

Mineral Interface Doping: a safer alternative to doping silicon substrates with phosphorus/arsenic without hazardous chemicals

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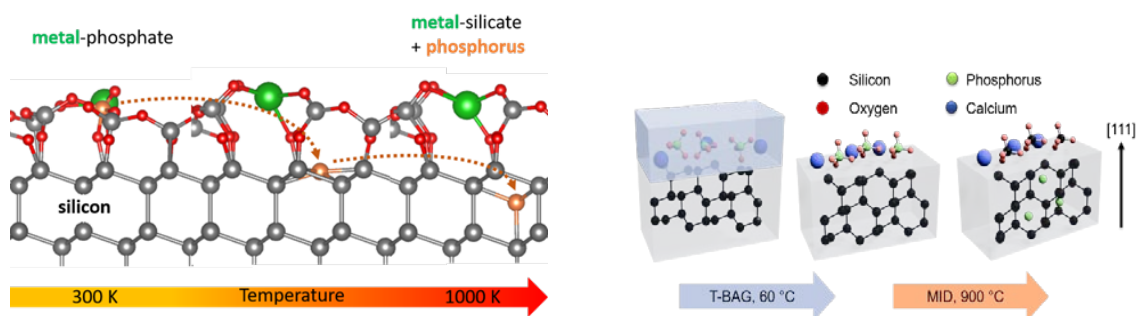
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This work explores Mineral Interface Doping (MID): a safer alternative that offers a simple, reproducible, and industry-relevant approach to doping without hazardous chemicals. MID is an incipient method based on the deposition of a mineral containing the dopant of interest on a silicon wafer, followed by a rapid thermal annealing (RTA) step. MID can utilize a variety of minerals, that effectively form metal silicates in contact with silicon oxide. For this specific application, a mineral should consist of three components: a metal ion (K^+ , Mg^{2+} , Ce^{3+} , ...), element that can be a source of electrons or holes in silicon bulk (such as P, As, B, etc) and oxygen/chlorine components. The proposed method uses ultra-thin films of minerals, for example Hydroxyapatite ($Ca_5(PO_4)_3OH$), Struvite ($MgNH_4PO_4 \cdot 6H_2O$), Cerium Orthophosphate ($CePO_4$), and Monopotassium Phosphate (KH_2PO_4), applied via the Tethering by aggregation and growth (T-BAG) process and activated by RTA. Infrared and Electrochemical Impedance Spectroscopy analyses confirm that phosphorus diffuses through native silicon oxide and into the silicon, altering its electrical properties. To further explain and investigate experimental doping processes using thin films of P-containing minerals, mineral interfaces were modelled and DFT calculations were performed. The Nudged Elastic Bands method provides us with the mechanism of phosphorus transport. Our findings reveal that the required doping temperature decreases with the charge density of metal ions, however there is a required minimum temperature to achieve diffusion of phosphorus into the silicon bulk. Finally, the metal silicates are removed post-doping using non-toxic acids, thus making the process broadly applicable.



Figures (left): Side views of the phosphorus transport into a silicon (111) lattice, (right) Schematic description of 1) T-BAG @ 60 °C and 2) MID @ 900 °C.

[1] Thissen, P.; Longo, R. C., Mineral Interface Doping: Hydroxyapatite Deposited on Silicon to Trigger the Electronic Properties, *Advanced Materials Interfaces* 2024 11 (31), 2400061.

[2] Konoplev-Esgenbourg, R.; Koenig, M.; Welle, A.; Bogner, A.; Longo, R.; Thissen, P., The Role of Metal-Ion Charge in Mineral Interface Doping, *ACS Appl. Mater. Interfaces* 2025, <https://doi.org/10.1021/acsami.5c09080>