doi:10.1017/S1431927622007413
Microsc. Microanal. 28 (Suppl 1), 2022

Direct Observation of Atomic Scale Diffusion Processes Using *in situ* HRSTEM

Peter Schweizer[1*], Laszlo Pethö[1], Emese Huszár[1], Lilian M. Vogl[1], Johann Michler[1], Xavier Maeder[1]

[1]Laboratory for Mechanics of Materials, Swiss Federal Laboratories for Materials Science and Technology (EMPA), Thun, Switzerland
*Corresponding author: Peter.Schweizer@Empa.ch

Diffusion is fundamentally important in materials synthesis, processing and application. While a deep un-derstanding of this process has been established over the centuries in many ways, there is still some gaps to fill when it comes to nanoscale diffusion effects. In particular the influence of size effects, and mechanisms of defect enhanced diffusion are not yet fully understood. Therefore new ways of directly probing diffusion mechanisms at the atomic scale are required. For this *in situ* transmission electron microscopy is the most promising technique as it provides the required spatial and at the same time temporal resolution.

In this work, we show the diffusion dynamics of individual impurity atoms at elevated temperatures using *in situ* High Resolution Scanning Transmission Electron Microscopy (HRSTEM). Impurities in the form of tungsten atoms are brought into an aluminum matrix via co-sputtering using large differences in sputter rate provided by a nanoparticle gun. With this, impurity concentrations in the range of 100 ppm are achieved with 10-20 nm thick Al films (See Figure 1 a for a 3D representation).

Due to the high difference in atomic number between Al and W, the impurity atoms are clearly visible using High-angle Annular Dark-field (HAADF) STEM as shown in Figure 1 b). The single atom contrast is confirmed by complementary image simulations using the PRISM algorithm [1] (see Figure 1 c). At elevated temperatures provided by *in situ* heating, volume diffusion is observed with impurities stochastically jumping from lattice site to lattice site (see Figure 1 d). For clarity the observed process is also shown as a 3D rendering in Figure 1 e and the combined trajectory in Figure 1 f. The process fits to the vacancy-assisted volume diffusion mechanism. Using the relation between distance traveled (x) and the time elapsed in the experiment (t) diffusion coefficients (D) can be worked out according to:

$$\frac{x^2}{4t} = D$$

In this relation, the 2D projection of the 3D atomic movement is taken into account. To get reasonable measures, the movement of atoms is tracked automatically using digital image correlation as shown in Figure 2 a exemplarily. By tracking several atoms simultaneously and repeating the experiment at different temperatures an Arrhenius relationship between temperature and apparent diffusion coefficient can be extracted (see Figure 2 b). There is a clear increase in diffusion speed with increased temperatures with the overall diffusion coefficients being above bulk values. Here, the influence of the electron beam has to be considered, which can stimulate diffusion [2]. By correlating dose- and temperature dependent diffusion coefficients, the influence of both effects can be delineated.

Besides evaluating the kinetics of volume diffusion we also used *in situ* HRSTEM to elucidate the mechanism of grain boundary diffusion. We observe the accelerated motion of impurity atoms along tilt boundaries (see Figure 2 c). Here the impurity atoms use grain boundary interstitial sites to move along the defect. For clarity the atomic columns and the tungsten impurity are marked in Figure 2 d. These

structures serve as direct input for correlative atomistic simulations. Overall, this approach shows great promise for furthering the understanding of diffusion effects on the atomic scale.

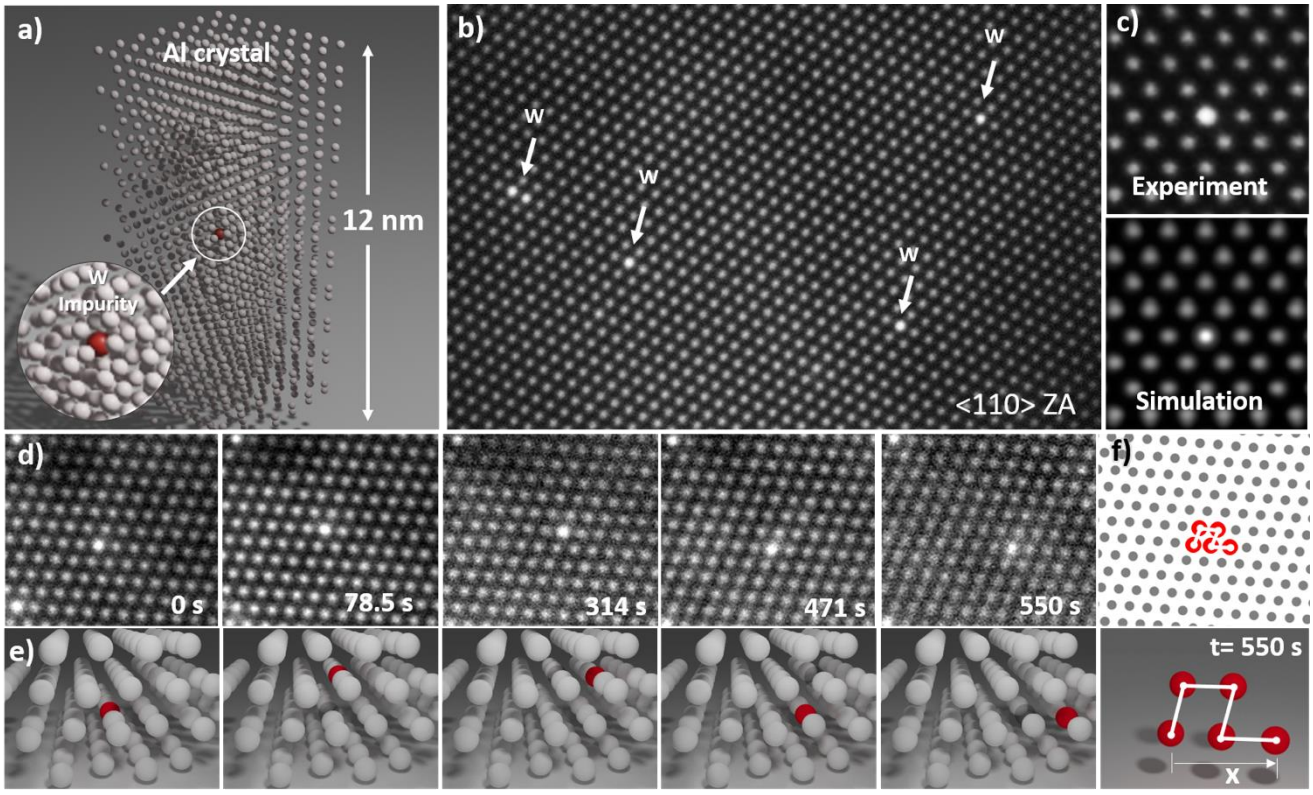
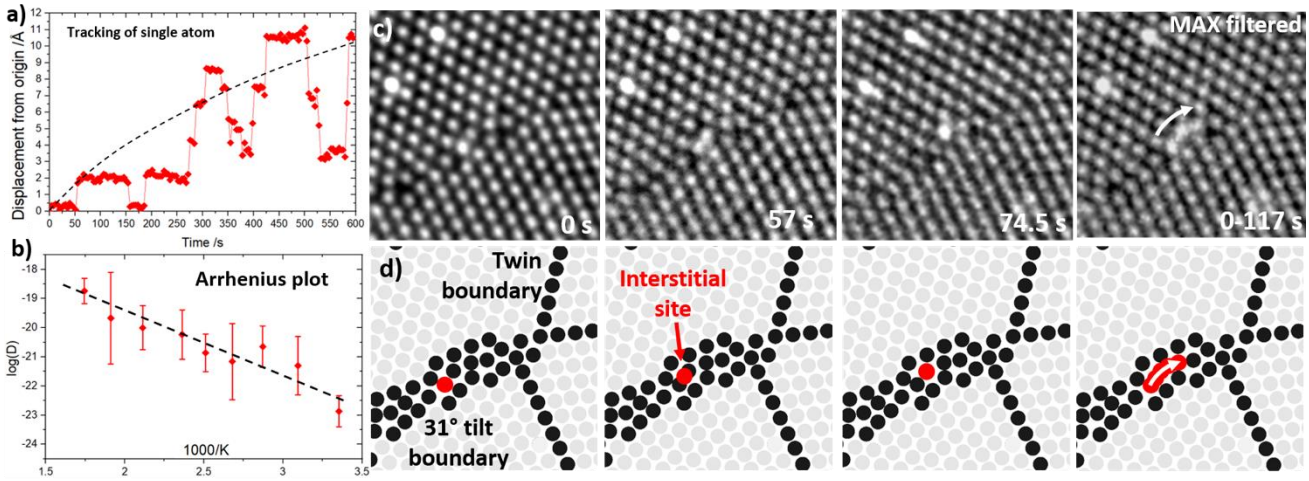


Figure 1: Overview of the sample system and experimental approach. a) 3D representation of a tungsten impurity in an Al thin film. b) HRSTEM image of several impurities in a sample. c) Comparison between experiment and simulation. d) Time series from an in situ heating experiment at 150°C showing hopping from lattice site to lattice site. e) 3D representation of the movement of the atom in the specific orientation. f) Combined motion of the atom over time.



https://doi.org/10.1017/S1431927622007413 Published online by Cambridge University Press

Figure 2: Tracking of atomic motion and grain boundary diffusion. a) Distance from origin over time for a single atom tracked via digital image correlation. b) Arrhenius plot based on such tracked atomic motions. c) Example of grain boundary diffusion in a tilt boundary where the impurity travels along the defect.

References:

[1] C Ophus, Advanced Structural and Chemical Imaging, **13** (2017), doi: 10.1186/s40679-017-0046-1

[2] R Ishikawa, R Mishra, A R Lupini, S D Findlay, T Taniguchi, Sokrates T. Pantelides, and S J Pennycook, Physical Review Letters, **113** (2014), doi: 10.1103/PhysRevLett.113.155501

https://doi.org/10.1017/S1431927622007413 Published online by Cambridge University Press