diffusion-fundamentals.org

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Diffusive Isotopic Fractionation: Implications for Diffusion Modeling in Crystalline Solids

Edmund G. Seebauer*, Ian I. Suni

Department of Chemical & Biomolecular Engineering
University of Illinois at Urbana-Champaign, Urbana, IL, USA
*Presenting author: eseebaue@illinois.edu

(Received: 2025/09/30, Published online: 2025/11/03)

The recent discovery [1] of strong isotopic fractionation of oxygen in a metal oxide semiconductor via "uphill diffusion" turns out to have unexpectedly broad implications for continuum models of defect-mediated diffusion in crystalline solids. Fig. 1 shows examples of such fractionation, which drives the concentration of ^{18}O in single-crystal rutile TiO_2 submerged in liquid water to well below natural abundance levels.

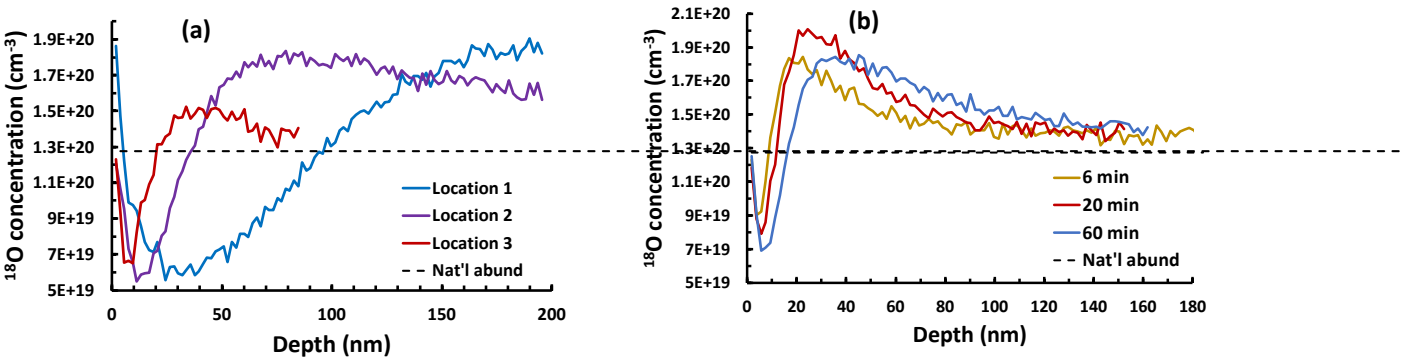

Fig. 1. (a) Example ^{18}O diffusion profiles near the rutile TiO_2 (110) surface measured by *ex situ* secondary ion mass spectrometry at several locations on one specimen. Diffusion transpired during immersion of TiO_2 single crystals immersed in isotopically labeled water with an applied bias V_{appl} = -0.4V vs Ag/AgCl at 30 °C for 60 min. Depth was measured with respect to the crystal surface. Despite the water being isotopically enriched to 10 at % ^{18}O, the profiles exhibit pronounced "valley" regions (having ^{18}O concentrations below natural abundance) up to 90 nm wide. The variability results from submonolayer amounts of surface impurities that inhibit injection of interstitial O atoms from the surface. (b) Example ^{18}O profiles vs diffusion time for the same material at V_{appl} = -0.4 V, 70 °C. Statistical analysis of many such profiles shows that most profile metrics do not vary appreciably outside the variability induced by poisoning as a function of time during the range examined. Straightforward numerical estimates of the time when uphill diffusion ceases suggest that the primary uphill diffusion features are already "baked in" by about 0.5 min.

Diffusion in crystalline solids is typically mediated by mobile atomic-scale defects that exchange atoms with the crystalline lattice. Unlike many examples of uphill diffusion in solids[2], fractionation in the isotopic systems exemplified by Fig. 1 is not driven by thermodynamic interactions between atomic species. Instead, steep chemical gradients of interstitial defects combine with the statistics of diffusional hopping by an interstitialcy mechanism to drive local imbalances at the nanometer scale between the isotopic composition of the defect population and the lattice. The imbalances are especially pronounced for minority species present at very low concentrations due to large departures of the effective diffusivity for the minority species from the hopping diffusivity of most interstitials. Conventional use of Fick's first and second laws as usually applied to simulate dopant diffusion cannot reproduce the observed uphill diffusion – even qualitatively – because local equilibrium is tacitly assumed.

The present work revises the conventional formulation of Fick's Laws in a way that explicitly accounts for strong gradients in defect concentration. The revised formulation can reproduce the main features of uphill isotopic diffusion, as exemplified in Fig. 2 for ^{18}O in TiO_2.

The effects of defect gradients and hopping statistics are understood most readily in such systems. For chemical dopants, an analogous approach applies, but the total concentration of mobile interstitials (dopant plus host) must be employed along with an effective diffusivity that represents a weighted average of the hopping diffusivities for dopant and host.

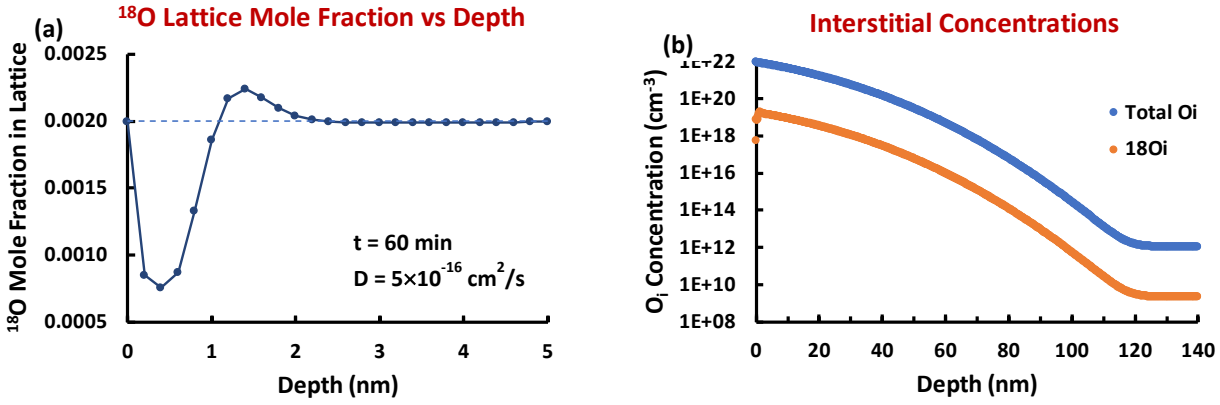

Fig. 2. (a) Example of a simulated ^{18}O diffusion profile near the rutile TiO_2(110) surface using the revised formulation of Fick's Laws. This formulation reproduces the valley-peak uphill diffusion structure seen in the experimental data of Fig. 1. (b) Corresponding concentrations of total O and ^{18}O interstitials as a function of depth. The simulation assumes Langmuir kinetics for interstitial injection and annihilation at surface. No interstitial trapping is included, and the model parameters have not been fitted to experimental data. The purified region is much shallower than the region of interstitial penetration.

Current practice for modeling diffusion of low-concentration minority species is adequate for simulation of many systems involving doping. Important exceptions occur, however, for:

- Chemical dopants at concentrations far outside where their behavior has been fitted to experimental data. This is important for semiconductor device fabrication by ion implantation.
- Chemical dopants whose pre-exponential factor for hopping diffusion has been computed from atomistic calculations by density functional theory, which is now feasible [3].
- Isotopic dopants present at very small mole fractions, as in Figs. 1 and 2.

Although these effects were discovered in connection with interstitial mediation, an analogous description should also apply for vacancy mediation, which is important for diffusion in metals. However, some of the equations need to be written in terms of the concentrations of mobile dopant and host atoms adjacent to vacancies, not the concentration of vacancies itself.

References

[1] H. Jeong, E.G. Seebauer, Strong Isotopic Fractionation of Oxygen in TiO_2 Obtained by Surface-Enhanced Solid-State Diffusion, J. Phys. Chem. Lett. 13 (2022) 9841–9847.

[2] V. Verma, C.H. Belcher, D. Apelian, E.J. Lavernia, Diffusion in High Entropy Alloy Systems – A Review, Prog. Mater. Sci .142 (2024) 101245.

[3] H. Jeong, E.G. Seebauer, E. Ertekin, First-principles description of oxygen self-diffusion in rutile TiO_2: Assessment of uncertainties due to enthalpy and entropy contributions, Phys. Chem. Chem. Phys. 20 (2018) 17448–17457.