

## Deterministic placement of doping atoms on hydroxylated surfaces

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### Abstract

An improved approach of semi-conductor doping by Molecular Layer Deposition (MLD) is investigated. Here, dopant-containing molecules are directly grafted onto silica-coated silicon wafers and optimized ligands can provide more effective dopant drive-in annealing. The grafting approach is validated on non-porous silica and successfully transferred onto silicon wafers.

### Introduction:

With the continuing shrinking of semiconductor devices, the randomness of dopant distribution within a device becomes more likely to critically impact their performance. Recent studies have aimed at making controlled positioning of dopants by advanced implantation,[1] in order to limit fluctuations in the threshold voltage, or by Molecular Layer Deposition of dopants on Si-H passivated Silicon[2] This latter approach efficiently tunes shallow junctions also for FinFet devices[3], but it requires SiO<sub>2</sub>-capping to avoid dopant evaporation during drive-in and activation annealing.

Here we evaluate the grafting of dopant-containing molecules on the Si-OH, present at the surface of silicon wafers, whose density can be tuned by thermal pre-treatment. We examine the effect of the type of ligands attached to the dopant atom on the resulting dopant density, in particular to avoid dopant evaporation during annealing and the use of post SiO<sub>2</sub>-capping step. (Fig. 1)

### Experiments

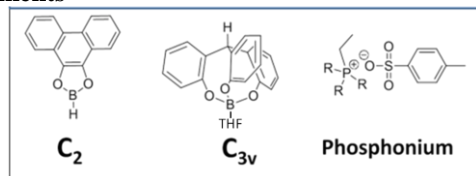


Fig. 1. Targeted molecules used in this study

First, the control of the dopant density was evaluated by grafting of B- and P-containing compounds having ligands of various sizes and symmetries (Fig. 1) on non-porous silica partially dehydroxylated at high temperatures (700 °C) as a simple and straightforward model.

The surface was then characterized through combined analytical techniques (IR-DRIFT, solid-state NMR and elemental analyses). Then the ligands were eliminated by a thermal treatment under dry air at 500°C (calcination). This

protocol was transferred on Silicon wafers covered by chemical oxide having surface SiOH. Grafted molecules with or without ligand elimination were then annealed by RTP at high temperature under inert atmosphere (>1000°C). ICPMS analysis of the grafted oxide treated with HF (VPD) was performed before and after annealing (Table 1). The resulting bare silicon surface was then analysed by ToFSIMS analysis, providing the amount of boron diffused into Silicon. Comparison of the results provided doping yield and the amount of evaporated dopant.

### Results and Discussion

Density of C<sub>2</sub>- and C<sub>3v</sub>-symmetrical B-containing molecules grafted on silica was shown to be directly related to the OH density and a result of the size of the ligand as the isolated SiOH disappear and B-loading is the same both cases. (Fig. 2)

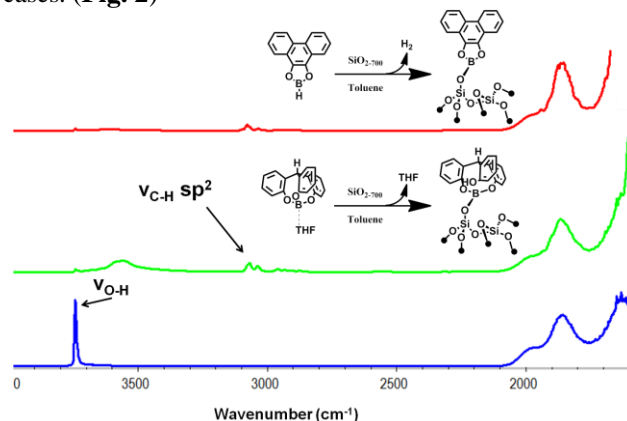
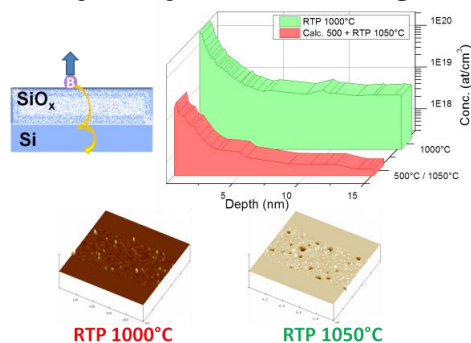


Fig. 2. IR-DRIFT of silica before and after grafting, showing disappearance of SiOH independently of molecule bulkiness

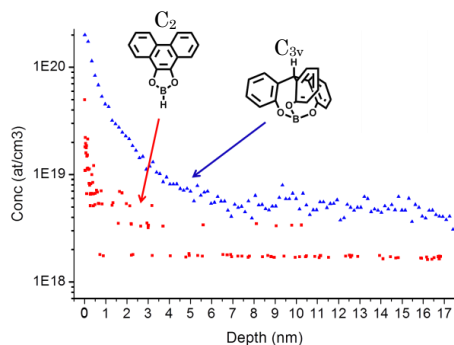
Then, calcination at 500°C under air led to the elimination of the ligands and the formation of BOH without inducing boron loss according to elementary analyses. In contrast, the same strategy applied to phosphorus-containing molecule originally led to some elimination of phosphorus when using phosphonium species. Tuning the P-containing molecule allows to avoid phosphorus loss. Since the diffusion of phosphorus through silica is less efficient than this of boron, we first transposed this grafting approach with boron onto silicon wafers for drive-in experiments. First, we evidenced that the annealing at high temperature of B-OH surface obtained after ligand removal at 500°C

provided poorer silicon doping efficiency compared to the direct annealing of the grafted molecules (**Fig. 3**)



**Fig. 3. Schematic of boron evaporation/diffusion-SIMS for  $C_2$  molecule RTP annealed w/ or w/o 500°C preanneal-AFM insert shows degradation of wafer after RTP at 1050°C**

Desorption of the ligands occurs at high temperature without boron evaporation, favouring its incorporation into  $SiO_2$ . Effect of organic moieties of  $C_{3v}$  and  $C_2$  molecules on doping efficiency after annealing was then compared. (**Fig. 4**)



**Fig. 4. ToF-SIMS profiles after annealing of the various Boron bearing molecules**

**Table 1** summarizes boron concentrations in  $SiO_2$  and Si after annealing at 1000°C-1050°C. The bulkier molecule  $C_{3v}$  allowed a better incorporation of boron and a better protection towards dopant evaporation upon annealing at 1000°C. Under these conditions, 100% of the initial boron was recovered within  $SiO_2$  and Si (versus only 8.4% for  $C_2$ ). Thus, we deduced that larger molecules prevented dopant evaporation without the need of post- $SiO_2$  capping. Boron segregation in Si led to the diffusion of ~12% of grafted boron into silicon from  $C_{3v}$ , making a shallow Boron profile with higher dopant surface concentration with  $C_{3v}$ .

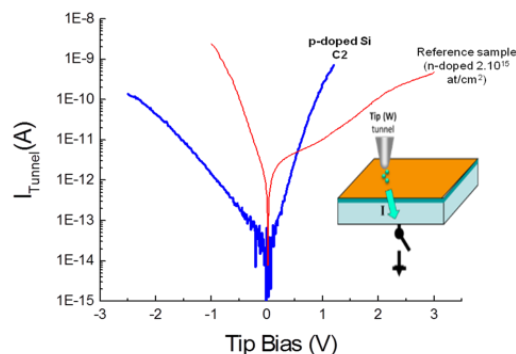
**Table 1. Surface Boron dose a) after 1000°C annealing on  $C_2$ - and  $C_{3v}$ -grafted wafers and b) after 1000°C and 1050°C annealing on  $C_{3v}$ -grafted wafers**

RTP T°C	Type	Reference ( $\times 10^{13}$ B/cm $^2$ )	B in $SiO_2$ ( $\times 10^{13}$ B/cm $^2$ )	B in Si ( $\times 10^{13}$ B/cm $^2$ )	Yield (%)
1000°C	$C_{3v}$	20.0	18.0	2.3	~100
	$C_2$	29.0	2.0	0.4	8.4

RTP T°C	Type	Reference ( $\times 10^{13}$ B/cm $^2$ )	B in $SiO_2$ ( $\times 10^{13}$ B/cm $^2$ )	B in Si ( $\times 10^{13}$ B/cm $^2$ )	Yield (%)
1000°C	$C_{3v}$	20.0	18.0	2.3	~100
1050°C	$C_{3v}$	20.0	3.3	1.6	24.3

Higher thermal annealing (1050°C) leads to boron loss, mainly due to dopant evaporation from the oxide layer because of  $SiO$  evaporation (**Fig. 3**). We concluded that optimal drive-in required bulky dopant-containing molecules and low annealing temperature (below 1050°C). Electrical measurements with a single tip in tunnel mode (sample grounded and bias voltage applied to the tip) evidenced the electrical activation of dopant. (**Fig. 5**). We then demonstrated that a very shallow junction can be obtained after annealing of optimized boron-containing molecules grafted on chemical oxide.



**Fig. 5. Current /voltage measurements of silicon doped by annealing of  $C_2$  molecule compared to N silicon reference at 750 pA**

## Conclusion

We have demonstrated the possibility to trigger boron diffusion into silicon using optimized B-containing molecules via grafting on the silanol present at the surface of the thin chemical oxide. While the size of the molecule does not affect the distribution of boron, showing that the primary factor determining B-density is the Si-OH density, it is critical to avoid the evaporation of boron from the  $SiO_2$  surface: the larger the molecule being better. This approach allows the incorporation of boron without the need of post  $SiO_2$  capping as previously used.[3] This grafting approach provides high concentration of dopants in a very shallow depth (5 nm), thus opening ways to control medium/high doping in shallow, deterministically doped junctions needed for future nano-devices. Phosphorus-containing molecules with optimized organic moieties are currently under further evaluations.

- [1] T. Shinada, M. Hori, Y. Ono, K. Taira, A. Komatsubara, T. Tani, T. Endoh, I. Ohdomari, in *Electron Devices Meeting (IEDM), 2010 IEEE International*, **2010**, pp. 26.25.21-26.25.24.
- [2] J. C. Ho, R. Yerushalmi, Z. A. Jacobson, Z. Fan, R. L. Alley, A. Javey, *Nat Mater* **2008**, *7*, 62-67.
- [3] K.-W. Ang, J. Barnett, W.-Y. Loh, J. Huang, B.-G. Min, P. Y. Hung, I. Ok, J. H. Yum, G. Bersuker, M. Rodgers, V. Kaushik, S. Gausepohl, C. Hobbs, P. D. Kirsch, R. Jammy, in *IEDM*, **2011**, p. 35.35.31.