic processes in deposition and annealing of ta-C films as predicted by molecular-dynamics simulations

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# related publications:


R. Gago, M. Vinnichenko, H.U. Jäger, A. Yu. Belov, I. Jiménez, N. Huang, H. Sun and M. F.Maitz,
**Evolution of *sp2* networks with substrate temperature in amorphous carbon films: Experiment and theory,**
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A.Yu. Belov and H.U. Jäger,
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A.Yu. Belov and H.U. Jäger,
**Elastic constants of tetrahedral amorphous carbon films: The effect of intrinsic stresses,**
Surface & Coatings Technology **151-152** (2002) 128

A.Yu. Belov and H.U. Jäger,
**Calculation of intrinsic stresses in amorphous carbon films grown by molecular dynamics simulation: From atomic to macroscopic scale,**
Computational Materials Science **24** (2002) 154

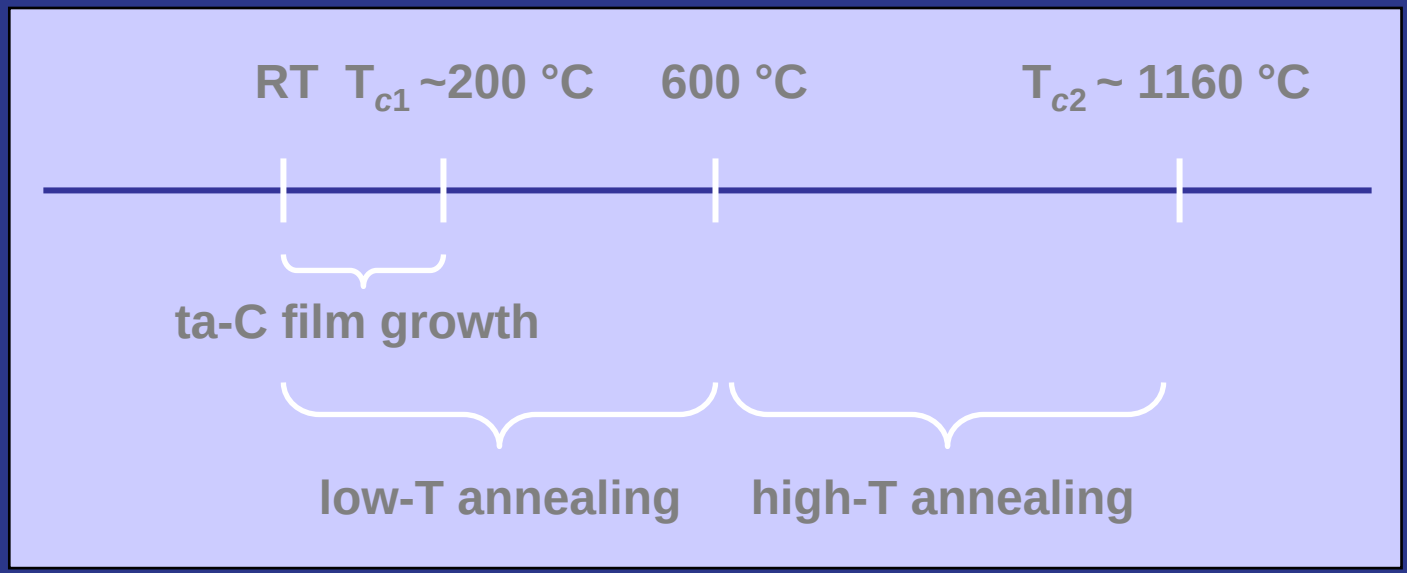
A.Yu. Belov and H.U. Jäger,
**Elastic properties of diamond-like amorphous carbon films grown by computer simulation of ion-beam deposition process,**
Mat. Res. Soc. Symp. Proc. **648** (2001) P6.53

H.U. Jäger and K. Albe,
**Molecular-dynamics simulations of steady-state growth of ion-deposited tetrahedral amorphous carbon films,**
J. Appl. Phys. **88** (2000) 1129

# Outline

- Introduction
  - temperature scales observed for the relaxation processes in ta-C
  - molecular-dynamics simulations
- Ion beam deposition simulations
  - film properties versus ion energy and substrate temperature
  - potential energy per bulk atom
  - time-resolved dynamics of film formation
  - $sp^2$ clusters and rings
- Simulation of post-deposition thermal annealing
  - stress relief, atomic volumes of $sp^3$ atoms
  - transition from ta-C to graphitic C
- Conclusions

# Temperature scales found for the relaxation processes in ta-C




## Film deposition

- 200 °C transition from ta-C → graphitic C

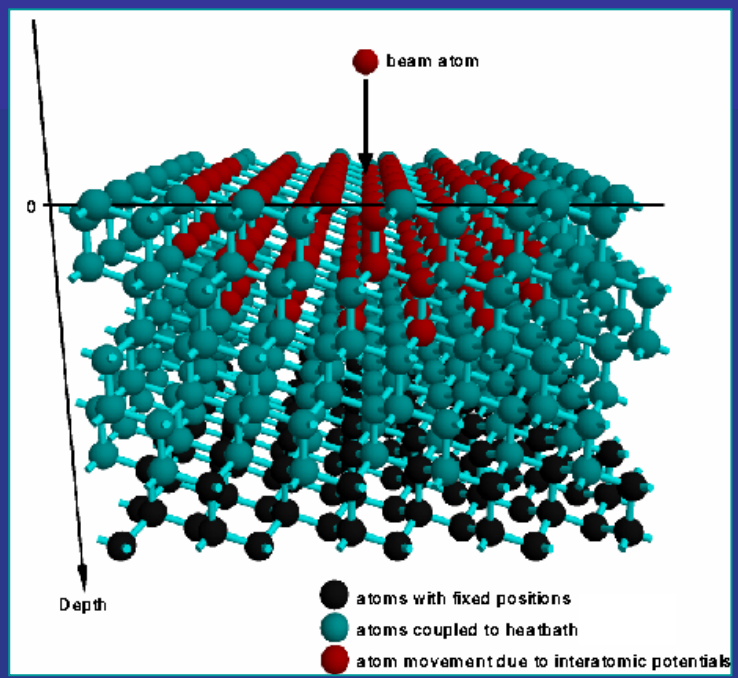
## Post-deposition thermal annealing

- 600 °C stress relief
- 1160 °C transition from ta-C → graphitic C

# Molecular-dynamics ion beam deposition simulations

Classical molecular dynamics - numerical solution of the classical equations of motion; time steps initially 0.05 - 0.15 fs

Empirical many-body potential of Brenner (for hydrocarbons, parameter set I) with increased C-C interaction range ( $R$, $S$ = 1.7, 2.0 Å ===> 1.95, 2.25 Å )




Simulation cell (initial stage)

1200-5000 impacts

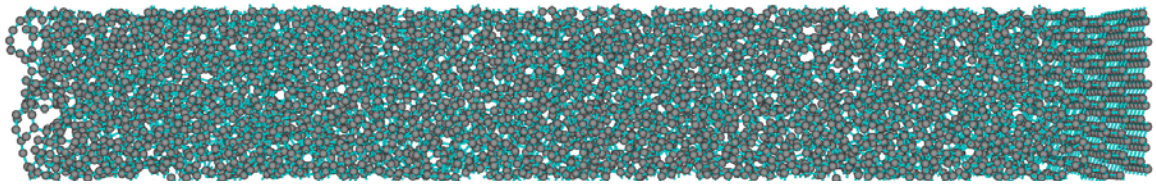
$E_{ion}$ = 10-80 eV, $T_s$ = 100-900 K

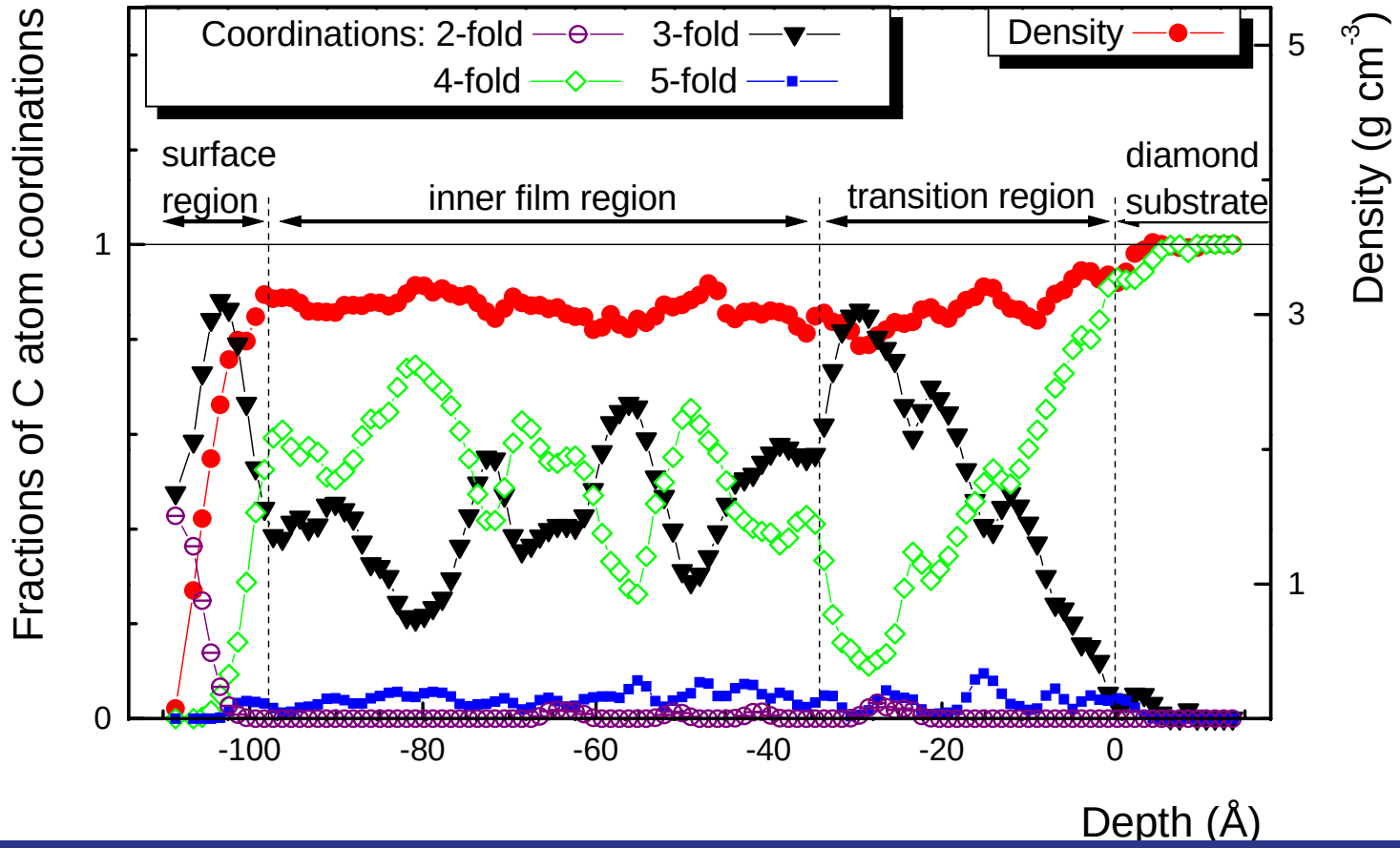
15 ps relaxation between impacts

Periodic boundary conditions for lateral directions

The „green“ atoms are coupled to a heat bath with $T = T_s$ (Berendsen method).

# MD deposition simulations: Depth profiles across a film





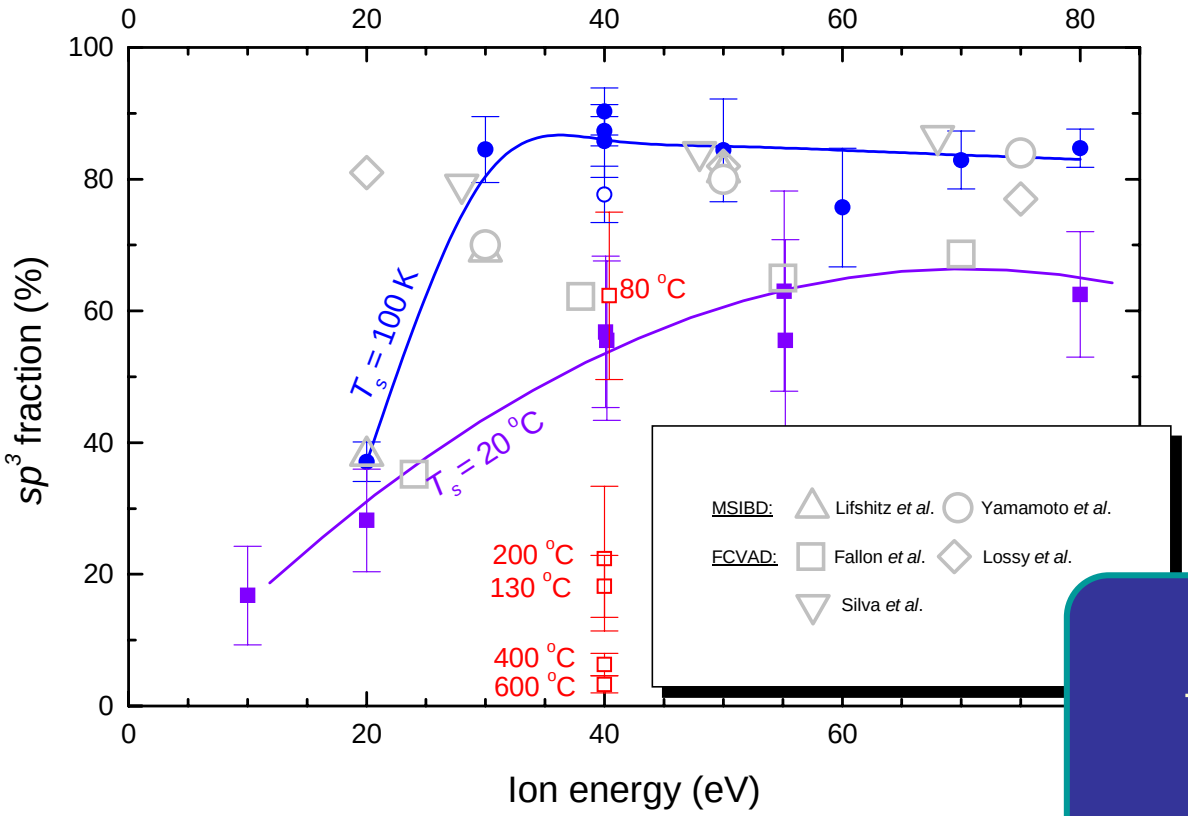

$E_{ion}$ = 40 eV

$T_s$ = 20 °C

5000 imp.

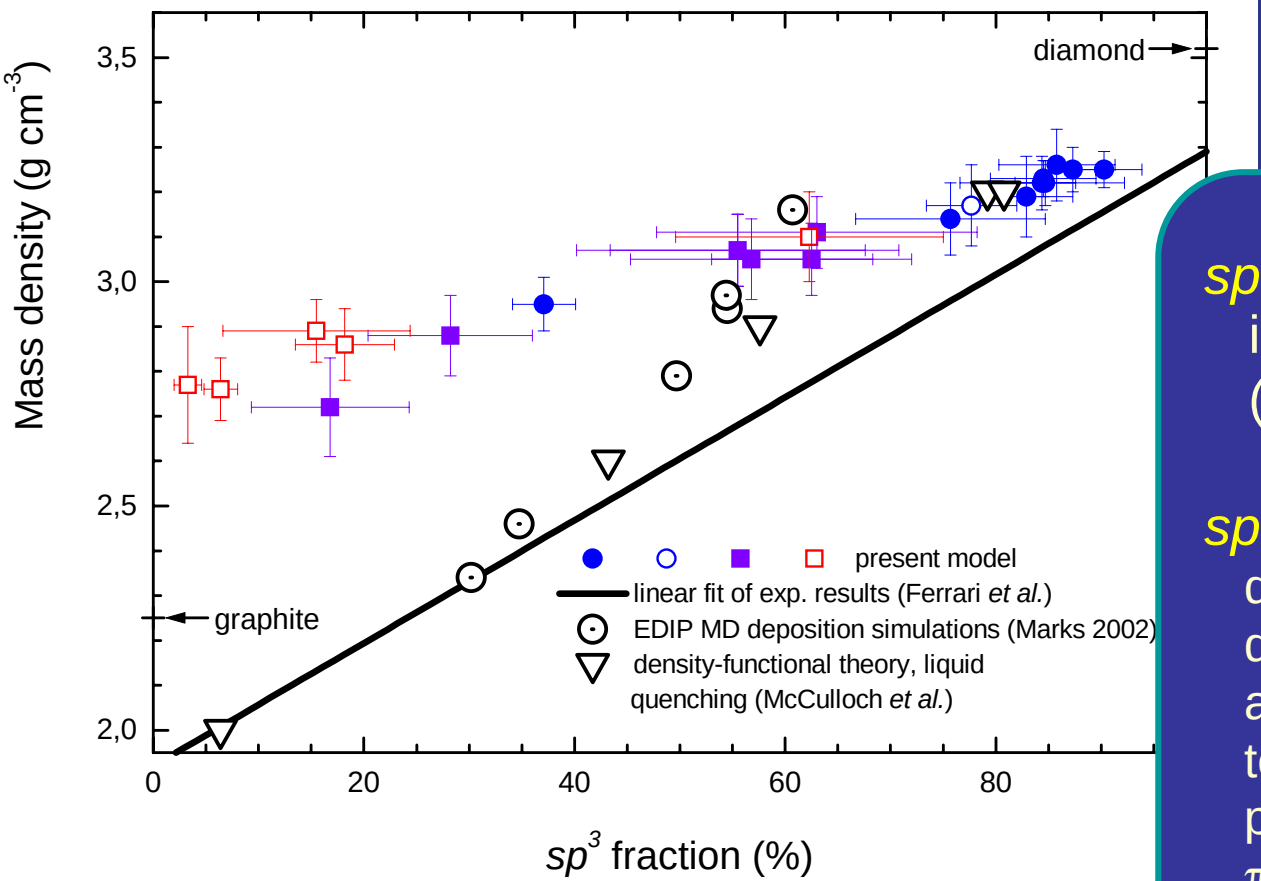
sputtered:
74 x C,
4 x $C_2$ ,
1 x $C_3$

# $sp^3$ fraction vs. ion energy and substrate temperature, simulation of the transition temperature $T_{c1}$




Sharp transition
ta-C ⇒ graphitic C
at $T_{c1}$ ~ 100 °C
( $E_{ion}$ = 40 eV )

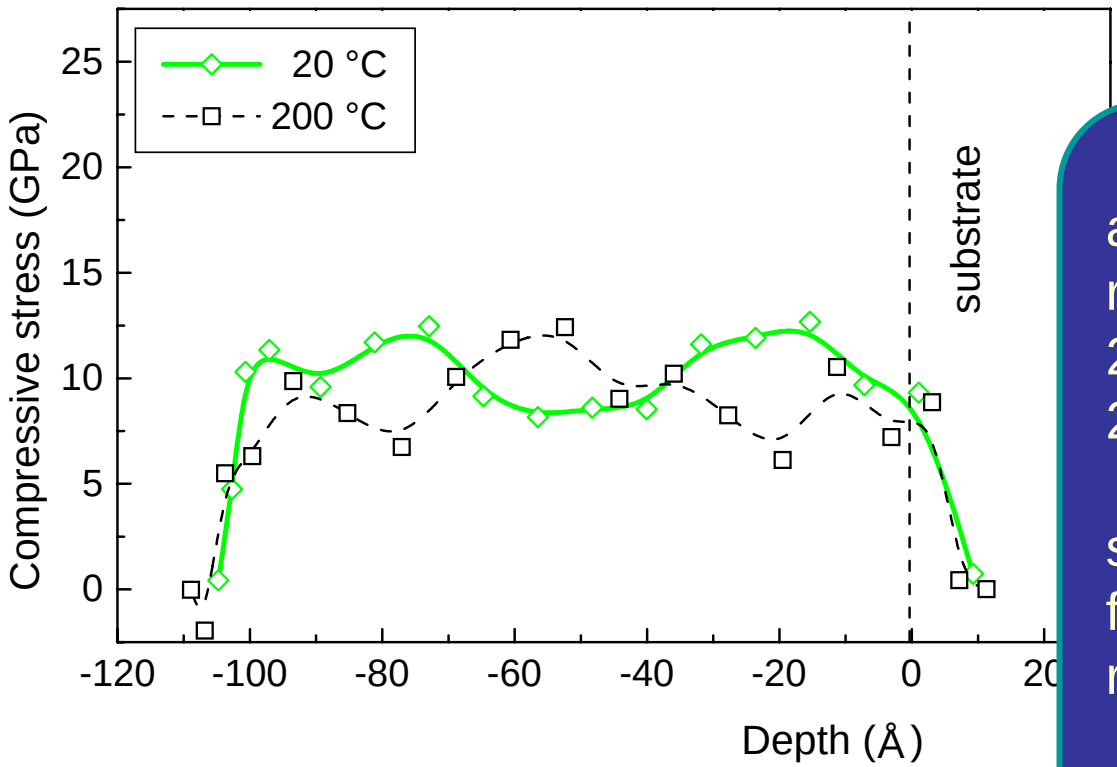
# Correlation of density and $sp^3$ fraction




$sp^3$ > 50% (ta-C):
in line with other models (and exp. data)

$sp^3$ < 50% (graphite-like):
density too large, due to the absence of adequate long-range terms in the empirical potential (non-bonded $\pi$ repulsion)

# Depth profile of intrinsic stress below and above the transition temperature $T_{c1}$



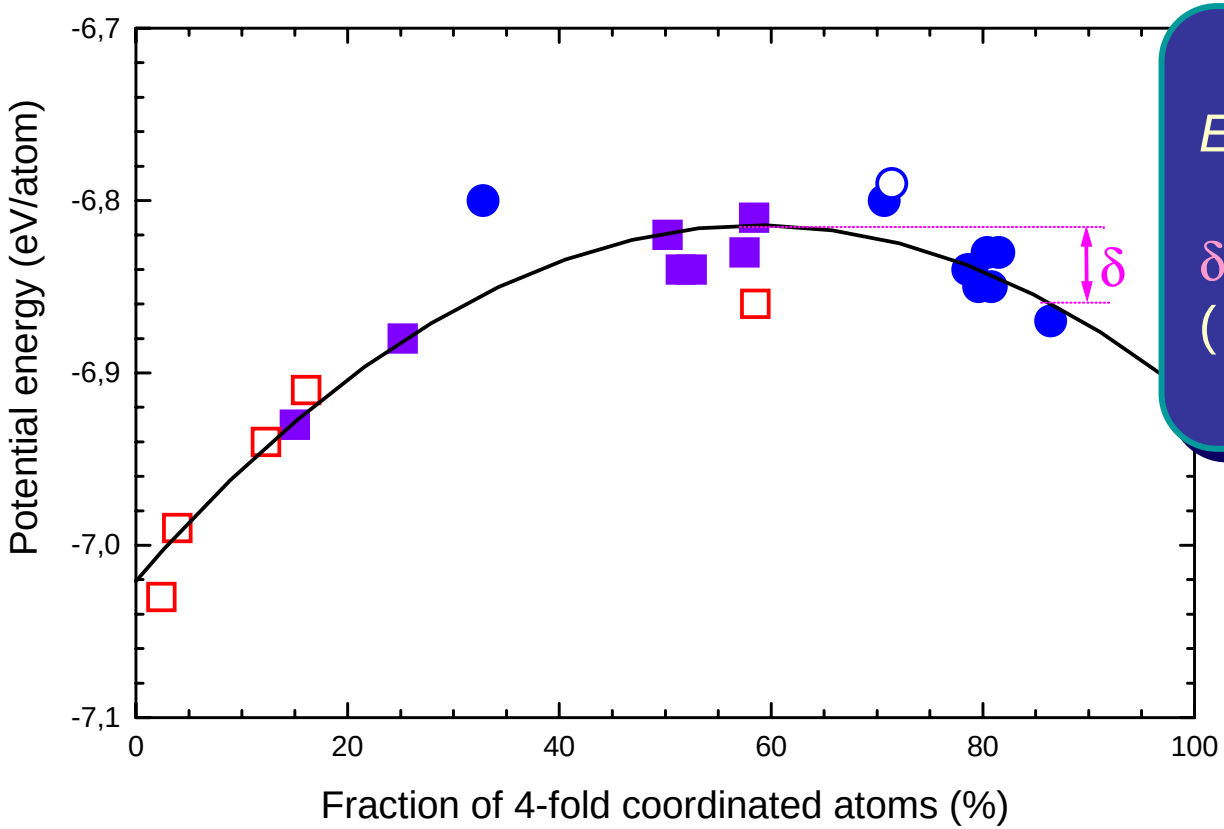

$E_{ion}$ = 40 eV

averaged over inner film region:
20 °C $\sigma$ = - 10.0 GPa
200 °C $\sigma$ = - 8.2 GPa

stress reduction (by 18%) follows exactly the density reduction

exp.: reduction by ~50%

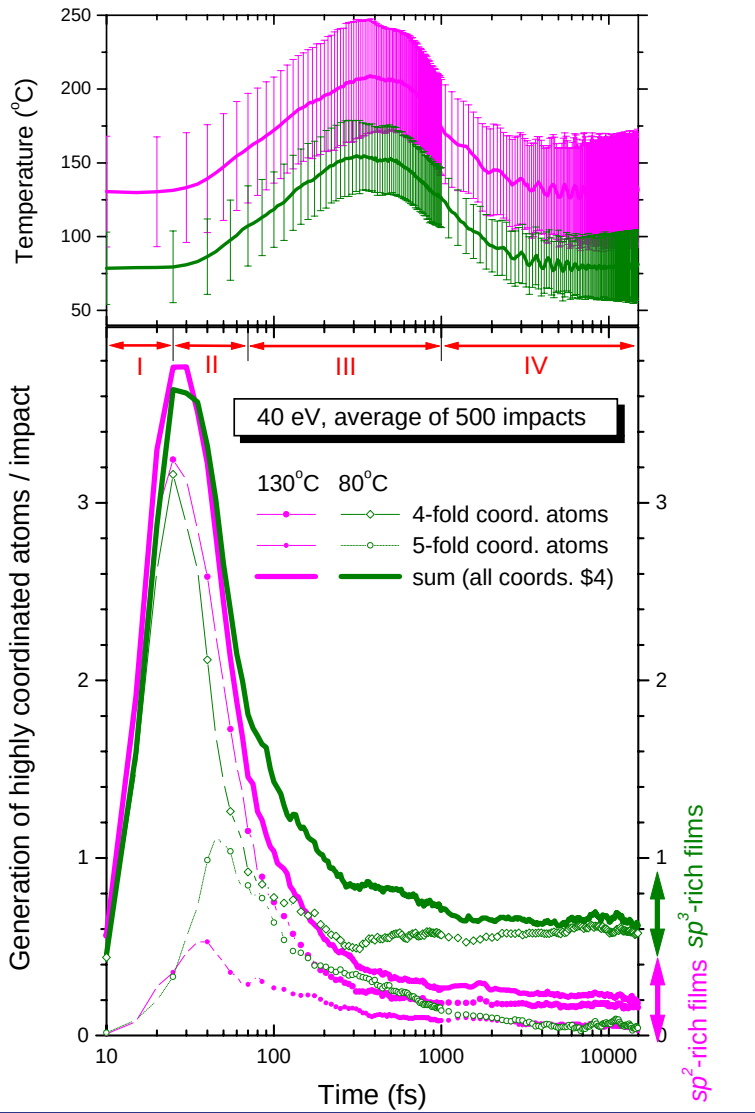
# Average potential energy per bulk atom




$E_P$(85% $sp^3$ ) ➲ $E_{P,max}$

δ ~ 0.04eV
( *i.e.* 400 K or 130 °C)

# Time-resolved dynamics of the film formation




Cell temperature and formation of highly coordinated atoms after a 40 eV $C^+$ ion impact for

$T_s$ = 80 °C (below $T_{C1}$) and 130 °C (above $T_{C1}$)

Time periods for basic processes:

(I) Subplantation ( t = 0-25 fs; $\rightarrow$ 20 eV )

(II) Stopping ( <2 eV ) and temperature-independent relaxation ( t = 25-70 fs )

(III) Temperature-dependent relaxation ( t = 70-1000 fs )

(IV) Temperature-driven stabilization ( t > 1 ps )

# $sp^2$ cluster size distributions

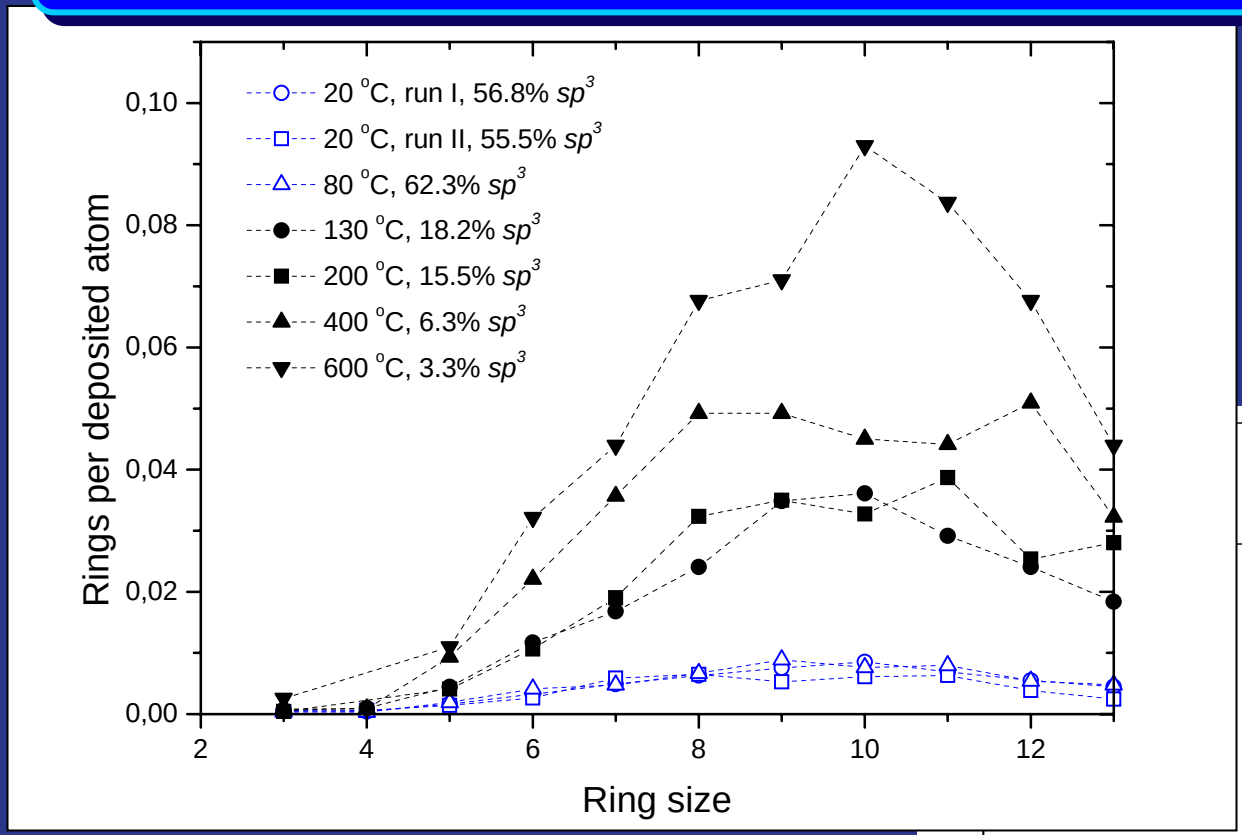
$E_{ion}$ = 40 eV

| $T_s$ (°C) | Ion impacts | Depos. atoms | $sp^3$ cont. (%) | $sp^2$ cluster size 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | Larger clusters (and location[b], if size > 50) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| -173 (run I) | 1200 | 1176 | 87.3 | 10 | 58 | - | 1 | 1 | 2 | 1 | - | - | 52 (tr), 160 (sr) |
| -173 (run II) | 1200 | 1175 | 90.3 | 11 | 53 | - | 1 | 2 | 1 | - | - | - | 199 (sr) |
| -173 (run III) | 1200 | 1180 | 85.8 | 14 | 72 | 1 | 1 | - | - | 1 | - | - | 158 (sr) |
| 20 (run I) | 5000 | 4915 | 56.8 | 32 | 176 | 5 | 1 | 3 | 2 | 1 | 1 | - | 28,30, 1836(wf) |
| 20 (run II) | 5000 | 4916 | 55.5 | 46 | 191 | 5 | 4 | 3 | 1 | 2 | - | 2 | 14,23,24,34, 1541 (wf) |
| 80 | 3200 | 3147 | 62.3 | 10 | 127 | 2 | 3 | 1 | 1 | - | 1 | - | 273(itr),782(sir) |
| 130 | 3200 | 3156 | 18.2 | 6 | 54 | 1 | 1 | 2 | - | - | - | - | 27, 2157 (wf) |
| 200 | 5000 | 4886 | 15.5 | 3 | 49 | - | - | - | - | - | - | - | 3790 (wf) |
| 400 | 1200 | 1178 | 6.3 | 3 | 13 | 1 | - | - | - | - | - | - | 988 (wf) |
| 600 | 1200 | 1183 | 3.3 | 1 | 8 | - | - | - | - | - | - | - | 1133 (wf) |

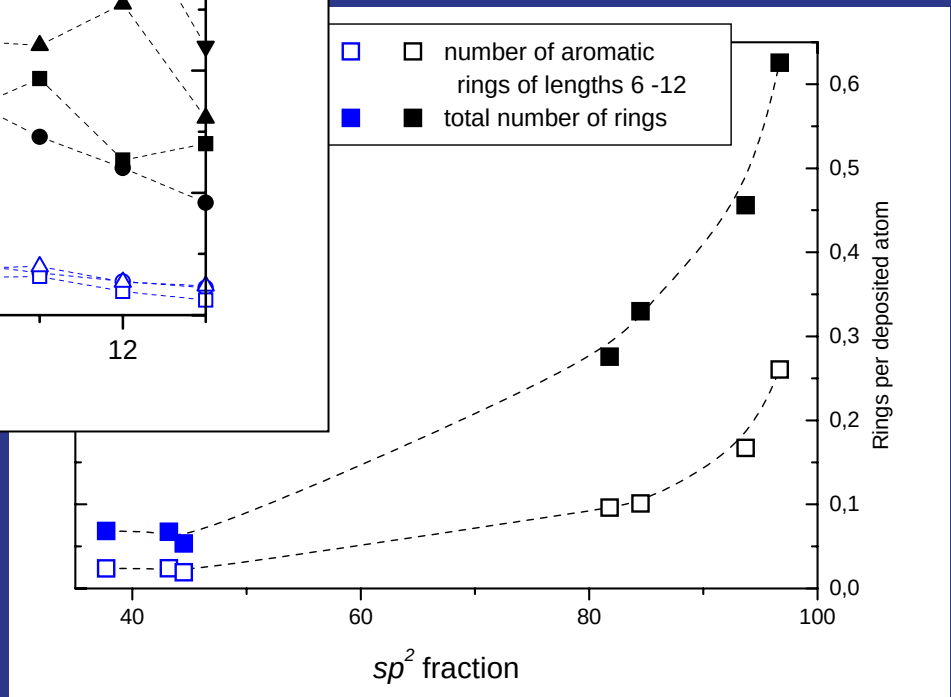
[b] tr - transition region near substrate, sr - surface region, wh - through the whole film, itr - from inner film region to transition region, sir - from surface to inner film region.

- Small clusters: pairs of $sp^2$ hybrids are prefered.
- $sp^2$ networks throughout the whole film (with rings!) - only for $sp^3$ fractions < 60-70%.

# $sp^2$ ring size distributions




for comparison with exp. data, see contr. of Jäger, Belov, Gago *et al. to* DIAMOND 2004 conf.




❒ pronounced increase of ring numbers for $sp^2$ fraction >80%

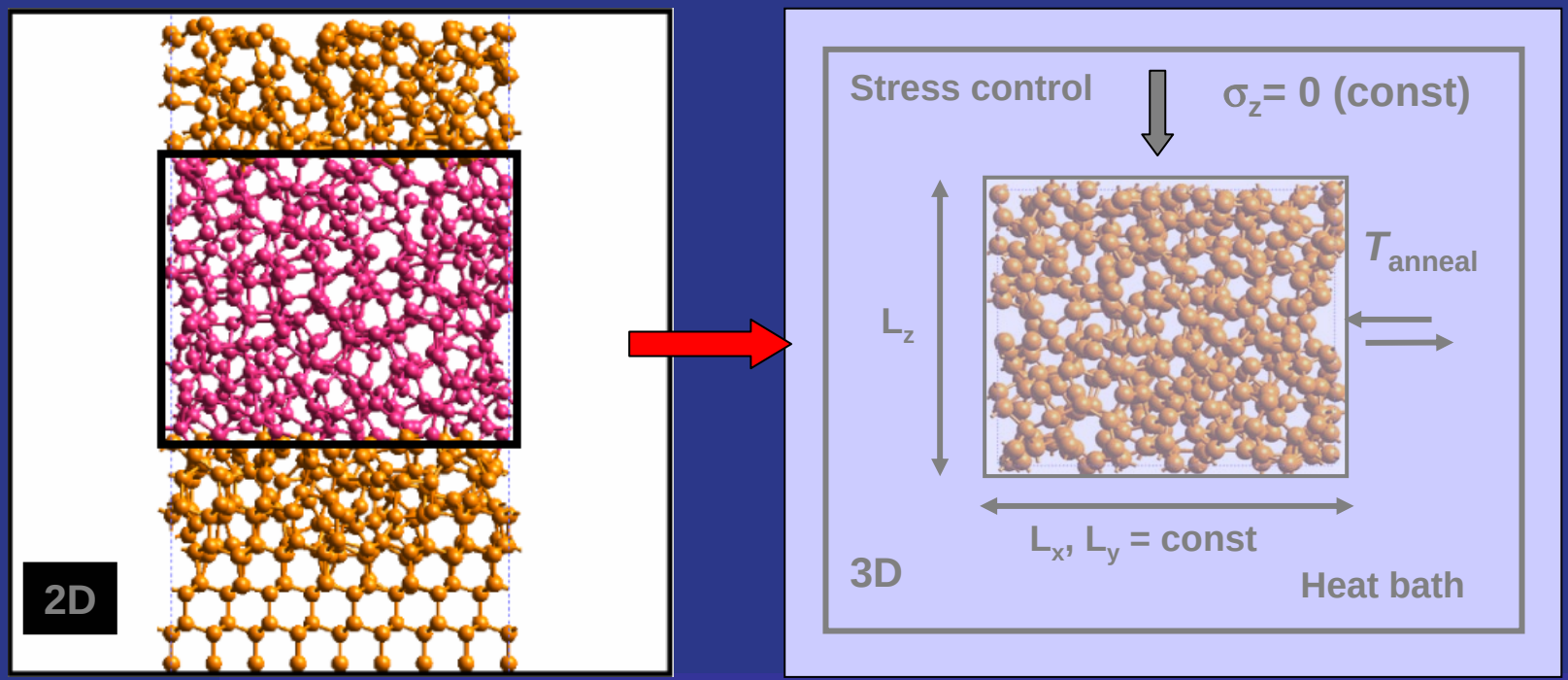
# MD thermal annealing simulations*

Heating schedule 300 K => $T_{anneal}$ => 300 K => 0 K

Annealing time $t_{anneal}$ = 1.1 ns ( = 8x10$^6$ $\Delta t$ )

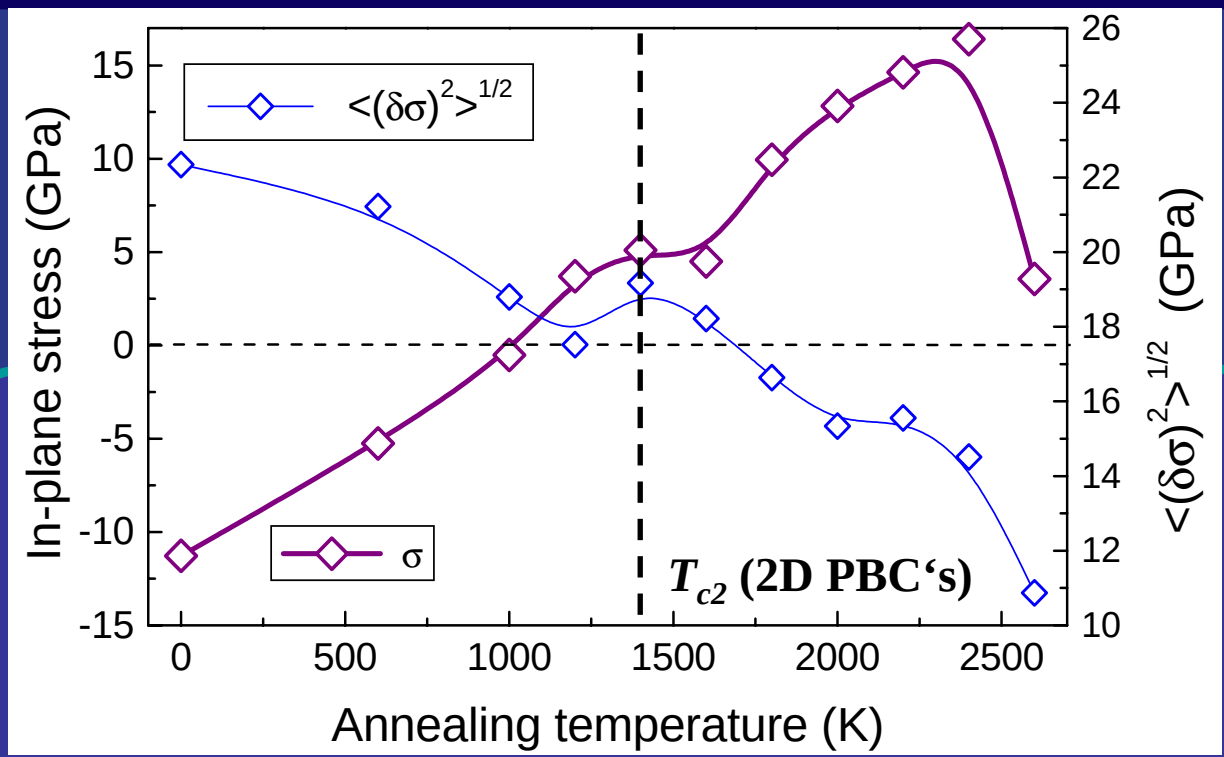
* for further results, see contr. of Belov and Jäger *to* DIAMOND 2004 conf.

## Periodic 3D models of 'bulk' ta-C:




Berendsen method to fix normal stress to $\sigma_z$ = 0 (optimization of $L_z$)

# Dependence of the in-plane stress on annealing temperature




ta-C : $\rho$ = 3.2 g/cm$^3$, 84% $sp^3$

3D PBC's

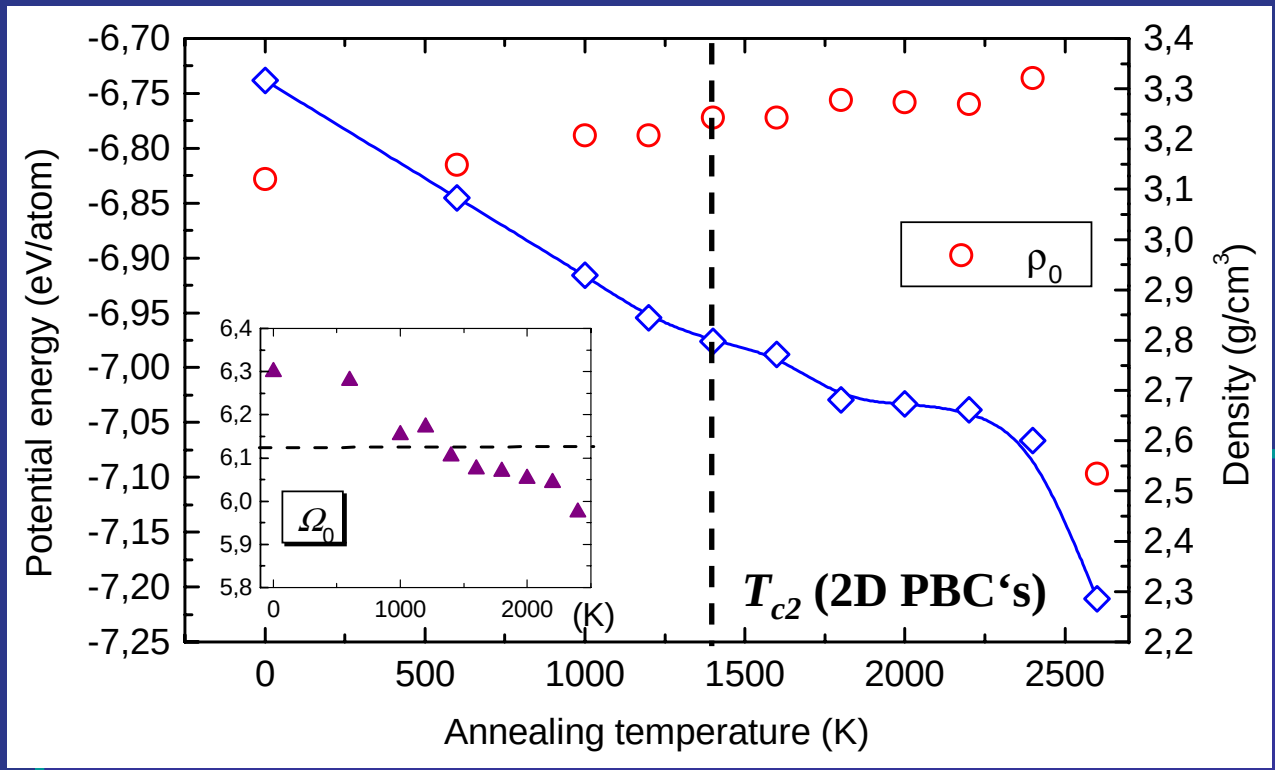
stress after cooling

- stress relief at ~ 1000 K.

(even tensile stress for $T_{anneal}$ > 1000 K, overestim. $\rho_{Graphite}$)

- The rms deviation of atomic-level stresses from their average value $\sigma$ illustrates a decrease in the structural disorder with $T_{anneal}$ .
- Stress relief is accompanied by a minor change in the short-range order. $sp^3$ content remains nearly constant.

# Densification of the $sp^3$ bonded constituent of ta-C




ta-C : $\rho$ = 3.2 g/cm³, 84% $sp^3$

3D PBC's

$\rho_0$ - density in the stress-free state

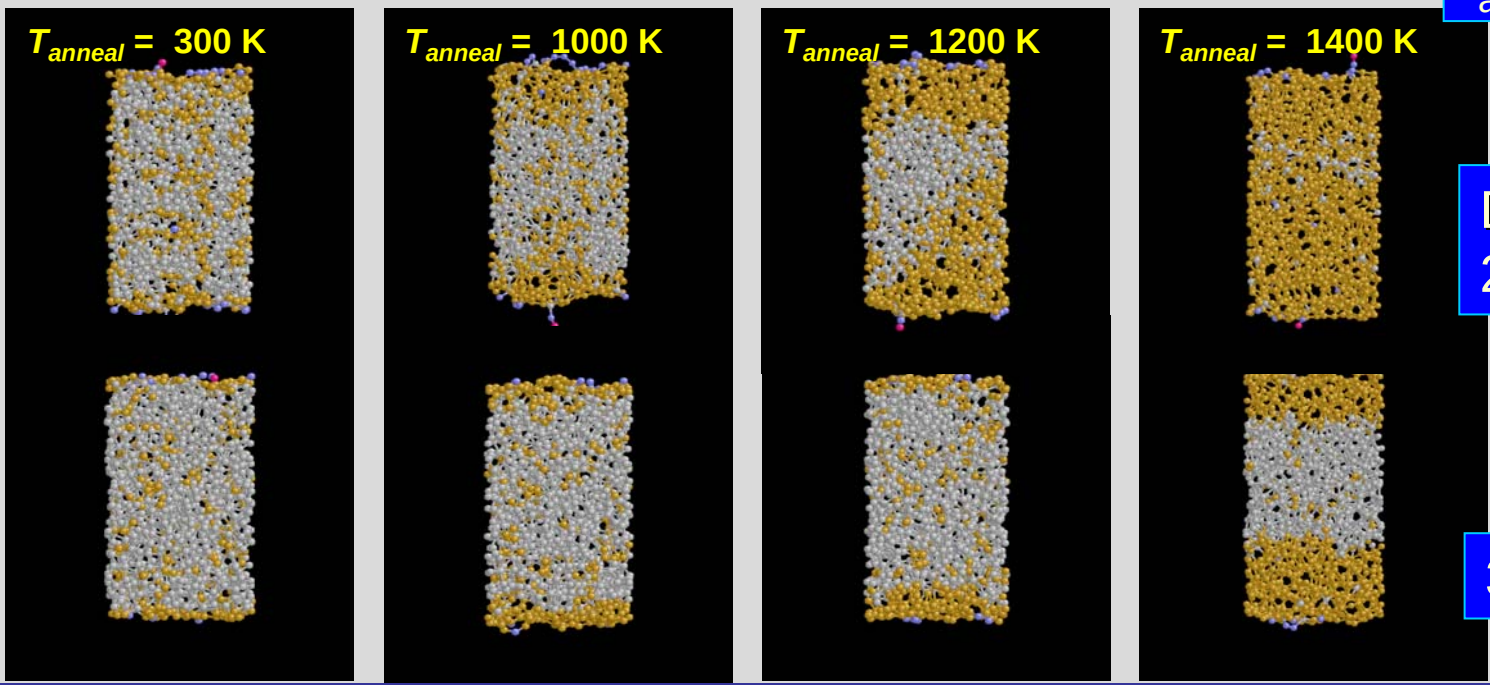
- The average atomic volume $\Omega_0$ of an $sp^3$-bonded atom in the stress-free state decreases with $T_a$.

- Upon annealing at 1000 K $sp^3$-bonded atoms do not expand as they would do in the case of pure elastic stress relief.
- Exp.: Reduction of the atomic volumes of $sp^3$ atoms - T.M. Alam *et al.*, PRB **67**(2003)245309

# Transition from ta-C to graphitic C (graphitization temp. $T_{c2}$ )

C coordinations: 1 2($sp^1$) 3($sp^2$) 4($sp^3$)

$t_{anneal}$ = 1.1 ns




Density
2.9 g/cm$^3$

3.2 g/cm$^3$

Annealing simulations with 2D PBC's for two ta-C slabs of different density

- Transformation from ta-C to graphitic C starts in the $sp^2$-rich surface layer, estimation : $T_{c2} \leq$ 1400 K ($\rho$ = 3.2 g/cm$^3$) and $T_{c2} \leq$ 1200 K ($\rho$ = 2.9 g/cm$^3$) .
- Annealing simulations with 3D periodic boundaries conditions provide higher values of $T_{c2}$ .

# Conclusions

## Deposition simulations

A transition from ta-C to graphitic carbon occurs within a narrow temperature range of ~50 $^{o}$C, confirming the experimentally observed sharp dependence of the $sp^3$ content on substrate temperature. At the time scale of about 0.5 ps the relaxation processes in growing films below and after $T_{c1}$ proceed differently, leading to ta-C or graphitic a-C.

Pairs of $sp^2$ hybrids are prefered in ta-C; pronounced increase of ring numbers for $sp^2$ fraction >80%.

## Annealing simulations

Low-temperature annealing simulations of ta-C with $sp^3$ ~ 84% :
A theoretical estimate for the stress relief temperature is ~ 1000 K. The stress relief is accompanied by a minor change in the short-range order, and a reduction of the atomic volumes of $sp^3$ atoms

In annealing simulations with 2D periodic boundaries the transformation from ta-C to graphitic C starts in the graphitic surface layer and sharply propagates into the bulk, graphitization temperature $T_{c2}$ ~ 1200-1400 K.