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En Sciences Pour l'Ingénieur

Amorphous-to-microcrystalline transition in a–Si:H under hydrogen-plasma

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Summary

- ☐ **Introduction**
- ☐ **Experimental setup**
- ☐ **Some results:**
  - ✓ **Crystallization of a-Si:H under H_2 plasma**
  - ✓ **Effects of doping on the amorphous-to-microcrystalline transition**
- ☐ **Conclusions**

Hydrogen in silicon based materials

- ☐ **µc-Si:H is an attractive material in large area applications :**
  - ✓ **Active material in photovoltaic devices.**
  - ✓ **Thin Film Transistors.**

- ☐ **Understanding the growth mechanism of µc-Si:H is essential for improving the device performances.**

Hydrogen in silicon based materials

❑ **Many ways to obtain μc-Si:H**

- ✓ **Thermal annealing (T~ 650 °C).**
- ✓ **Laser annealing (T~ 1400 °C).**
- ✓ **Metal-induced crystallization (T~ 500 °C).**
- ✓ **Hydrogen plasma exposure (T < 300 °C).**

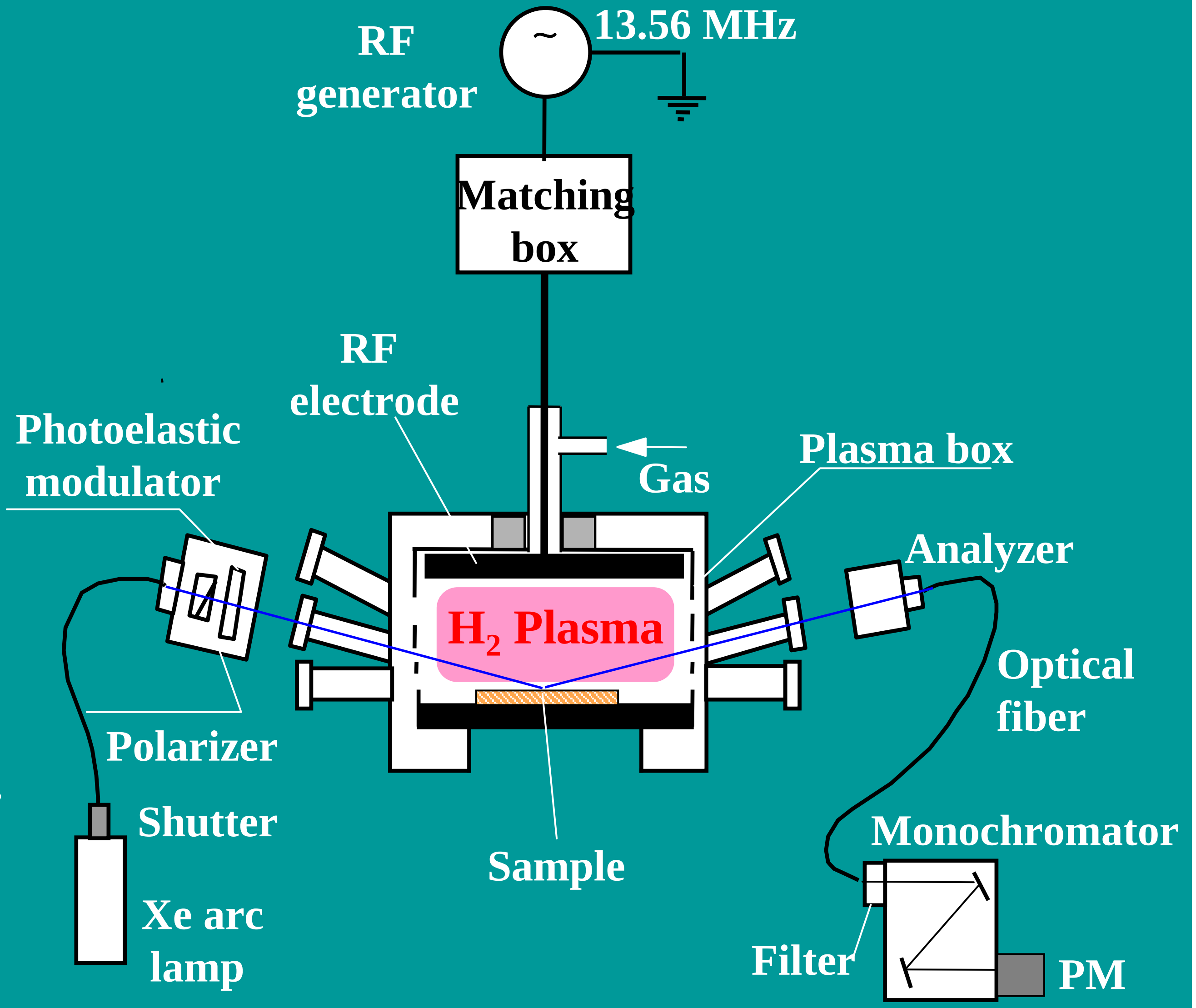
Hydrogen in silicon based materials

❑ **Complex interaction H → Si**

- ✓ **Surface :**
  - **Adsorption and desorption**
  - **H abstraction**
  - **Etching of Si surface**
  - **…**
- ✓ **Bulk :**
  - **In-diffusion in the Si network**
  - **Breaking of weak Si–Si bonds**
  - **Insertion in Si–Si bonds**
  - **…**

Experimental setup

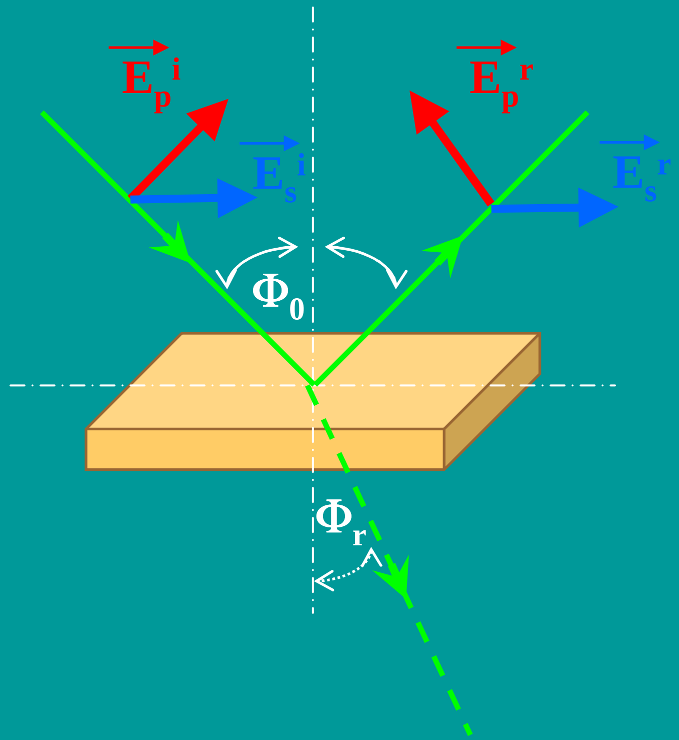
- ☐ H_2 plasma treatment just after deposition.
- ☐ *In situ* detection of H-induced modifications.



Experimental setup

- Sensitive and non-disruptive optical technique based on the change in the polarization of the incident light :

$$\rho = \frac{r_p}{r_s} = \tan\Psi \; \exp\left(i\,\Delta\right)$$

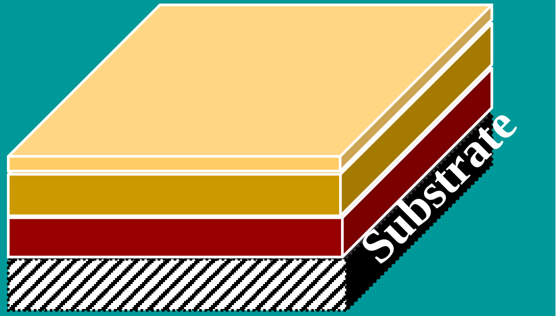


- We measure the pseudo-dielectric function < ε > of the whole sample :

$$\langle\varepsilon\rangle = \langle\varepsilon_1\rangle + j\,\langle\varepsilon_2\rangle = \sin^2(\Phi_0) + \left(\frac{1-\rho}{1-\rho}\right)^2 \sin^2(\Phi_0)\,\tan^2(\Phi_0)$$

Experimental setup

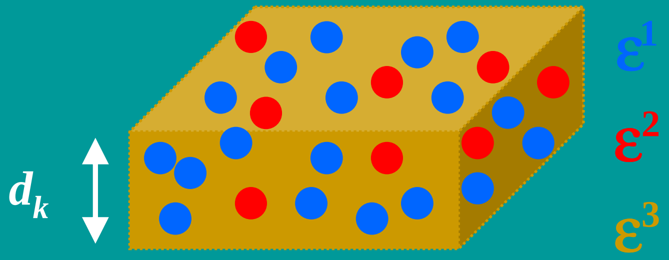
☐ **Modeling of the optical de la response :**
Multilayer system (d_k , ε^{eff}).



☐ **Dielectric function ε^{eff} → Effective medium theory :**

$$\sum_k f_k \frac{\varepsilon^k - \varepsilon^{eff}}{\varepsilon^k - 2\varepsilon^{eff}} = 0$$

$$\sum_k f_k = 0$$

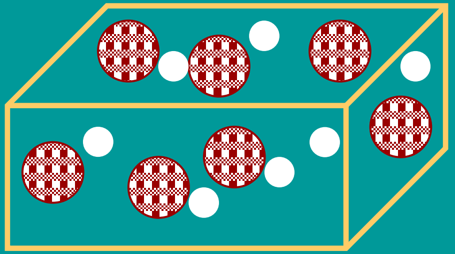


☐ **Dielectric function ε^k of each component :**
- **Experimental reference (measured, literature, …)**
- **Dispersion law (Tauc's Lorentz model for a semiconductor)**

Experimental setup

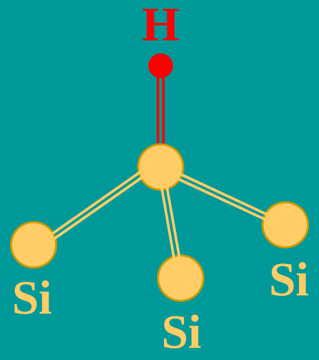
☐ **Microcrystalline silicon (μc–Si:H) :**

- **a-Si:H matrix : volume fraction f_a**
- **Crystallites : volume fraction f_c**
- **Void : volume fraction f_v**



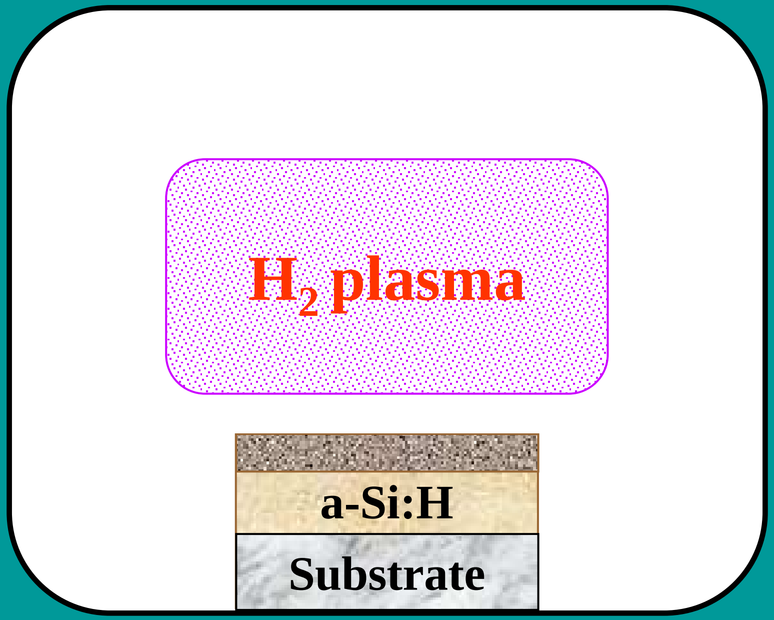
☐ **Hydrogen modified layer :**

- **Only bonded hydrogen contributes to the optical response.**
- **a-Si:H matrix : volume fraction f_a**
- **Excess of $Si–Si_3–H$: volume fraction f_H**

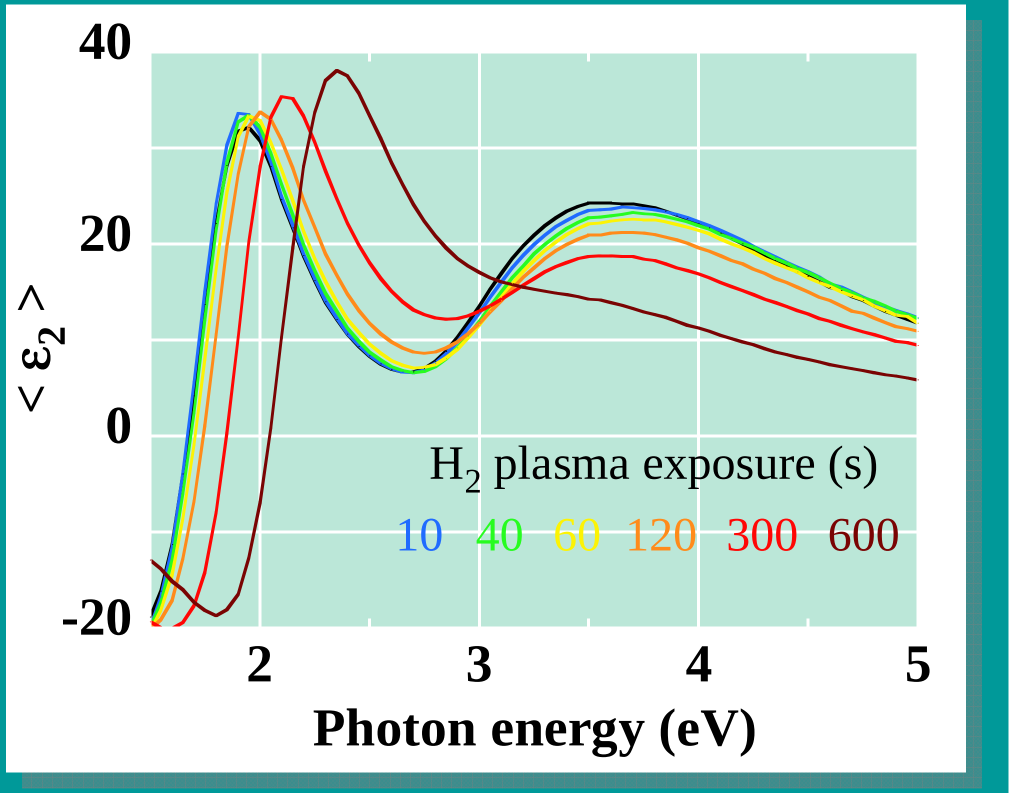


H-induced crystallization

- Can H **alone** induce crystallization of a-Si:H ?



Clean walls

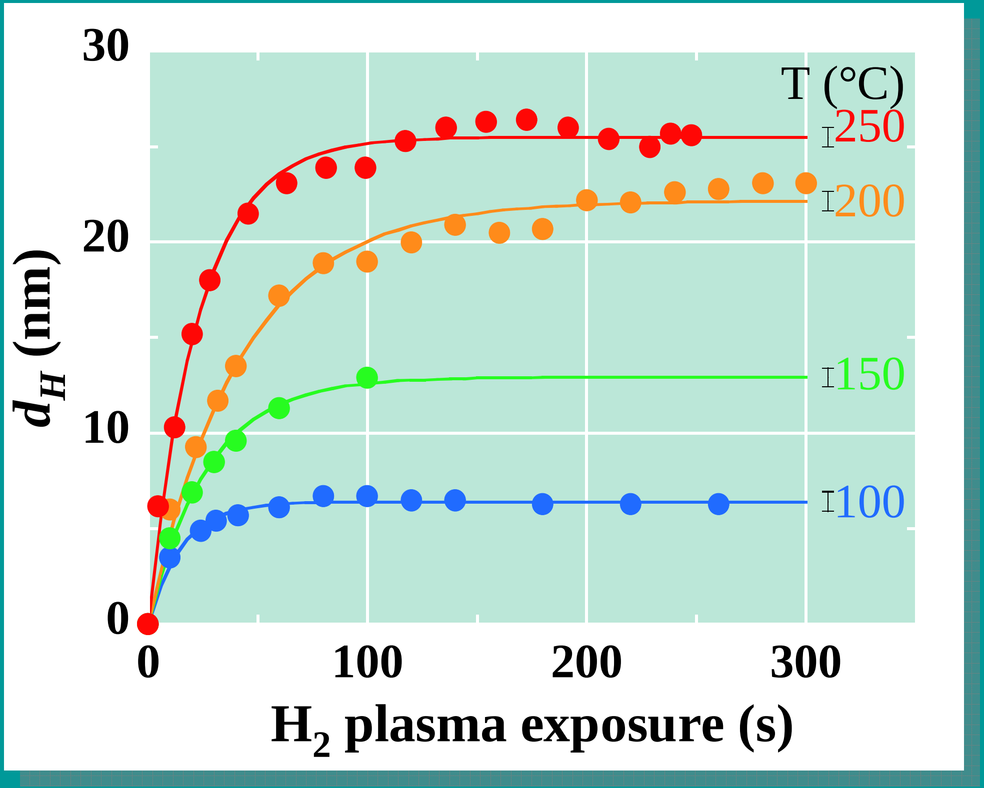


Etching of a-Si:H

H-induced crystallization

- H alone ⇒ etching of a-Si:H !!!
  - The formation of the H-rich layer : a competition between H insertion and diffusion and SiH_4 production (etching process at a rate r_e).

$$d_H(t) = d_H^{0}\left[1 - \exp\left(-\frac{t}{\tau}\right)\right]$$



  - The H-modified layer forms at a rate r_H.

$$r_H = \frac{d_H^{0}}{\tau}$$

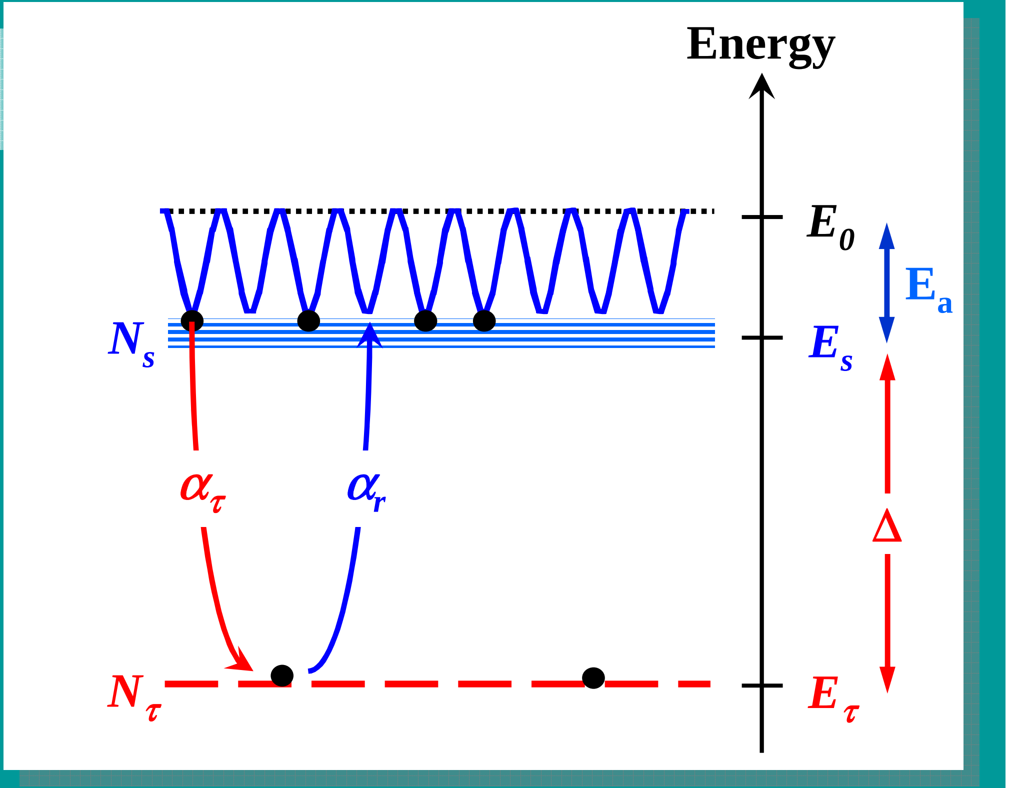
H-induced crystallization

- ☐ **H alone ⇒ etching of a-Si:H !!!**

- ☐ **Trap-limited diffusion of H**

$$D_H\ (\mathrm{cm^2s^{-1}}) = 2.7\ 10^{-11}\ exp(-0.22/kT)$$

$$N_\tau\ (\mathrm{cm^{-3}}) = 1.4\ 10^{13}\ exp(0.43/kT)$$



H-induced crystallization

❑ H alone ⇒ etching of a-Si:H !!!

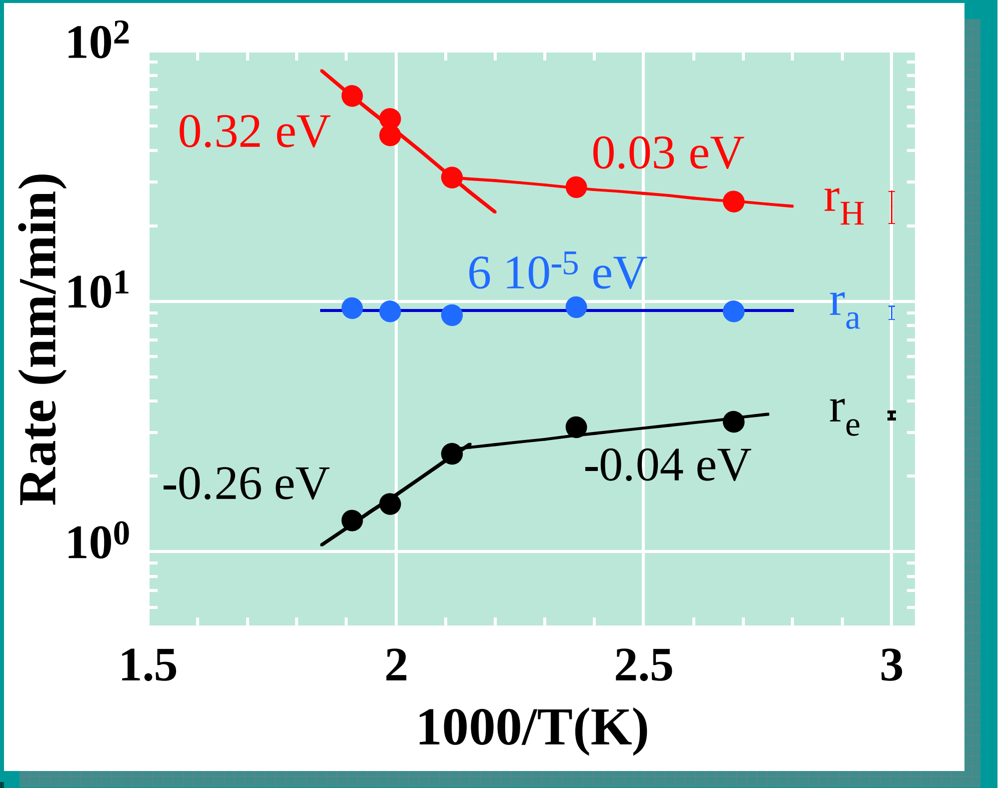
- The H-modified layer forms at a rate r_H.

$$r_H = \frac{d_H^{\,0}}{\tau}$$

- A particular temperature dependence at both sides of T = 200 °C of both r_H and r_e.

❑ The geometric average r_a rate remains constant :

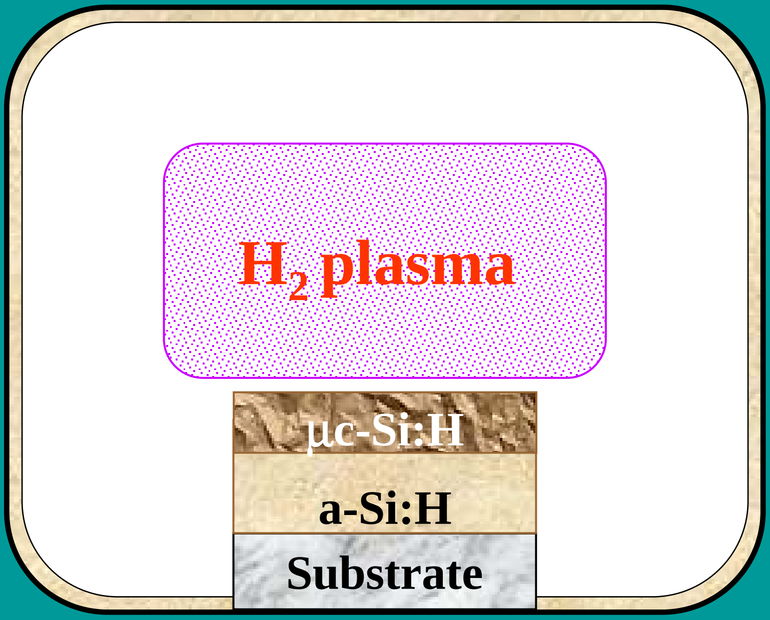
$$r_a = \sqrt{r_e r_a}$$



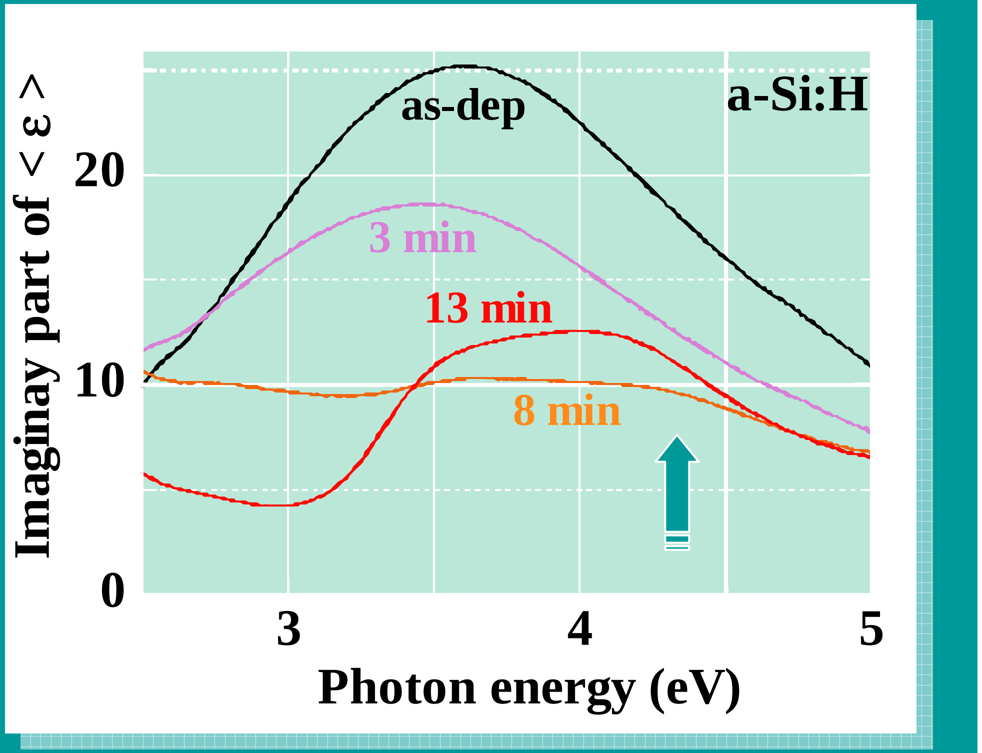
❑ Balance between hydrogen insertion and film etching : $(\mathrm{Si}-\mathrm{Si})_{\mathrm{weak}} + \mathrm{H}_{\mathrm{gas}} \leftrightarrows \mathrm{Si}-\mathrm{H} + \mathrm{SiH}_4$

H-induced crystallization

- H is essential but not suffiicient for the crystallization of a-Si:H.

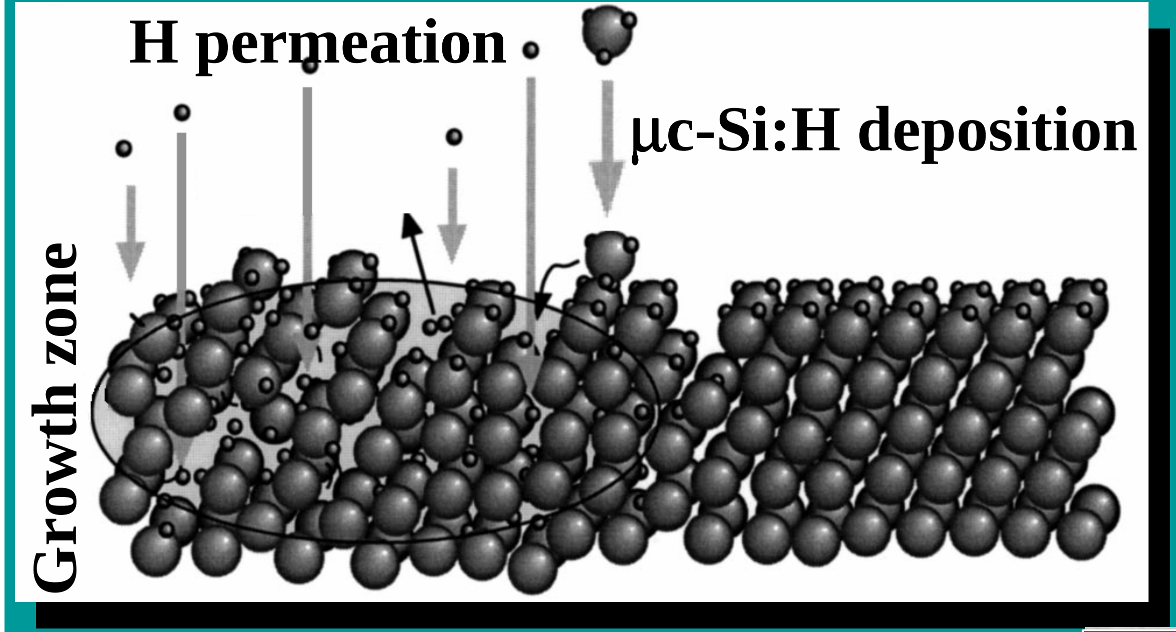


a-Si:H covered walls



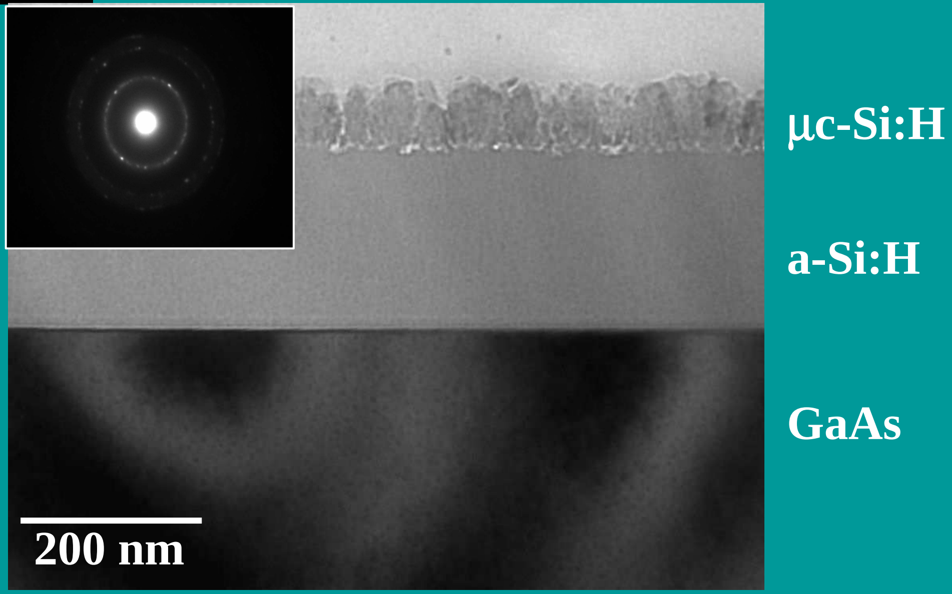
Growth of μc-Si:H

H-induced crystallization

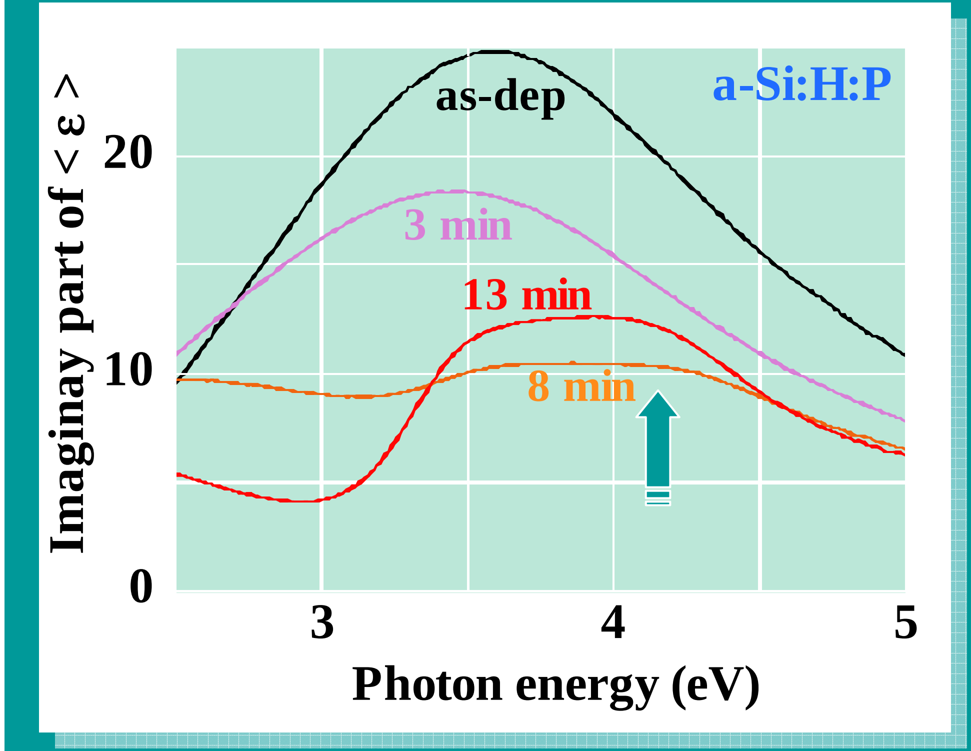


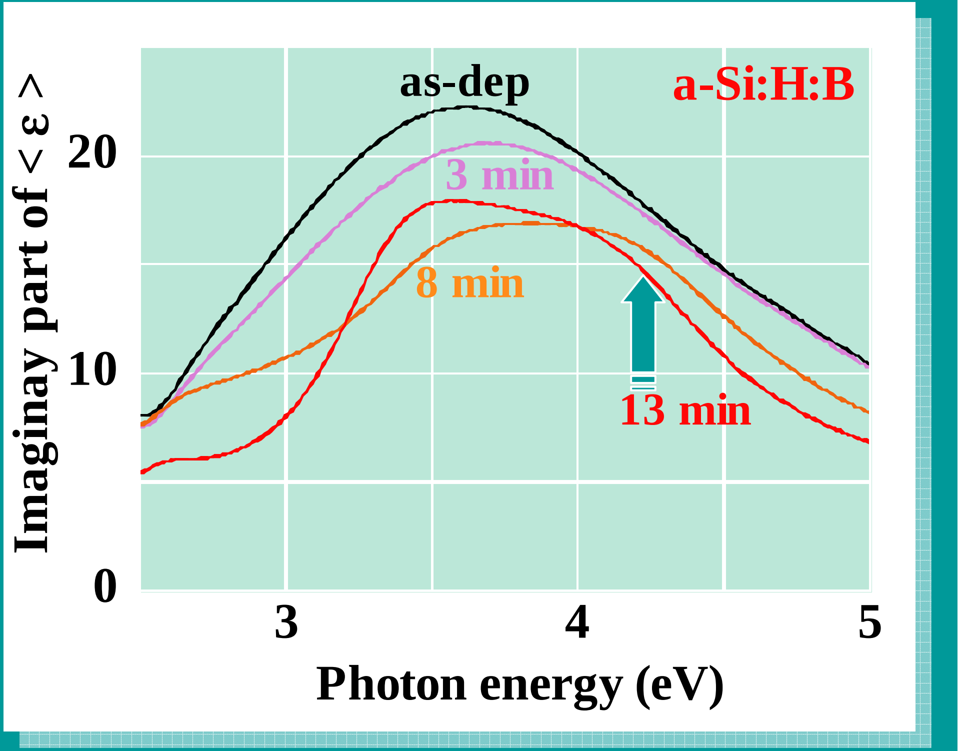
- ☐ H_2 plasma
  - 1 Torr H_2
  - 230 °C
  - 22 W RF power

- ☐ Chemical transport of Si radicals from the walls of the reactor provides conditions similar the deposition of μc-Si:H from silane diluted (< 1 %) in H.



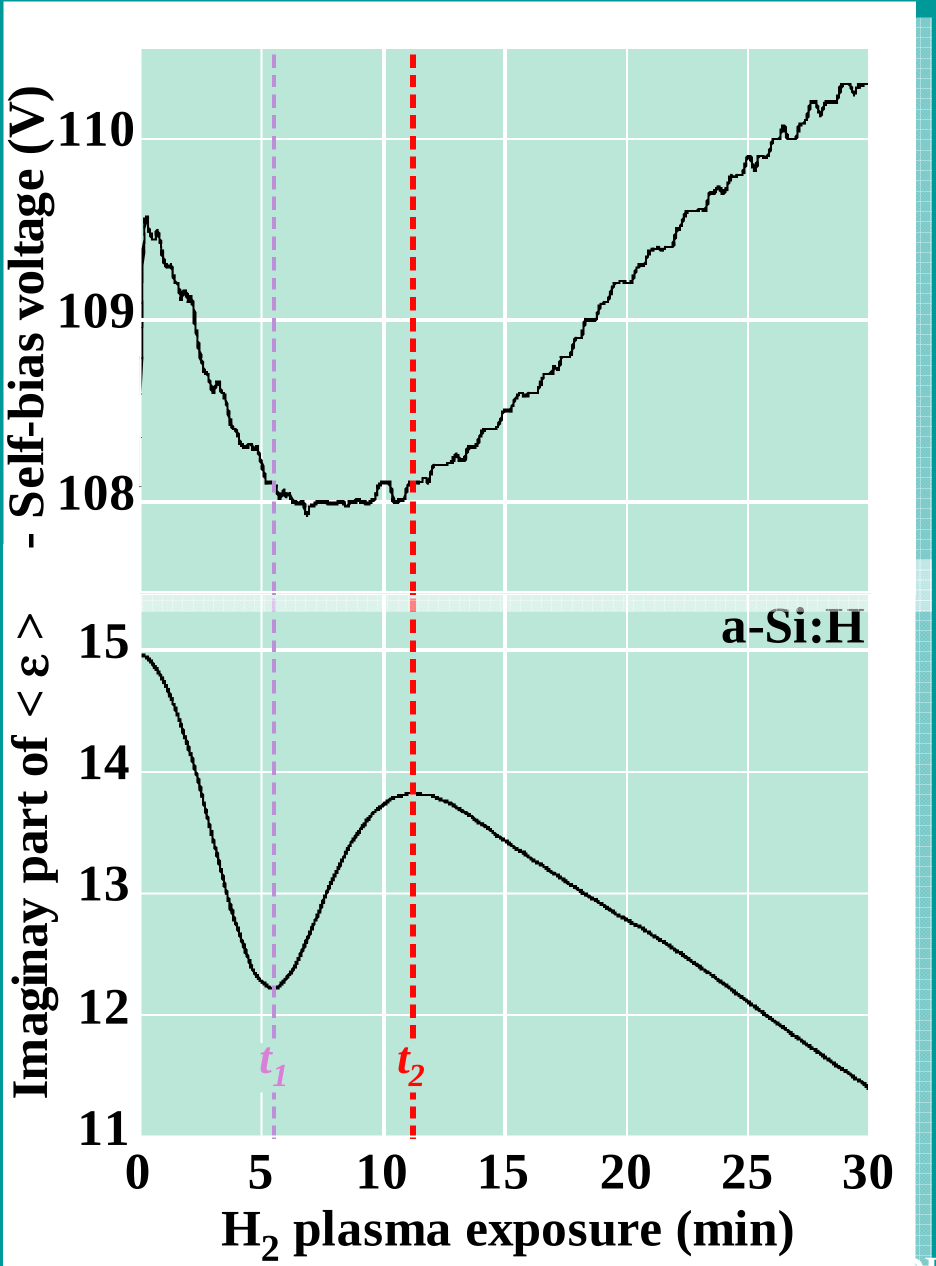
Doping effects





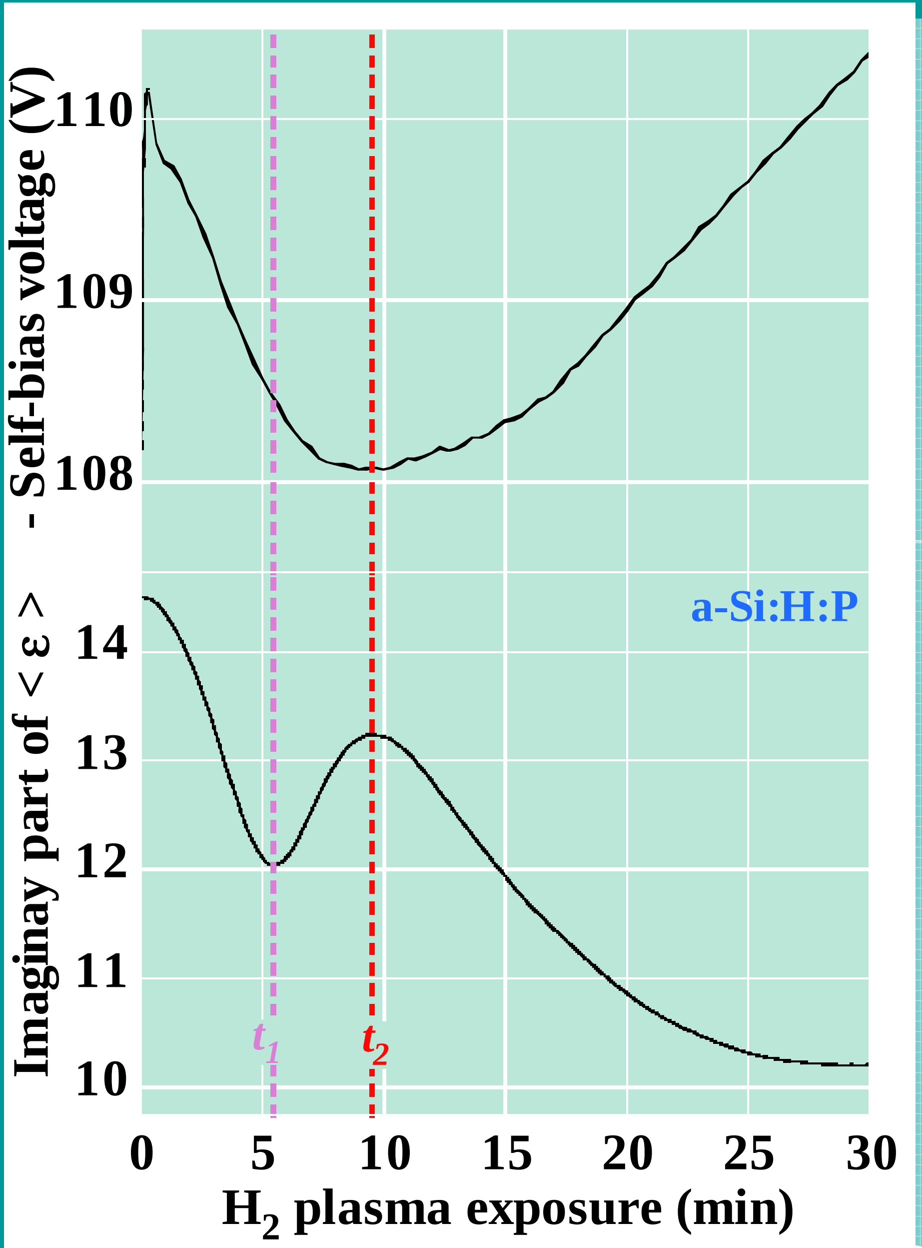
- ❑ **Phosphorus-doped a-Si:H: Similar behavior as undoped material.**
- ❑ **Boron-doped a-Si:H: Higher amplitude of the <ε_2> peak and a well–defined feature at 4.2 eV.**

Doping effects



- ☐ Undoped a-Si:H:
  - t_1 ~ 5 min : hydrogen diffusion and etching, which provide the necessary conditions for crystallites nucleation.
  - Correlation between V_{dc} and the solid-phase transformation of a-Si:H.
  - V_{dc} can be used as a diagnostic tool to detect the a → μc transition in undoped a–Si:H.

Doping effects

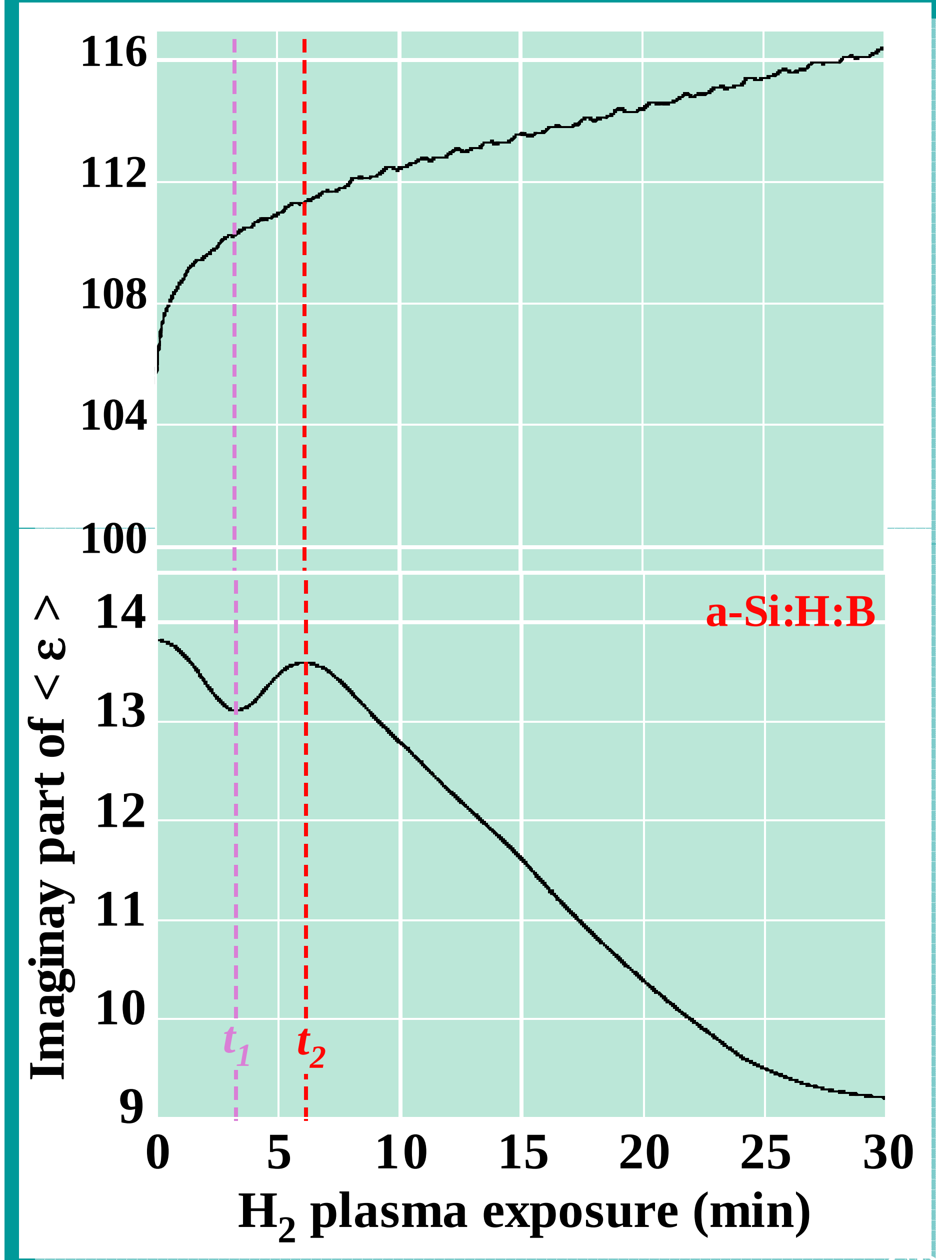


❑ **Phosphorus-doped a-Si:H**

- **Kinetics of a → µc transition as in undoped a-Si:H (t$_1$ ~ 5 min and t$_2$ ~ 10 min).**

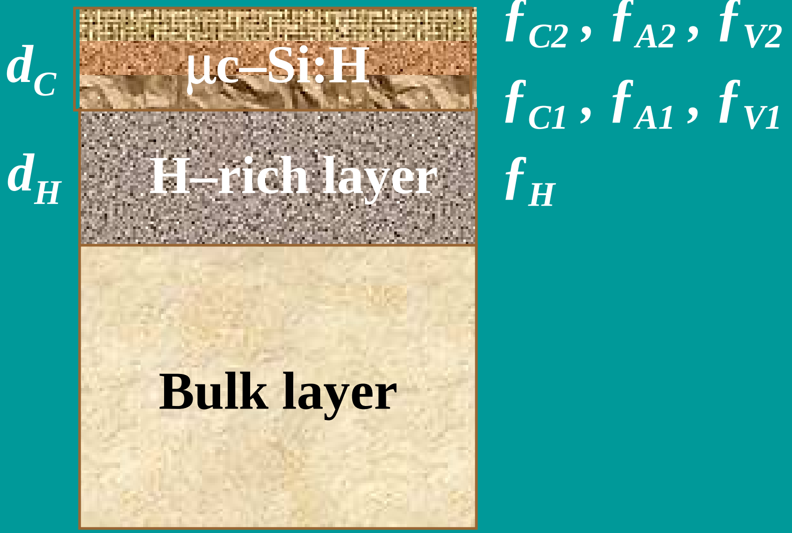
- **Same correlation between V$_{dc}$ and <ε$_2$> as in undoped a-Si:H.**

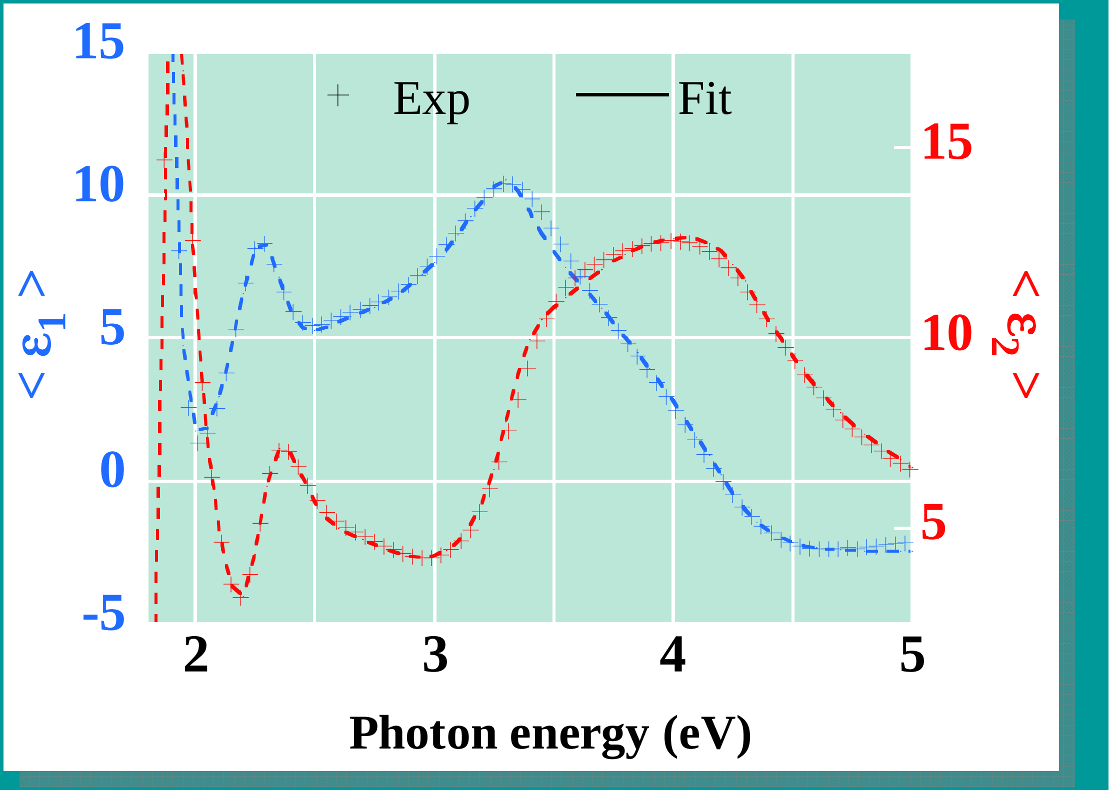
Doping effects



- ☐ **Boron-doped a-Si:H:**
  - **An earlier a → μc transition (t_1 ~ 3 min).**
  - **A faster a → μc transformation (t_2 ~ 6 min).**
  - **No clear correlation between V_{dc} and $<\varepsilon_2>$.**

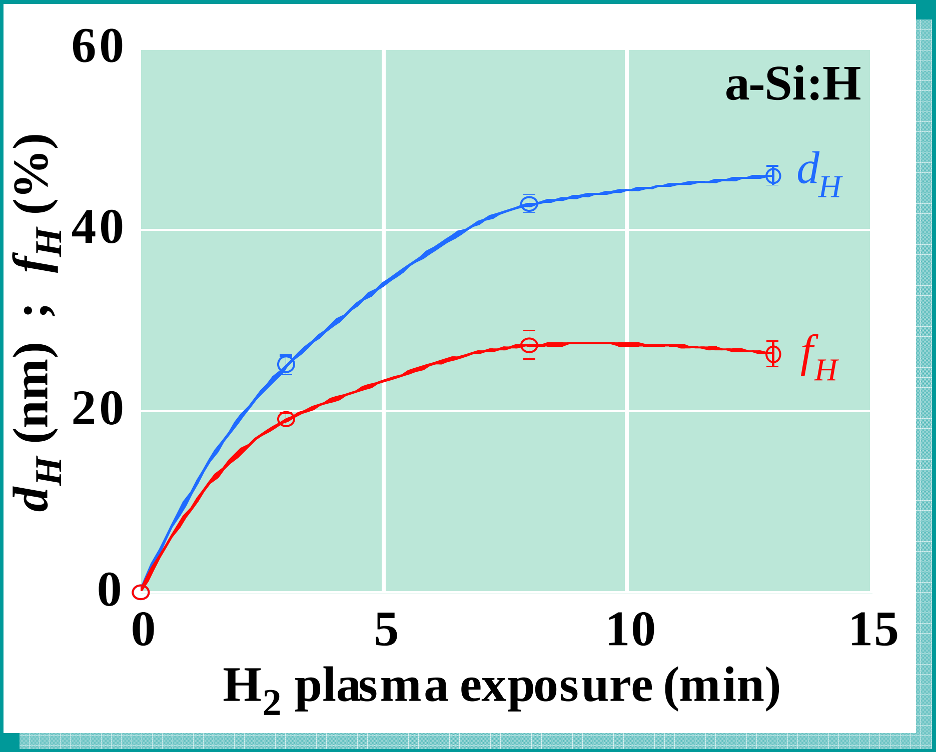
Doping effects

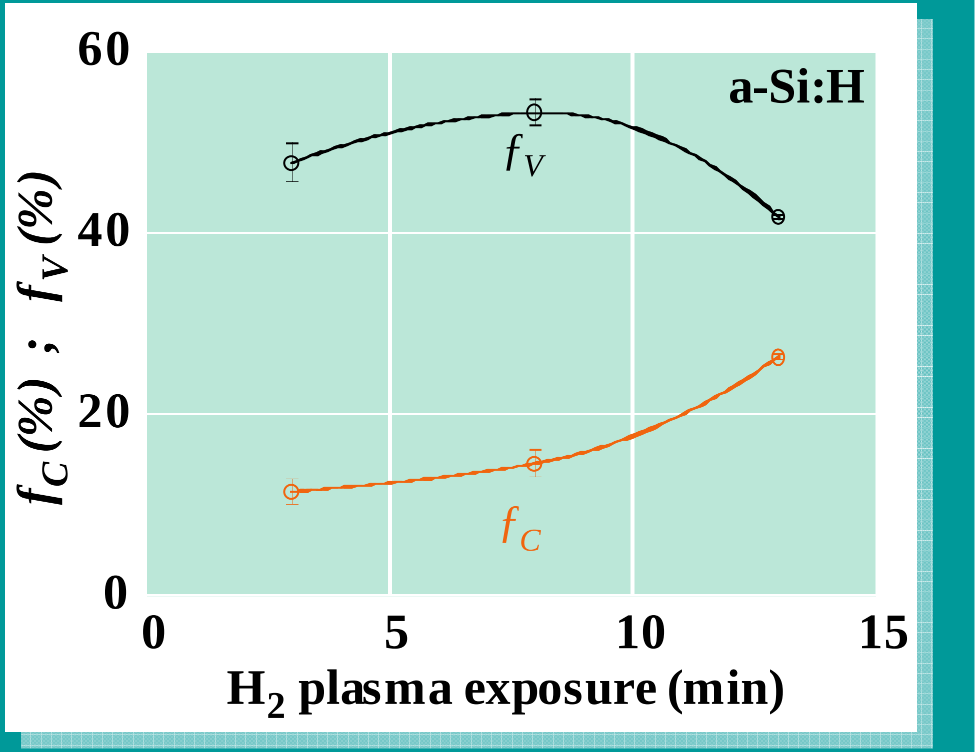




- ☐ Formation of a H-rich subsurface layer (thickness d_H and excess of hydrogen f_H) and the growth of a μc–Si:H layer (thickness d_C).
- ☐ The μc–Si:H layer is represented by a linearly graded layer: f_{C1}, f_{A1}, f_{V1}, at the bottom side and f_{C2}, f_{A2}, f_{V2} at the top side.

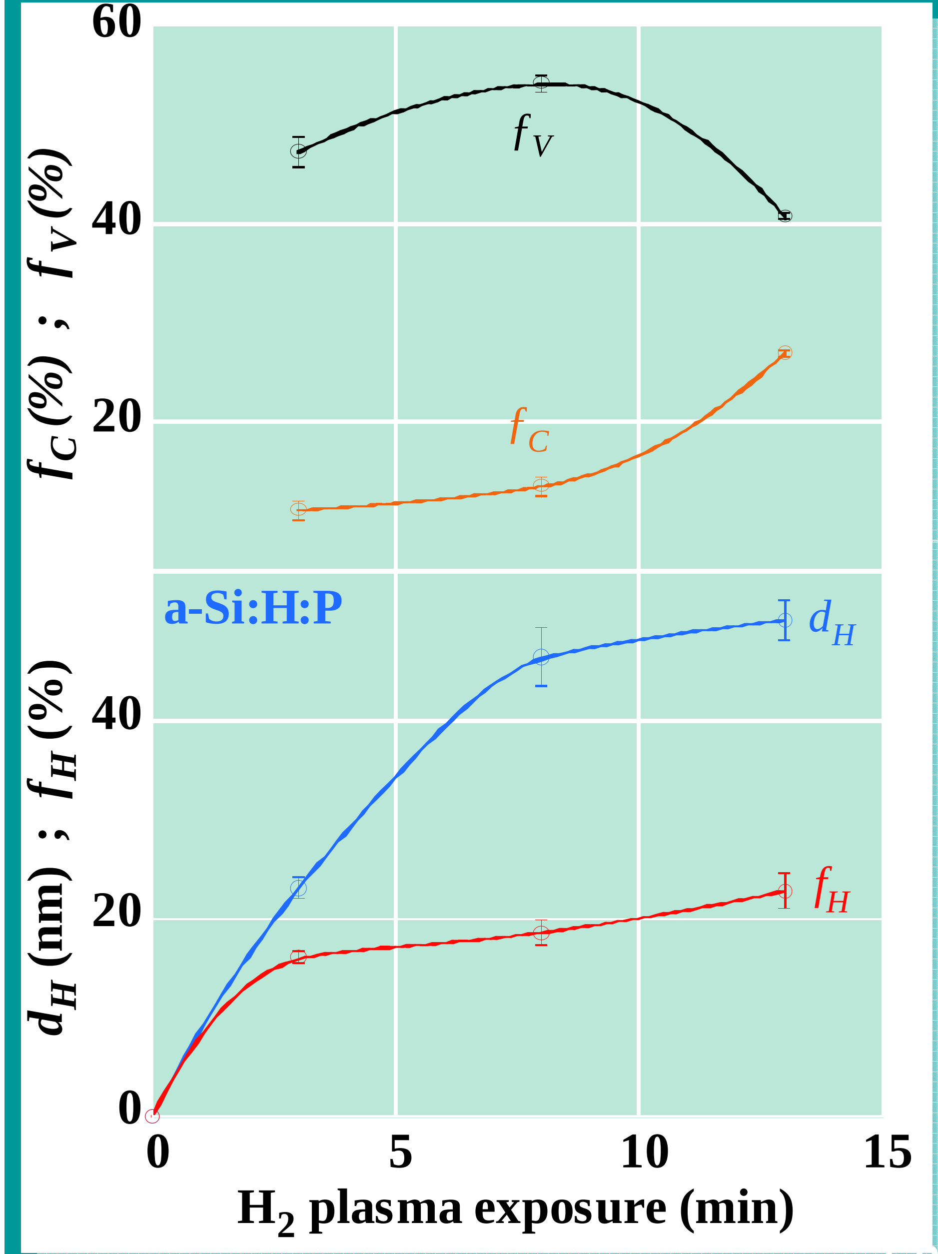
Doping effects





- d_H and f_H increase during the first 10 min to reach values close to 45 nm and 25 %, respectively
- An early nucleating process (f_C = 10 %) since 3 min with high and constant void fraction.

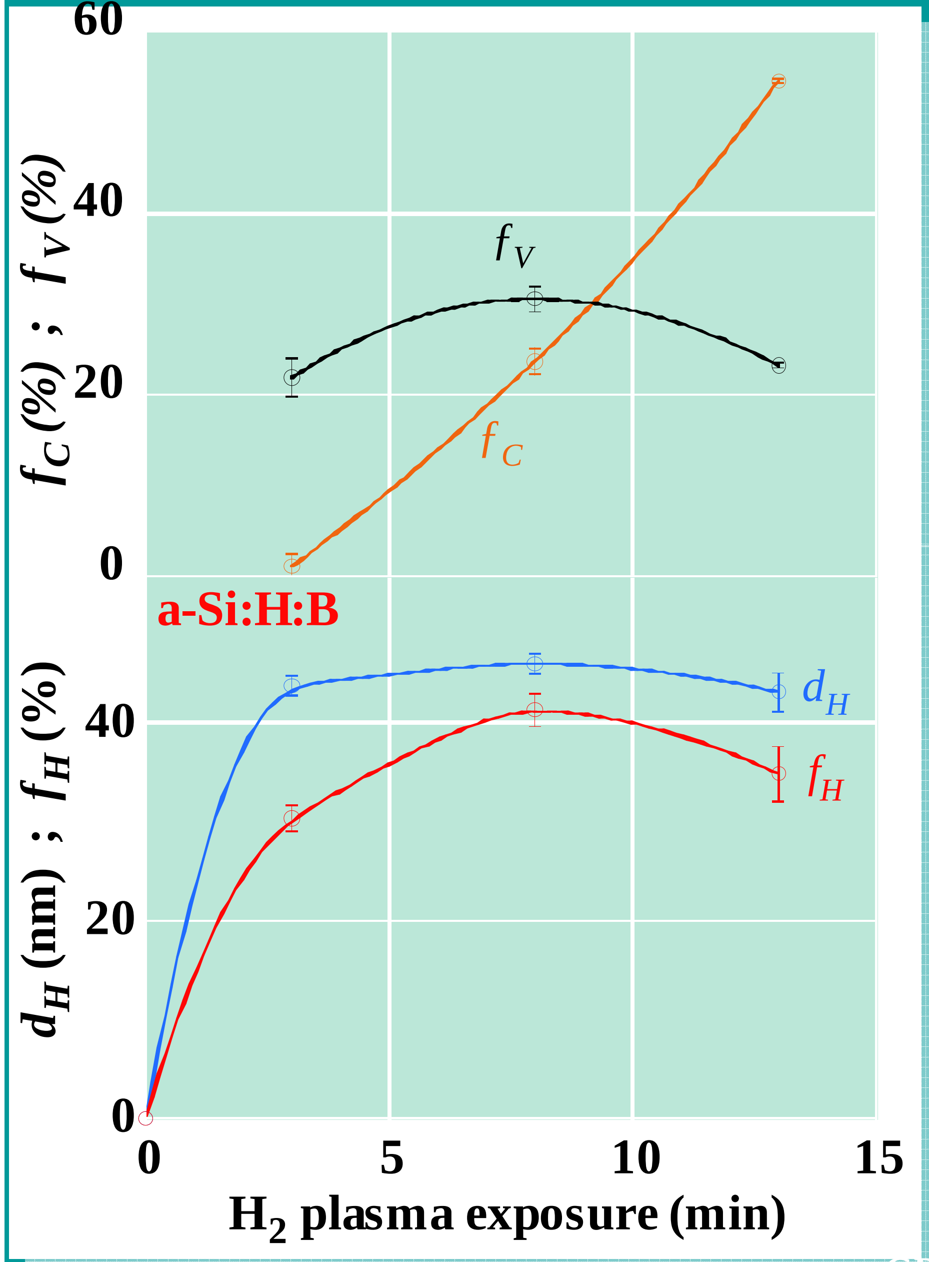
Doping effects



❑ **Phosphorus-doped a-Si:H:**

- **Same time-evolution of d_H and f_H as function of the plasma treatment time.**
- **Same kinetics of μc-Si:H growth.**

Doping effects



- ☐ Boron-doped a-Si:H:
  - d_H sharply increases and reaches a higher saturation value of 46 nm while f_H reaches 40 % .
  - The crystalline fraction, low at the beginning, rapidly increases to exceed 50 %. The fraction of voids keeps a low value (f_V ~ 20 %).

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Conclusions

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- ✓ **The combination of ellipsometry and V_{dc} measurements gives complementary information on the transition layer and the following growth of the μc-Si:H layer.**
- ✓ **Hydrogen diffuses within 40 – 50 nm of the a–Si:H substrate. The H diffusion is faster in boron–doped material and leads to a higher hydrogen excess up to 40 %.**
- ✓ **Hydrogen plasma produces an early porous nucleating layer in intrinsic and n–type a–Si:H. The nucleation arises later for the p–type substrate within a more compact layer.**
- ✓ **The hydrogen action at both sides of the μc–Si:H layer leads to a non-uniform crystalline and void fractions along the growth direction, especially for intrinsic and n–type a–Si:H.**

A fruitful collaboration with LPICM (Ecole Polytechnique, Palaiseau)

Appl. Phys. Lett. **94** 061909 (2009).
J. Vac. Sci. Technol. **A 28** 309 (2010) .
J. Appl. Phys. **108** 093705 (2010).