Atomic-scale simulations of LEPECVD-grown nc Si film

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L-NFSS



Nanophoto final meeting, Como 2008.

LEPECVD growth



Gas phase presursor: SiH₄ Reactive plasma -> radicals, ions Several substrates: Si, glass, oxide



We learned with POLIMI that the surface is almost fully hydrogenated

After performing Car-Parrinello MD simulations[1-3], we now know that SiH_3 sticking on $Si(001)(1\times2)$:H is negligible, while SiH_2 is unitary

S. Cereda, M.Ceriotti, F.Montalenti, M. Bernasconi, L.Miglio PRB 75, 235311 (2007)
S. Cereda, PHD Thesis, University of Milano-Bicocca, December 2007
S. Cereda, F. Zipoli, M. Bernasconi, L. Miglio, and F. Montalenti, PRL 100, 046105 (2008)

SiH₃ needs a db!

SiH₃ adsorbs on db at Si(100)(2x1):H



 $SiH_3 (g) + H (a) -> SiH_4 (g) + db$ direct abstraction (p ~ 60 % *) SiH₃ (g) + db -> SiH₃ (a) (p = 100 %)

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SiH₂ **does not!** SiH₂ adsorbs on Si(100)(2x1):H













S. Cereda, PHD Thesis, University of Milano-Bicocca (2007)



What is the barrier for incorporation into crystalline sites (DFT needed)?

The adsorbates are completely <u>motionless</u> on fully Si(001)(2x1):H



no altrusion (E_D > 2eV) no incorporation (E_D =2.6eV)

GROWTH

Role of impinging atomic hydrogen

Totally motionless species ($E_D > 2 \text{ eV}$)



- Car-Parrinello MD simulations
- Impinging H at 0.1 eV
- Substrate 200 °C



S. Cereda, F.Zipoli, M. Bernasconi, L.Miglio, F. Montalenti, Phys. Rev. Lett. (2008,)

Processes induced by H atoms hitting a SiH_3 adsorbed on a db H abstraction from recoil neighbouring dimers $E_D \sim 1.64 \text{ eV}$ 0 0 0 6 epitaxial H removal **2**× SiH₄ desorption $\sigma \sim 4 \text{ Å}^2$



Incorportation after etching: Ein=1.0 eV

200 °C
$$\tau_i = \frac{1}{v_0} e^{E_i / k_B T} = 4.5 \,\mathrm{ms}$$

300 °C $\tau_i \approx 0.1 \,\mathrm{ms}$

If the average time between subsequent atom landing at a given site is τ_{dep} , then the necessary condition to be satisfied in order to obtain crystalline growth is:

$$au_{i} << au_{dep}$$

If there is hydrogen available in the gas phase, lowering the incorporation barrier, formation of crystalline sites is possible

From atomic-scale mechanisms to film growth: Kinetic Monte Carlo simulations

H Si substrate

Cartoon is in 1+1D, the real model considers the diamond lattice in 3D

Two families of processes considered, each with its own time constant. At each KMC step I consider the mechanism with the correct statistical weight (fast processes occur first!)

Si substrate

Cartoon is in 1+1D, the real model considers the diamond lattice in 3D

Family I: Deposition of H, SiH₂, or SiH₃; time constants given by the deposition fluxes (ML/s) as given by the POLIMI model, based on experimental Φ_{SiH4} and Φ_{H2}



Si substrate

Species-dependent adsorption probabilities controlled via sticking coefficients, provided by our Car-Parrinello MD simulations. Possible adsorption site picked randomly.

Family II: Incorporation processes for adsorbed radicals (remember that the initial site is the same)

SiH₃

 $\tau_i = \frac{1}{\nu_0} e^{E_i / k_B T}$

Si substrate

Incorporation barrier computed by DFT. Barrier = 2.6 eV (never surmounted), unless ...

Family II: Incorporation processes for adsorbed radicals (remember that the initial site is the same)

 $\tau_{i} = \frac{1}{v_{0}} e^{E_{i}/k_{B}T}$ SiH₃ Si substrate

a hydrogen hits the adsorbed radical removing one hydrogen with the probability computed by Car-Parrinello MD simulations. In this case the barrier is lowered to 1eV, and it is possible to surmount it. The sequence leading to creation of a new crystalline site is therefore ...

I) SiH_2 or SiH_3 is successfully adsorbed

SiH₃



III) SiH₂ incorporates by surmounting a barrier of 1 eV

Si substrate Si substrate IV) If, before incorporating, new neighboring radicals are adsorbed, we declare this site irreversibly amorphous

> Si substrate a=amorphous Si substrate

By simulating the deposition of several layers WITHOUT WORRYING ABOUT THE EFFECTS OF SITES BECOMING MORE AND MORE AMORPHOUS ...

APPLIED PHYSICS LETTERS 93, 061902 (2008)

Physical mechanisms of hydrogen-enhanced onset of epitaxial growth of silicon by plasma-enhanced chemical vapor deposition

X. Tan and G. W. Yang^{a)}

Good agreement with exp. is found in terms of crystallinity, but the morphology is rather random



FIG. 2. (Color online) Surface morphologies of the silicon film's structure growing upon PECVD at various temperatures: (a) 75 K, with H₂ dilution, (b) 250 K, with H₂ dilution, (c) 475 K, with H₂ dilution, and (d) 475 K, without H₂ dilution. Black, red, green, blue, and cyan dots represent adsorbed species I, II, III, IV, and V, respectively.

Suppose we have this configuration. The situation is now very different from the one considered in the DFT calculations!

- 1) It does not make sense to create one crystalline site, in an amorphous environment
- 2) The barrier for crystallization must be higher in an amorphous environemnt

We count the number N of "bad supporting" neighbors, and we change the incorporation barrier to

$$E_{in} = 1 \text{eV} + \text{N} \times \Delta \text{E}$$

The additional barrier is used as a free parameter to fit (0.21eV) the experiments

If this higher barrier is surmounted, then the site occupied by the radical and the neighboring amorphous ones are all transformed to crystalline

> ()()

Crystallinity and microstructure in PECVD-grown Si films: a simple atomic-scale model validated by experiments

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3 G. Isella,
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1, \ddagger

Submitted to Appl. Phys. Lett.

Results: hydrogen promotes crystallinity



Results: high T and/or low silane fluxes promote crystallinity



Results: columnar structures, typical of nc Free surface

 Φ_{SiH4} =20 sccm; T=280°C; d=30%



Dark gray= crystalline Light gray=amorphous

Crystalline substrate

Latest results: application to non-crystalline substrates.

Flux-dependent non-crystalline buffer layer



Yellow= non-crystalline substrate

Higher T in KMC: buffer layer too thick to be simulated in experiments



I should consider all processes contributing to the average H coverage. This prevents simulation of a significant amount of layers



Since we know that the hydrogen coverage is very high, what do I loose if I force each surface site to be always hydrogenated? Let us look at adsorption ...



To overcome the problem it is sufficient to assign to SiH_3 a probability corresponding to the average db coverage (0.1 in the following)

The problem could be incorporation, since on clean surfaces radicals can incorporate without the etchant action of hydrogen [Ceriotti et al, submitted]. But the probability of having "clean regions" is very low

SiH₃

Si substrate

TABLE I: Deposition rates of SiH₃, SiH₂ and H in monolayers per second, as a function of the silane flux Φ_{SiH_4} and the dilution ratio d, based on the gas-phase model of Ref.¹⁵. Values are given only for the set of parameters explored in this work.

$\Phi_{\rm SiH_4}$	Species		d	
[sccm]		30%	50%	100%
12	SiH_3	16.1	19.4	-
	SiH_2	6.4	7.8	-
	Н	34.9	32.2	-
16	SiH_3	18.7	23.3	27.1
	SiH_2	7.5	9.3	10.8
	Н	38.6	36.2	31.0
20	SiH_3	20.6	26.4	-
	SiH_2	8.2	10.6	-
	Н	41.3	39.2	-