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A Semi-quantitative Predictive Model for SnO_2 Adatom Diffusion & Its Application to Exit Wave Reconstruction

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Aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM) in conjunction with exit wavefunction reconstruction (EWR) are routinely used to investigate 2D and 3D chemistry, crystallography, and defective structural features of inorganic nanoparticles at atomic resolution [1,2]. EWR is often implemented by acquiring a series of 20-30 HRTEM images while varying the focus of the objective lens. This long exposure can be detrimental to the structural integrity of radiation-sensitive materials, especially nanoparticles because they can easily undergo thermal- and beam-induced surface damage [3,4]. Surface atom dynamics induced by knock-on effects, hinder direct correlation of structural, chemical, and crystallographic properties with the surface of restored exit wave phase. Therefore, methods to predict and prevent atomic motion during AC-HRTEM are essential for electron-imaging-based nanostructural quantification using EWR.

Typically, measuring the extinction of high spatial frequency reflections is used to estimate the rate of transformation of nanoparticles during imaging [5]. However, this method is difficult to implement for very beam-sensitive nanomaterials. Egerton [4,5] developed an alternative calculation-based semi-quantitative method to estimate surface diffusion of adatoms on a substrate. Adatom displacement rates are predicted by applying electron elastic scattering equations to model knock-on displacements at the surface.

At 300 keV, typically used in this study, adatom motion is primarily driven by elastic knock-on displacement [3], which can be slowed by using low beam currents. However, this approach significantly reduces the signal-to-noise ratio of images, which results in loss of structural detail, low contrast, poor image registration and subsequently inaccurate exit waves. Depending on the specimen, electron beam damage can be mitigated while maintaining the resolution of the exit wave by carefully adjusting either the dose rate or cumulative dose [6].

Applying Egerton's predictive model to EWR we found that the optimum dose rate, which minimises beam damage but enables both Sn and O atoms to be resolved, is between 1000 e Å^{-2} s^{-} and 5000 e Å^{-2} s^{-} (Figure 1). This method also predicts that at room temperature thermal-induced displacement rates, $\mathbf{R_t}$, should be greater than beam-induced displacement rates, $\mathbf{R_e}$, at dose rates between 1000 e Å^{-2}s^{-} to 10000 e Å^{-2}s^{-}. Furthermore, upon cooling the specimen to liquid nitrogen temperature, thermal displacements should be negligible, if the adatoms are chemisorbed on the substrate ($\mathbf{E_{sd}}$ >0.2 eV) (Figure 2). Here, $\mathbf{E_{sd}}$ is the activation energy of surface diffusion, signifying the strength of the interaction between the substrate and the adatom [4]. In the chemisorption regime, for heteroatomic nanoparticles, the element with the highest atomic mass has the limiting beam-induced damage rate, as summarised in Table 1.

It follows that to acquire a focal series of 30 images without a single displacement, at 77 K and under optimal dose rates between 1000 – 5000 e Å^{-2} s^{-}, framerates of above 200 fps must be used. High speed cameras are available for fast image acquisition and are therefore promising tools to advance current EWR techniques. In this work, we show how low temperature and fast imaging, using experimental

conditions designed from the predictive model can be used as a starting point to significantly reduce beam damage while maximising exit wave resolution.

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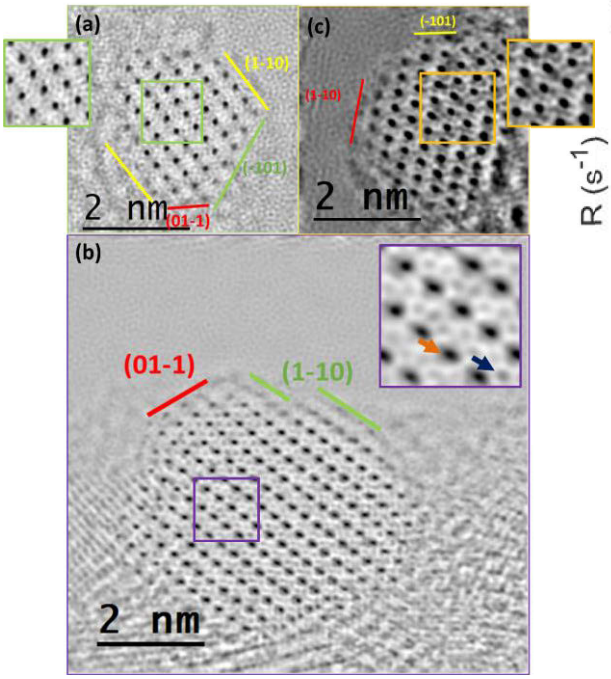

Figure 1. Experimental exit wave phases of [111] SnO_2 nanoparticles obtained using dose rates of a) 1000 eÅ^{-2} s^{-1}, b) 5000 eÅ^{-2} s^{-1}, c) 10 000 eÅ^{-2} s^{-1}. Blue and orange arrows in b) show O and Sn atoms, respectively.

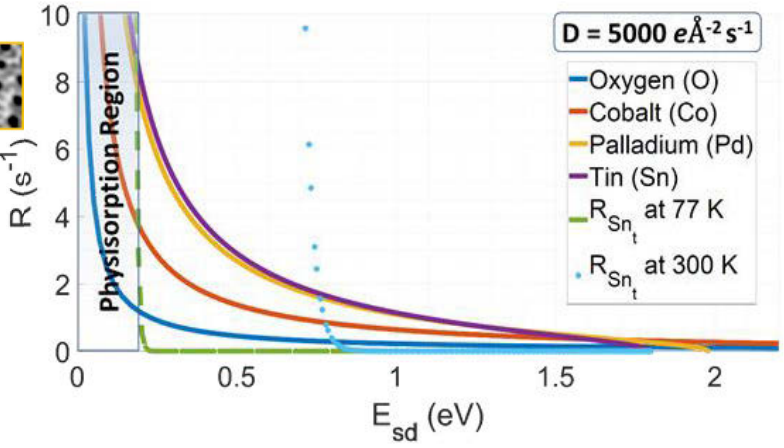

Figure 2. Beam-induced displacement rates for different surface atoms at an incident electron energy of 300 keV and at a dose rate of 5x10^3 eÅ^{-2}s^{-1}. A comparison between thermal-induced displacement rates at temperatures of 77 K (green) and 300 K (light blue) is also shown for Sn atoms.

Dose rate (e□$^{-2}$ s^{-1})	Re (O) s^{-1}	Re (Co) s^{-1}	Re (Pd) s^{-1}	Re (Sn) s^{-1}
1 000	0.15	0.3	0.6	0.7
5 000	1.5	3	6	7
10 000	3	6	12	14

Table 1. Summary of the different adatom displacement rates as a function of dose rate

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