18th Conference on **Gettering and Defect Engineering in Semiconductor Technology,** Zeuthen, Germany, September 22-27, 2019

Diffusion of phosphorus and boron from ALD oxides into silicon

S. Beljakowa[1], P. Pichler[1,2,a], B. Kalkofen[3], R. Hübner[4]

[1] Chair of Electron Devices, Friedrich-Alexander-University Erlangen-Nuremberg, Erlangen, Germany
[2] Fraunhofer Institute for Integrated Systems and Device Technology IISB, Erlangen, Germany
[3] Institute for Micro and Sensor Systems (IMOS), University of Magdeburg, Magdeburg, Germany
[4] Helmholtz-Zentrum Dresden - Rossendorf (HZDR), Institute of Ion Beam Physics and Materials Research, Dresden, Germany
[a] corresponding author: peter.pichler@fau.de

Motivation

- ➢ Technology of high-density 3D-integrated semiconductor devices requires ultra-shallow junctions with low sheet resistances and conformal doping[1, 2]
- ➢ Low-energy implantation of dopants in semiconductor leads to damage-related and ion-beam shadowing effects [3, 4]
- ➢ Deposition of a dopant source by atomic layer deposition (ALD) followed by a drive-in process – a viable alternative

Aim of this work:

- ➢ Study of dopant transport phenomena from ALD-grown oxides into silicon

Experimental

- Boron-doped (5 – 22 Ωcm) and phosphorus-doped (8 – 12 Ωcm) 710 µm thick <100> Cz-Si wafers
- Deposition of Sb_2O_5 oxides and B_2O_3/Sb_2O_5, P_2O_5/Sb_2O_5 oxide stacks by ALD onto Si
- RTA annealing in N_2 at 1000 °C for annealing times from 4 to 64 s with a ramp of 15 °C/s

Characterization methods:

- X-ray photoelectron spectroscopy (XPS)
- Transmission electron microscopy (TEM)
- Secondary ion mass spectrometry (SIMS)
- Sheet resistance

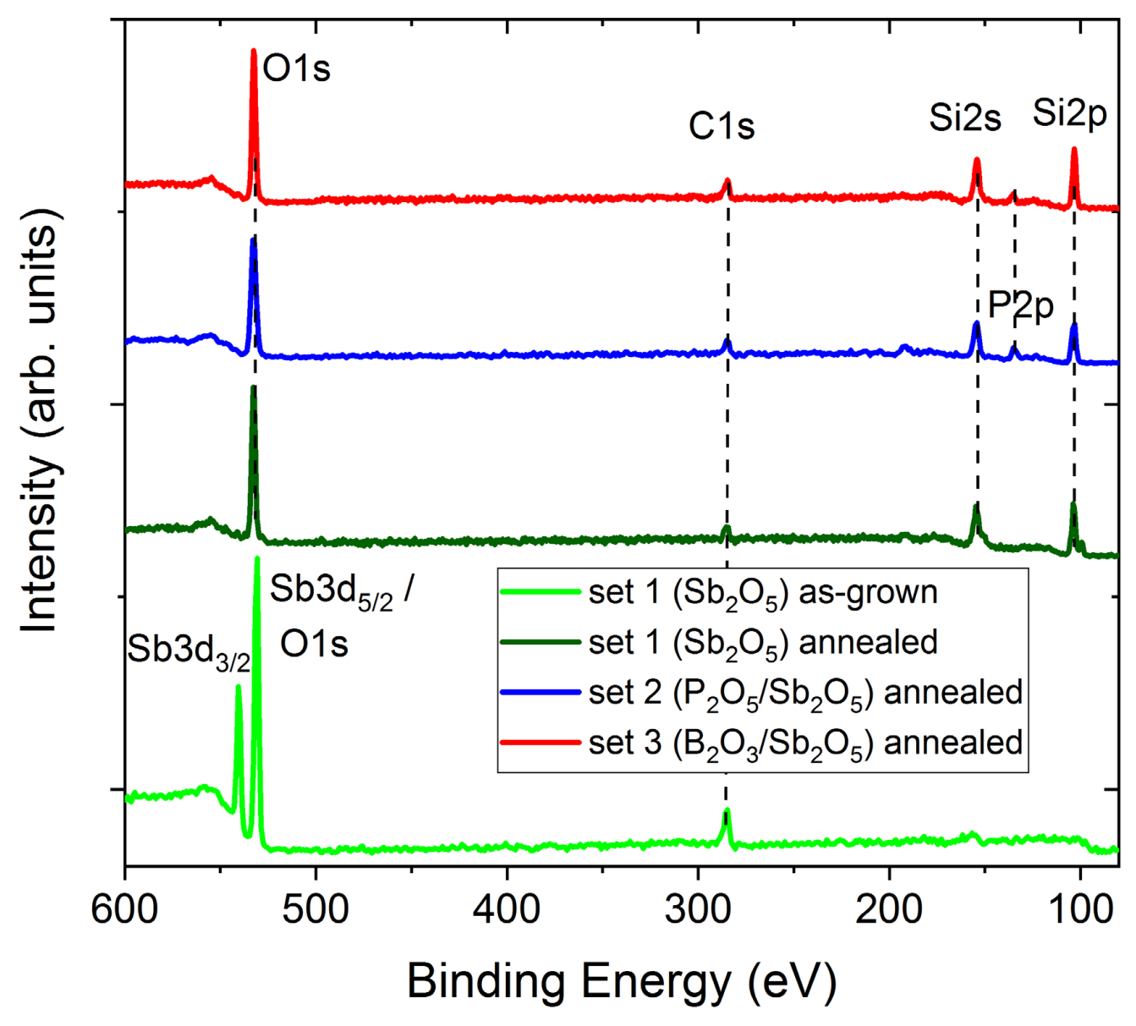
Numerical simulation of experimental doping profiles using Sentaurus Process of Synopsis

Parameters of investigated samples

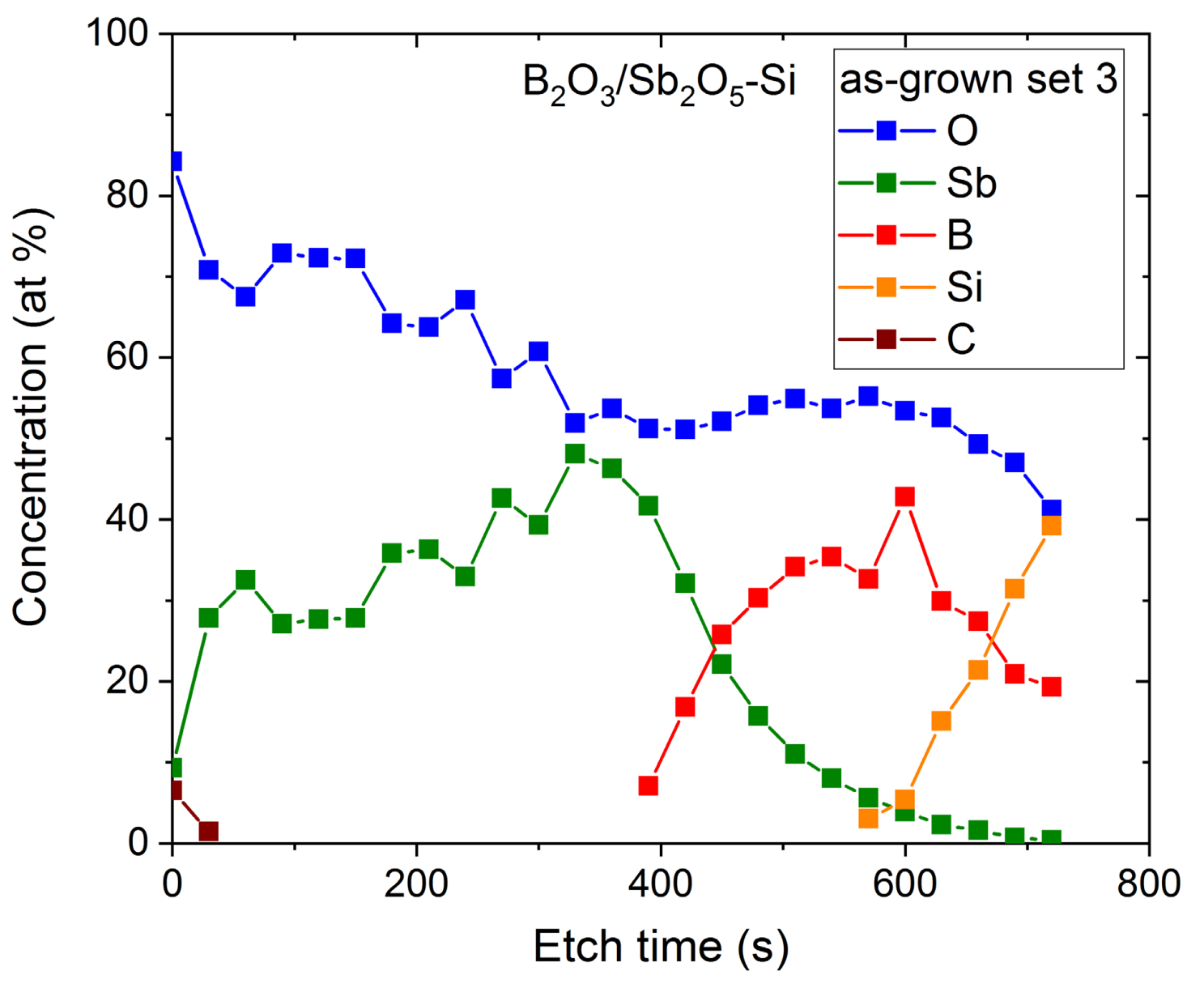
set	ALD-grown oxide thickness [nm]			RTA time [s]
	B_2O_3	P_2O_5	Sb_2O_5	
1			64	20
2		81	64	20
3	28		63	20
4		10	20	4 / 16 / 64
5	10		20	4 / 16 / 64

Experimental results

XPS-spectra of annealed samples

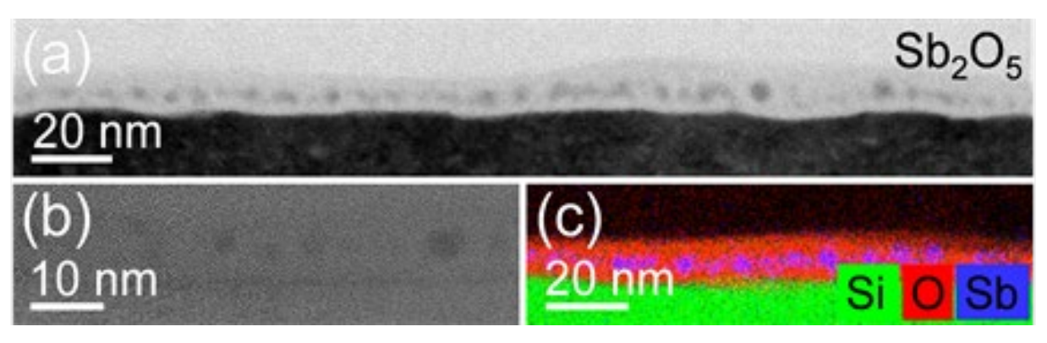


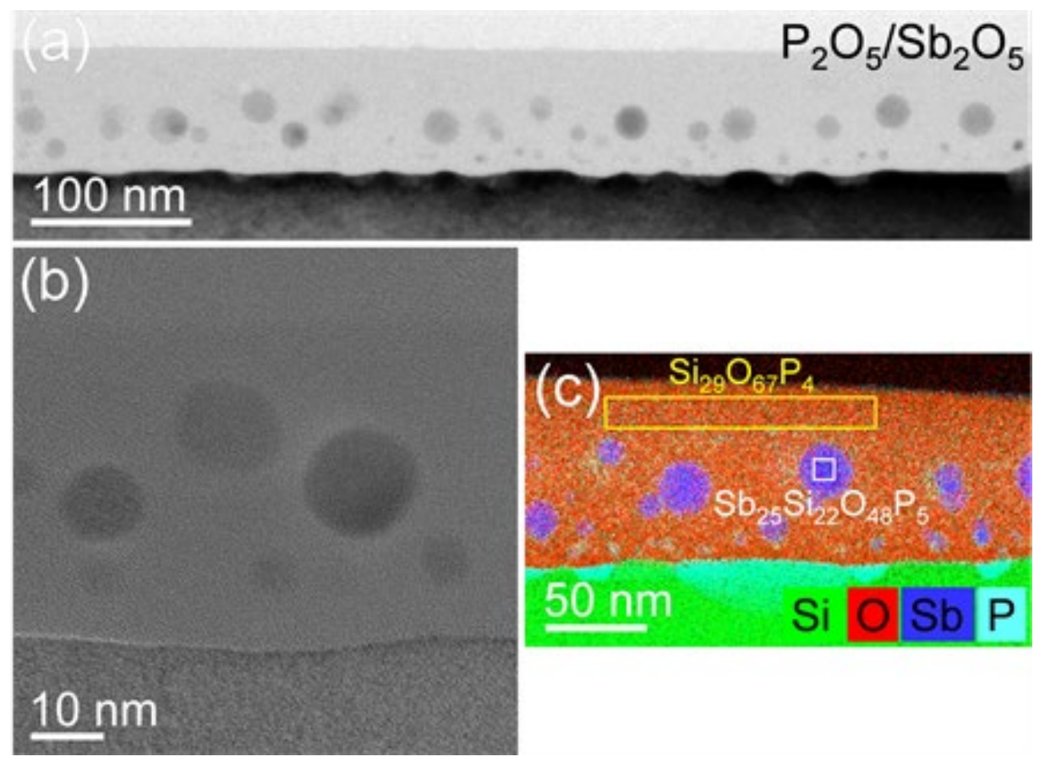
XPS depth profiles of as-deposited B_2O_3/Sb_2O_5-Si sample

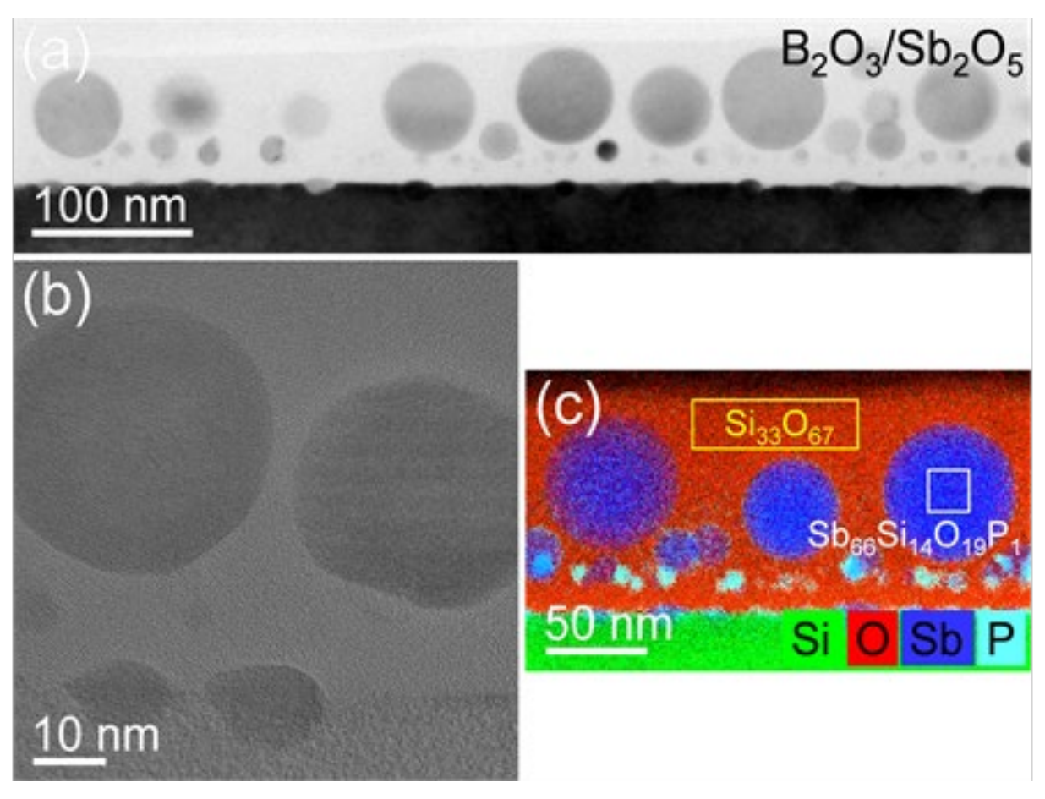


- Presence of phosphorus in annealed samples
- Residual phosphorus in the RTA set-up – source of contamination
- Oxide composition of annealed samples at the surfaces close to $SiO_{2.4}C_{0.4}(P_{0.1})$

Cross-sectional TEM images of annealed samples







(a) Overview bright-field image
(b) High-resolution image
(c) Element distributions obtained by EDXS analysis

- Presence of spherical, partially crystalline particles embedded in an amorphous matrix of SiO_2
- Formation of Si-P precipitates at the oxide/Si interfaces in the B_2O_3/Sb_2O_5-Si and P_2O_5/Sb_2O_5-Si samples
- No precipitates, clusters or structural defects deeper inside the silicon substrate

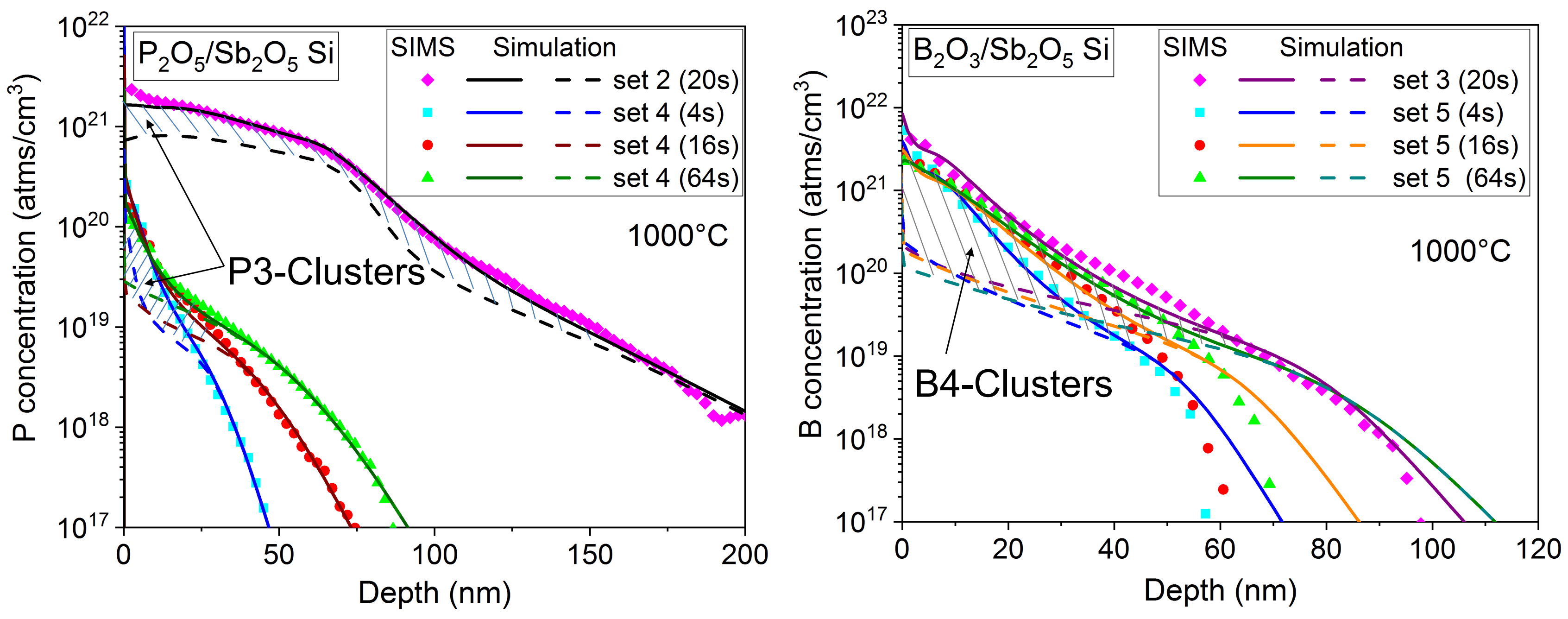
SIMS results and simulation

Calibration of the “React” diffusion model

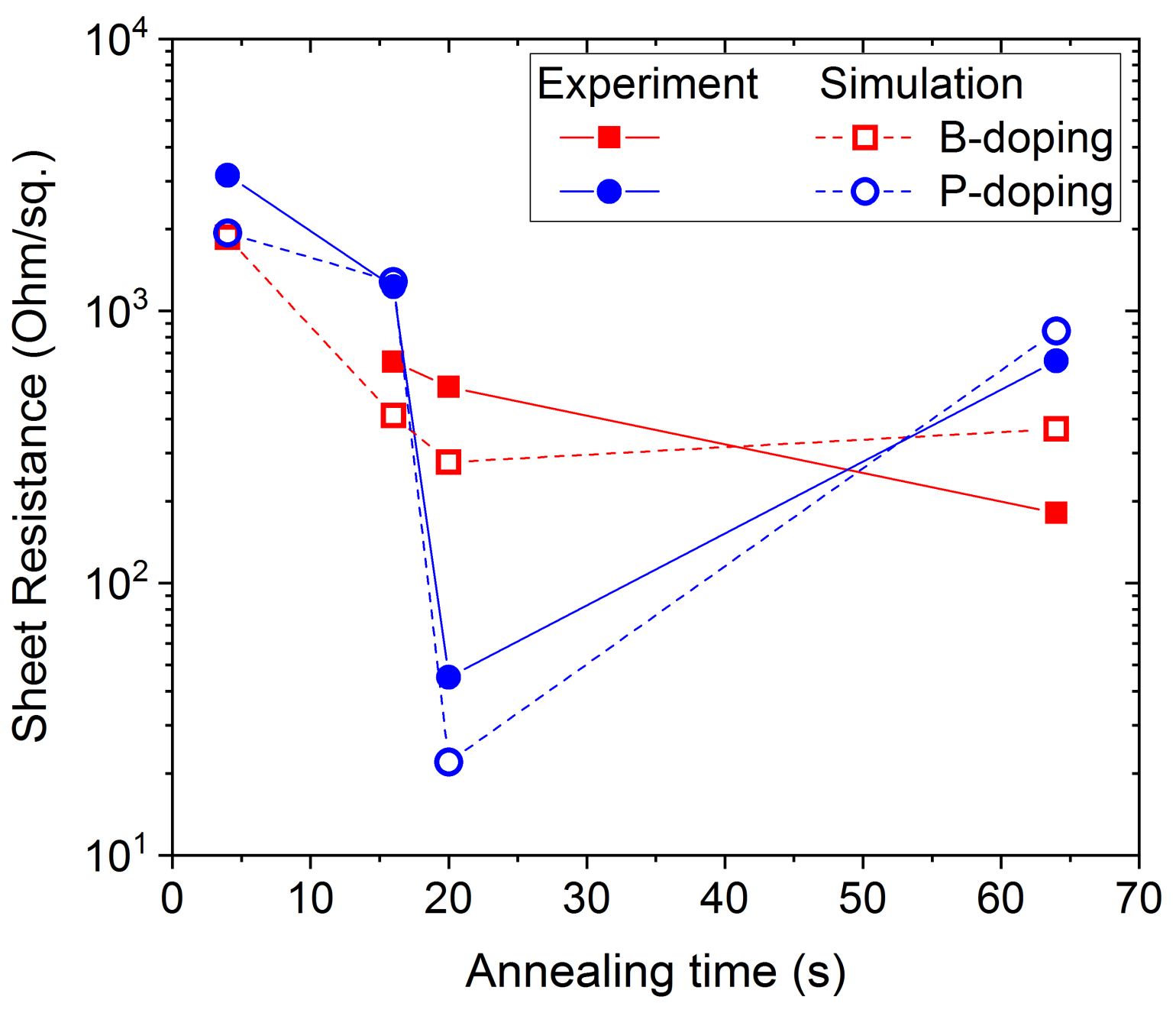
- Highly doped SiO_2 – oxide source
- “Two-phase segregation” model
- Dynamical defect clustering via P_3 and B_4
- “Transient” activation model – activation kinetic of the dopants
- Adjustment of forward-clustering reaction rate & the forward and backward reaction factors of the transient model
- Simulation parameters:

Parameter	Dopant	
	Boron	Phosphorus
Dopant concentration in SiO_2 [cm^{-3}]	$(1.0 \div 1.5)x10^{22}$	$(0.95 \div 8.3)x10^{21}$
Dopant diffusion coefficient in SiO_2 [cm^{-2}]	$2.7x10^{-4}exp(-3.3eV/(kT))$	$5.6x10^{-1}exp(-3.32eV/(kT))$
Solubility in Si [cm^{-3}]	$(6.5 \div 7.5)x10^{20}exp(-0.2eV/(kT))$	$(4.5 \div 8.1)x10^{20}exp(-0.06eV/(kT))$

SIMS and simulated total (solid lines) & electrically active (dashed lines) concentration profiles



Sheet resistance values



- Deviation of SIMS and simulation of boron profiles below $1x10^{19}$ cm^{-3} due to an overestimation of interstitials in simulation
- Estimated fractions of electrically active dopants ≈ 15% for phosphorus and ≈ 5% for boron
- Low dopant activation due to the clusters

Summary

- ➢ **Complete transformation of the ALD-oxides into a silicon oxide during annealing at 1000°C**
- ➢ **Formation of spherical, partially crystalline particles in the oxide & Si-P precipitates at the oxide-Si interface**
- ➢ **High-concentration shallow phosphorus (>$1x10^{20}$ cm^{-3}) and boron (>$1x10^{21}$ cm^{-3}) profiles in Si were realized**
- ➢ **SIMS phosphorus and boron profiles as well as sheet resistances were reproduced by simulations considering dynamical dopant-defect clustering**
- ➢ **Immobile dopant clusters formed during the drive-in processes affect the diffusion of phosphorus and boron and cause a low activation ratio of the dopants in Si**

References & Acknowledgements

[1] B. S. Murty. P. Shankar, B. Raj, B. B. Rath, J. Murray, Textbook of Nanoscience and Nanotechnology (Springer, Berlin), pp. 107-148, 2013
[2] H. H. Radamson, Y. Zhang, X. He, H. Cui, J. Li, J. Xiang, J. Liu, S. Gu, G. Wang, Appl. Sci. 2017, 7 (10), 1047
[3] Y. Sasaki, K. Okashita, B. Mizuo, M. Kubota, M. Ogura, O. Nishijima, J. Appl. Phys. 2012, 111, 013712
[4] L. A. Larson, J. M. Williams, and M. I. Current, Rev. Accel. Sci. Technol. 2011, 4, 11

The authors gratefully acknowledge the support by the Deutsche Forschungsgemeinschaft (DFG)