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LPCVD SYNTHESIS FROM SILANE OF SILICON NANODOTS FOR FLASH MEMORY  
DEVICES

Vanessa Cocheteau LGC/ENSIACET/INPT, 5 rue Paulin Talabot, BP1301, 31106 Toulouse  
Cedex 1 –France  
Tel: 33 5 34 61 52 52 fax: 33 5 34 61 52 53 email: Vanessa.Cocheteau@ensiacet.fr

Brigitte Caussat LGC/ENSIACET/INPT, 5 rue Paulin Talabot, BP1301, 31106 Toulouse  
Cedex 1 -France  
Tel: 33 5 34 61 52 11 fax: 33 5 34 61 52 53 email: Brigitte.Caussat@ensiacet.fr

Pierre Mur CEA-DRT-LETI – CEA-GRE, 17 Avenue des Martyrs, 38054 Grenoble Cedex 09  
- France  
Tel: 33 4 38 78 56 64 fax: 33 4 38 78 30 34 email: pierre.mur@cea.fr

Emmanuel Scheid LAAS, Avenue du Colonel Roche, 31077 Toulouse Cedex - France  
Tel: 33 5 61 33 64 59 fax: 33 5 61 55 35 77 email: scheid@laas.fr

Patricia Donnadiou LTPCM/ENSEEG, 1130 Rue de la Piscine, 38402 Saint Martin D'Hères  
Cedex - France  
Tel: 33 4 76 82 66 86 fax: 33 4 76 82 66 44 email: Patricia.Donnadiou@ltpcm.inpg.fr

Thierry Billon CEA-DRT-LETI – CEA-GRE, 17 Avenue des Martyrs, 38054 Grenoble  
Cedex 09 - France  
Tel: 33 4 38 78 36 80 fax: 33 4 38 78 30 34 email: thierry.billon@cea.fr

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# LPCVD SYNTHESIS OF SILICON NANODOTS FROM SILANE AND FOR FLASH MEMORY DEVICES

V.Cocheteau<sup>1</sup>, B.Caussat<sup>1</sup>, P.Mur<sup>2</sup>, E.Scheid<sup>3</sup>, P.Donnadieu<sup>4</sup>, T.Billon<sup>2</sup>

1)LGC/ENSIACET/INPT, 5 rue Paulin Talabot, BP1301, 31106 Toulouse Cedex 1 - France

2)CEA-DRT-LETI – CEA-GRE, 17 Avenue des Martyrs, 38054 Grenoble Cedex 09 - France

3)LAAS, Avenue du Colonel Roche, 31077 Toulouse Cedex - France

4)LTPCM/ENSEEG, 1130 Rue de la Piscine, 38402 Saint Martin D'Hères Cedex - France

## ABSTRACT

The increase of microelectronic device potentialities essentially derives from the reduction of feature size down to the nanometer scale. Multi-nanocrystals memories are one illustration of this trend.

A multi-field study is reported, aiming to better understand phenomena involved in silicon nanocrystals elaboration. A first objective is to better control the density and the size of silicon nanocrystals formed during Low Pressure Chemical Vapor Deposition (LPCVD).

Some experimental results will be presented, aiming a reliable estimation of densities and sizes of nanocrystals using several techniques: ellipsometry measurements, SEM and TEM image analysis.

These experimental data have been simulated at the reactor scale using the Computational Fluid Dynamics (CFD) code FLUENT. A new kinetic scheme has been developed, which considers the various chemisorption sites existing on SiO<sub>2</sub> substrates. This new modelling approach allows to correlate in transient mode the local composition of the gas phase near the substrate with the various sites number and with the density and the size of nanocrystals.

## INTRODUCTION

Nanometer-sized structures are increasingly attracting attention because their unique physical properties, especially quantum mechanical effects, allow to develop new Si-based functional devices, like resonant tunnel components, one dimensional transport devices and single electron transistors.

The industrial application and production of devices based on silicon nanodots properties will require the control of silicon nanocrystals (nc-Si) size, size distribution and density. Various methods have been proposed for nc-Si elaboration such as chemical vapor deposition(1), ion implantation(2), aerosol(3), ... However the main drawback with nanoscale structures is that the elaboration processes have difficulties in controlling densities and sizes of as-deposited nc-Si. In that respect, Low Pressure Chemical Vapor

Deposition (LPCVD) seems to be the most efficient way to form Si nanocrystals for industrial applications.

Nevertheless, in order to reach a better control of densities and sizes of nc-Si elaborated by LPCVD, the understanding of phenomena involved during deposition must be improved. We present here experimental and theoretical investigations concerning a LPCVD conventional process to form nc-Si from silane  $\text{SiH}_4$ .

First, a comparative structural study based on Transmission Electron Microscopy (TEM) and Field Effect Gun Scanning Electron Microscopy (FEG-SEM) analysis is presented in the case of nc-Si deposition. Considering the size and the density of the nanocrystals, both high resolution techniques have here to be used to get a reliable structural information.

The experimental data have then been simulated at the reactor scale. Using the CFD code Fluent, a new heterogeneous chemical mechanism for the initial stages of deposition will be proposed aiming to take into account the nature of the chemical bonds present at the surface of the substrate and their impact on silicon adsorption, surface diffusion, chemisorption, desorption ...

## EXPERIMENTAL

### Elaboration features

Silicon nanocrystals have been elaborated in an industrial tubular hot wall LPCVD reactor as schematically presented in figure 1.

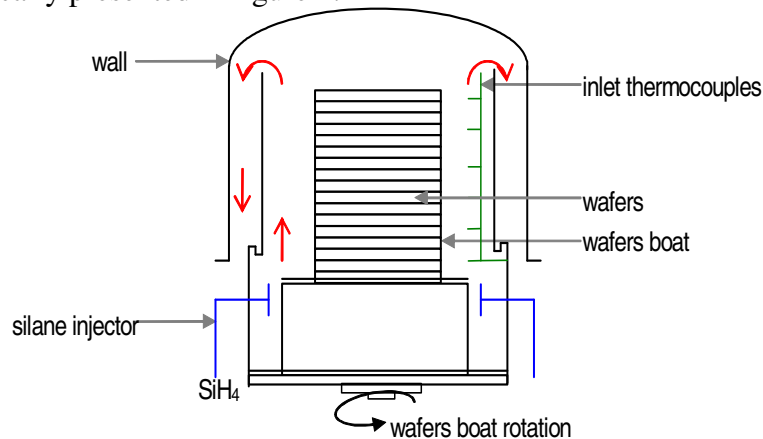


Figure 1 : The LPCVD tubular reactor

The tubular reactor can simultaneously treat 170 wafers of 8' in diameter.

Two sets of substrates have been studied, both corresponding to thermally oxidised silicon wafers. The first set, named "untreated substrates" stands for Si wafers of as-formed  $\text{SiO}_2$ . The second one, named "treated substrates" corresponds to the substrates on which a HF treatment has been applied (3), the objective is to form more reactive chemical bonds at the substrate surface.

## Dots characterizations

FEG SEM and TEM were carried out on a microscope Hitachi S5000 and on a microscope Jeol3010 respectively. The nc-Si density has been measured by direct counting on FEG-SEM images. From spectroscopic ellipsometry, we have determined the thickness and the silicon fraction of a continuous layer including vacuum and silicon. The thickness of the as-deposited nc-Si has been calculated from these informations. By considering nanocrystals as hemispherical, their mean diameter  $D$  has then been calculated using the following formulation:  $\pi \cdot D^3 / 12 = e_{Si} / d_{dot}$  where  $e_{Si}$  is the thickness of an equivalent layer of Si and  $d_{dot}$  is the nc density.

TEM analyses have been carried out only on some nc-Si samples because of the difficulties of samples preparation. The TEM samples consists of plane view of the nc-Si deposit on the Si oxidized substrate. Polishing and ion beam thinning are done only the Si substrate side. During ion beam thinning, care must be taken to protect the Si deposit which can be very reactive in particular with Cu. The TEM images of the nc-si deposit shows a phase object contrast. To extract information, focal series have been taken and further analyzed according to the so called phase retrieval method described in (4).

## CFD SIMULATIONS FEATURES

### Basic Principles

Experiments are simulated using the commercial CFD software Fluent. Fluent is a pressure-based, implicit Reynolds Averaged Navier Stokes solver that employs a cell-centered finite volume scheme having second-order spatial accuracy. This software discretizes any computational domain into elemental control volumes, and permits use of quadrilateral or hexahedral, triangular or tetrahedral and hybrid meshes.

Gas flow, heat and mass transfers including homogeneous and heterogeneous chemical reactions have been calculated. The gas flow is assuming as laminar and isothermal, the gas is considering as ideal and the heats of reaction are neglected.

Owing to the axisymetry of the tubular reactor, a 2D model of 25 000 meshes is developed. Simulations have been performed in transient mode, due to the duration of the transitory step at the onset of deposition, as explained elsewhere (5).

A rigorous analysis showed that polysilanes of order higher than two can be neglected in our conditions, only the first reaction involved in silane pyrolysis ( $\text{SiH}_4 \leftrightarrow \text{SiH}_2 + \text{H}_2$ ) has been considered for the homogeneous phase. The kinetic constants of Fayolle(6) have been used if the total pressure is lower than 1 Torr and those of Kleijn(7) for higher pressures.

Consequently, the two following heterogeneous reactions have been considered,  $\text{SiH}_4 \rightarrow \text{Si} + 2\text{H}_2$ , named (R1) and  $\text{SiH}_2 \rightarrow \text{Si} + \text{H}_2$ , called (R2). For (R1) the overall empirical kinetic law of Wilke et al.(8) has been used. For (R2), to take into account of the very high reactivity of the unsaturated silylene molecule ( $\text{SiH}_2$ ), in agreement with the literature, a sticking coefficient equal to 1 has been assumed, using the kinetic theory of gases.

It is worth noting that this kinetic model has been first validated by the excellent agreement observed when comparing experimental and calculated deposition rates for conventional thick layers of silicon (100 nm minimum in thickness).

In a second step, the whole experiments of nc-Si deposition has been simulated. A general important result is that the simulated deposition rates have always been higher, sometimes of one order of magnitude, than the experimental ones.

The kinetics of fundamental steps of CVD like physisorption, adatom surface diffusion, desorption and chemisorption during the first times of deposition are then slower than the kinetics of those occurring on a fresh silicon surface. The reason is that the chemical bonds on a SiO<sub>2</sub> surface (SiOH and SiOSi) are much less reactive than fresh silicon dangling bonds. Some authors (9-12) express this phenomenon by the existence of an incubation time, delaying the onset of the deposition. Of course, the kinetic of these first deposition steps dominate the kinetic of nc-Si formation, which is not the case for thicker films.

Consequently, it seems logical that the classical heterogeneous laws established for conventional thick layers were no more valid in the case of ultrathin films like nc-Si.

### Presentation of a new kinetic heterogeneous model

This is the reason a new kinetic heterogeneous model accounting for specific reactivities of the gaseous precursors on the various chemical bonds existing on SiO<sub>2</sub> during the first times of deposition has been developed.

Its fundamental assumptions are the following:

- An experimental nucleation rate is calculated from the corresponding experimental nc densities, sizes and deposit durations,
- 3 kinds of chemisorption sites are considered, SiOSi epoxy bonds, SiOH silanol bonds on the SiO<sub>2</sub> surface and fresh Si bonds due to deposition,
- An “untreated” SiO<sub>2</sub> substrate is ideally represented as covered exclusively by epoxy bonds whereas a “treated” substrate is supposed to be fully covered by silanol bonds.
- The total number of sites remains constant during deposition; in a first approach, it has been taken equal to that of  $\beta$ -cristobalite, i.e  $3.9 \cdot 10^{14} \text{ cm}^{-2}$ ,
- Nucleation corresponds to Si chemisorption on a substrate site (SiOH or SiOSi),
- Growth corresponds to Si chemisorption on a fresh Si bond,
- Due to its intrinsic high reactivity whatever the surface sites, the unsaturated SiH<sub>2</sub> molecule in priority contributed to nucleation,
- If this contribution is not high enough regarding the experimental nucleation rate, the SiH<sub>4</sub> contribution is then taken into account (this fraction of silane deposition is called  $x_{\text{nucleation}}$ ),
- The remaining part of physisorbed silane on SiOH or SiOSi sites can then diffuse on surface to chemisorb on a fresh Si site, or desorb (these fractions of silane deposition are respectively called  $x_{\text{diffusion}}$  and  $x_{\text{desorption}}$ ).
- The flux of silane involved in these two phenomena is calculated by mass balance from the total number of Si atoms experimentally deposited.

The considered new kinetic heterogeneous laws are given in Table I. The original Wilke et al. formulations and the kinetic theory of gases have been kept respectively for

silane and silylene. A balance in terms of types of sites and considering the various phenomena described in the assumptions has been added.

Deposition rate from SiH <sub>4</sub>	On site i (i=SiOSi or SiOH) [nucleation]	$K_1PSiH_4/(1+K_HPSiH_4+K_SPSiH_4)^* \frac{n_i}{n_{total}} * X_{nucleation}$
	On fresh Si [growth]	$K_1PSiH_4/(1+K_HPSiH_4+K_SPSiH_4)^* \frac{n_{Si}}{n_{total}}$
	After surface diffusion [growth]	$K_1PSiH_4/(1+K_HPSiH_4+K_SPSiH_4)^* \frac{n_{Si}}{n_{total}} * X_{diffusion}$
Desorption rate from SiH <sub>4</sub>	On site i (i=SiOSi or SiOH)	$K_1PSiH_4/(1+K_HPSiH_4+K_SPSiH_4)^* \frac{n_i}{n_{total}} * X_{desorption}$
Deposition rate from SiH <sub>2</sub>	On site i (i=SiOSi or SiOH) [nucleation]	$(1/(2*\pi M_{SiH_2}RT))^{1/2} * \frac{n_i}{n_{total}}$
	On fresh Si [growth]	$(1/(2*\pi M_{SiH_2}RT))^{1/2} * \frac{n_{Si}}{n_{total}}$

Table I : New formulation of the heterogeneous kinetic laws in which  $n_i$  is the number of site i and  $n_{total}$  is the total number of sites

## EXPERIMENTAL RESULTS

Among the whole experimental results obtained, only the more representative ones will be presented here. Sample 1 has been elaborated at 873 K for a duration of 7 s. Samples 2 to 4 have been elaborated at 773K for durations ranging between 60 s and 180 s. In all case, nc-Si have elaborated on “treated” substrates.

Some of the TEM and SEM images are shown in figure 2, whereas TEM and SEM nanocrystals densities and diameters for the four samples are given in Table II. The TEM and SEM techniques appear as very complementary since TEM is able to measure small nc-Si size (i.e. below 4 nm) while the density given by SEM combined to ellipsometry is very reliable when the dot size is correct.

	TEM density (nc/cm <sup>2</sup> )	SEM density (nc/cm <sup>2</sup> )	TEM diameter (nm)	SEM diameter (nm)
sample 1	1 10 <sup>12</sup>	8.6 10 <sup>11</sup>	4.0	4.8
sample 2	6 10 <sup>12</sup>	not measurable	2.8	not measurable
sample 3	2 10 <sup>12</sup>	5.9 10 <sup>11</sup>	5.0	5.8
sample 4	4 10 <sup>12</sup>	9 10 <sup>11</sup>	3.3	6.6

Table II : nc densities and diameters from SEM and TEM analysis

A general result is that nc-Si densities are higher on “treated” than on “untreated” substrates. Nc-Si densities and sizes increase with deposition duration as can be seen for samples 3 and 4 (run durations respectively equal to 60 and 180 s), until coalescence. An increase in silane partial pressure tends to increase sizes as shown for samples 2 and 3 for same temperatures and durations (silane pressure of sample 3 is twice that of sample 2). According to TEM results densities decrease with silane partial pressure.

Another general trend is that nc diameters measured by TEM are smaller than those measured by SEM and that densities are higher. This result can be explained by the higher level of resolution offered by TEM. As an example, if a quite good agreement is obtained for samples 1 and 4, this is no more the case for samples 2 and 3. For sample 3,

the difference is due to the fact that TEM analysis reveals the presence of very small nc-Si (< 2 nm), not visible by SEM. For sample 3, a density of  $6 \cdot 10^{12}$  nc/cm<sup>2</sup> has been measured by TEM. To our knowledge, this is the highest density ever measured for silicon nanocrystals. For this sample, nc-Si are hardly detectable by SEM as can be seen in figure 2. The fact the TEM nc-Si size is as low as 2.8 nm confirms that the level of resolution of FEG SEM may reach its limits for some specific nc samples.

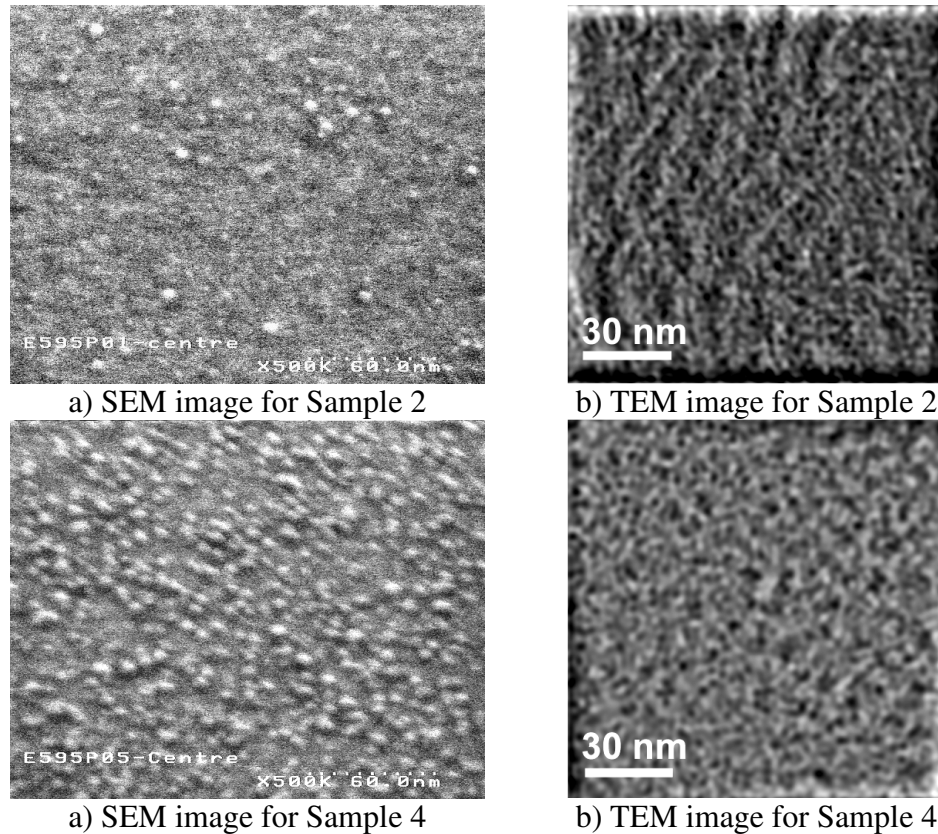


Figure 2 : Nc elaborated in the tubular reactor

a) SEM images and b) phase image obtained by image analysis of the TEM image

## SIMULATION RESULTS

As characteristic examples, the simulation results for a run performed on an untreated substrate at 873K and 0.2 Torr are shown in figures 3 to 5.

First, figure 3 gives the evolution with time of the SiOSi and fresh Si site numbers. One can observe an increase with time for fresh Si sites number whereas the reduction of the number of SiOSi sites is quite low.

As illustrated by figures 4 and 5, this is due to the fact that silicon deposition for these conventional LPCVD conditions is mainly due to silane itself and that silane contribution to nucleation is negligible (less than 0.2 %).

Indeed, roughly 1/6<sup>th</sup> of the substrate SiOSi sites are covered after 20 s of deposition. By extrapolation, for these conditions, 2 min (i.e 6 nm deposit thickness) would be

necessary to entirely saturate the SiOSi sites. This time increases when the silane partial pressure decreases, since 10 min (i.e 22 nm Si film thickness) are necessary for a silane pressure of 0.06 Torr. This information is original and very valuable since these values directly correspond to the deposition times and film thicknesses from which the intrinsic kinetic laws become valid.

Second, figure 4 gives the evolution with time of silane and silylene deposition rates on SiOSi and Si bonds. It can be noted that the total silylene contribution to deposition is about 100 times lower than that of silane. The silylene contribution to nucleation (deposits on SiOSi sites) decreases with time since the sites number decreases. Logically, the silylene contribution to growth (deposition on fresh Si sites) increases with time, as that of silane.

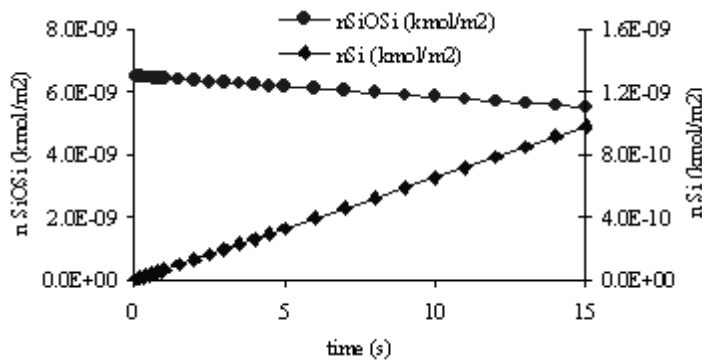


Figure 3 : Evolution of the number of deposit site

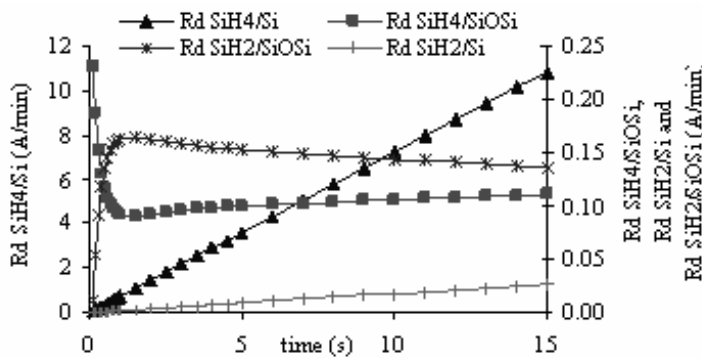


Figure 4 : Deposition rates of silane and silylene on SiOSi bond and Si dangling bonds

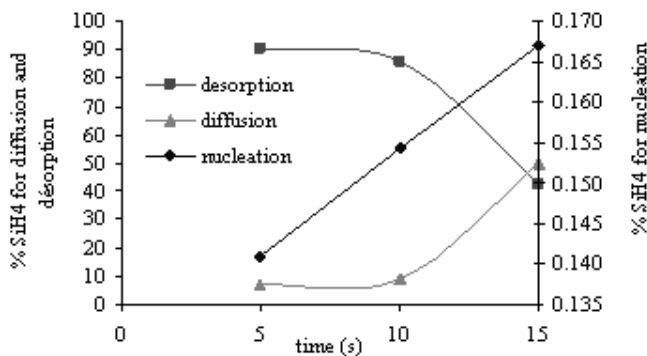


Figure 5 : Silane participation to nucleation, surface diffusion/chemisorption and desorption

Finally, results presented on figure 5 confirm our assumption that the unsaturated silylene is sufficient to account for nucleation. During the first 10 s of deposition, 90% of silane deposited on SiOSi has to desorb and 10% has to diffuse on a fresh Si site to chemisorb, so as to balance the experimental number of deposited silicon atoms.



The silane participation to nucleation has been calculated from an experimental nucleation rate which is constant with time. The silane and silylene deposition rate on SiOSi decrease with time. It is then logical that the silane participation increases with time. Because of deposition, the fresh Si sites number increases with time, and thus Si sites present around adatoms increase. The probability that an adatom diffuses on surface and chemisorbs on a fresh Si bond then increases with time. Finally, the silane participation to desorption logically decreases with time.

## CONCLUSIONS

Some experimental and modelling results of silicon nc deposits have been presented. The fact that deposits are ultrathin (< 5 nm) and imply very short durations (< 60 s) generates experimental and modelling problems.

First a comparison between FEG SEM and TEM reveals that FEG SEM tends to over estimate nc sizes and to under evaluate nc-Si densities. The level of resolution of SEM seems to reach its limits to detect nc-Si of diameters lower than 2 nm. The TEM phase retrieval method is then particularly valuable for nc characterization. Though TEM remains of limited use because of sample preparation problems.

All experimental conditions have then been simulated using the CFD code Fluent with a kinetic heterogeneous scheme especially developed for ultrathin films. Some original modelling results have been presented confirming the slowness of the first stages of deposit and the necessity to adapt the heterogeneous kinetic scheme when simulating LPCVD nc-Si formation.

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