Bayesian Inference of Metal Oxide Ultrathin Film Structure from Surface X-Ray Diffraction Data

Surfaces and interfaces are where useful functionalities appear, but it is not easy to examine the atomic arrangement at these locations. Surface X-ray diffraction is a potentially useful method because of its non-contact and high-resolution nature, although the difficulty of data analysis makes it a rather special technique. Various methods such as phase retrieval [1-3] have been developed to facilitate the analysis. We have applied the Monte Carlo-based technique to the analysis of surface X-ray diffraction data on the basis of Bayesian inference [4]. It correctly identified the interfacial structure from a crude initial model for a perovskite ultrathin film.

Transition metal oxides show various functionalities originating from the strong electron correlation. At the surfaces or interfaces of such oxides, the electron-electron interaction must be altered, which leads to a new functionality (see **Fig. 1**). Since the 3*d* electrons couple with the lattice strongly, one can study the interfacial phenomena through the interfacial structure. The required accuracy of the structural parameters is usually 0.1Å, because the typical change in metal-oxygen bond length caused by the change in valence is 0.1Å. Transmission electron microscopy is a powerful tool for studying interfacial structure, however, its resolution is typically only slightly better than 1Å, which is often insufficient to obtain a detailed physical insight. Instead, high-resolution surface X-ray diffraction can greatly assist studies of metal oxide interfaces.

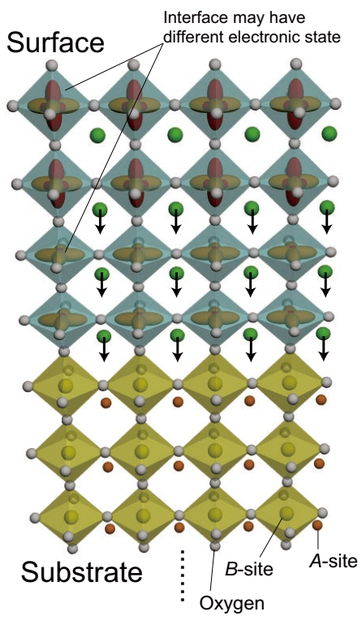

Figure 1: Schematic view of a perovskite oxide interface. The interfacial region may have a special electronic state.

The main difficulty of using surface X-ray diffraction for practical oxide studies is the phase problem. For single-crystal structure analysis, powerful direct methods are available. However, no such methods have been developed for cases with surface diffraction. Instead, holographic [1, 2] or iterative [3] methods, which utilize knowledge of the bulk structure, have been used. As a result, strict constraints such as positivity, atomicity, and the position of the sample surface as well as the bulk structure, are required to obtain a stable answer from a surface diffraction dataset. This requirement can be fulfilled by using specific atomic arrangements instead of phasing the surface diffraction intensity profiles, leading us to develop a real-space based analysis method [4].

The structure determination process is reduced to finding the most probable set of the structural parameters $\boldsymbol{\Theta}$, i.e., atomic positions and occupancies, under the condition of given intensity distribution $I(\boldsymbol{Q})$. Unfortunately, the conditional probability, $P(\boldsymbol{\Theta}|I(\boldsymbol{Q}))$, is not easy to calculate. In contrast, the conditional probability $P(I(\boldsymbol{Q})|\boldsymbol{\Theta})$, which is the probability of obtaining the experimental result from the structure $\boldsymbol{\Theta}$, is easily calculated. According to Bayes' theorem, $P(\boldsymbol{\Theta}|I(\boldsymbol{Q}))$ is proportional to $P(I(\boldsymbol{Q})|\boldsymbol{\Theta})\ P(\boldsymbol{\Theta})$, where $P(\boldsymbol{\Theta})$ is the probability that the structure $\boldsymbol{\Theta}$ happens. Mathematically, we can obtain the most probable structure by calculating $P(I(\boldsymbol{Q})|\boldsymbol{\Theta})\ P(\boldsymbol{\Theta})$ for all possible structures. Practically, it is impossible to calculate the probability for all possible structures; instead, we can do *sampling* by using the Monte Carlo (MC) method with varying the atomic positions and occupancy for the sites close to the surface or interface. We defined the cost function to be minimized during the MC calculation as $-\log[P(\boldsymbol{\Theta}|I(\boldsymbol{Q}))]$. The expression for the cost function resembles the ordinary χ^2, but is not exactly the same.

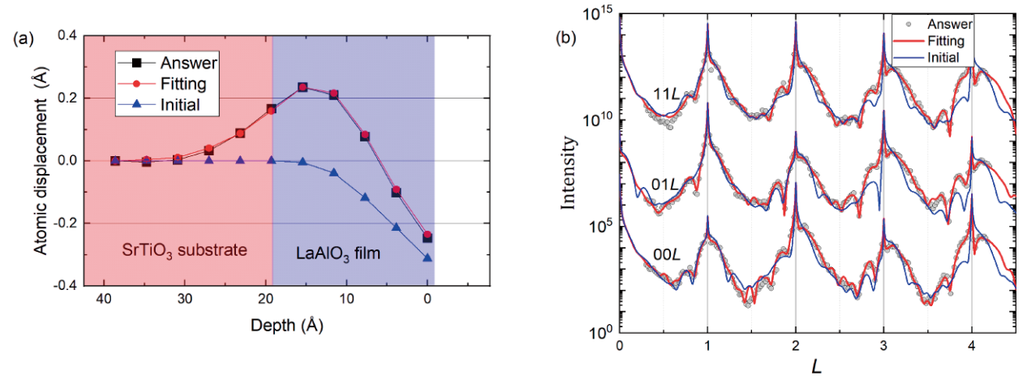

Figure 2: (a) Atomic displacement along the surface normal direction of the answer structure, initial model, and the result of MC fitting. The displacement is measured from the substrate lattice. **(b)** Intensity profiles along 00*L*, 01*L* and 11*L* lines for the answer structure, initial model, and the result of the MC fitting.

In order to examine the efficiency of the curve fitting based on the MC method (MC fitting), the method was applied to artificial intensity profiles calculated from the reported structure parameters of a five-unit-cell-thick $LaAlO_3$ film on a TiO_2-terminated $SrTiO_3$(001) substrate [5]. **Figure 2 (a)** shows the atomic displacement from the substrate lattice. Black and blue symbols show those of the answer structure and initial model, respectively. Panel **(b)** shows the calculated surface diffraction intensity profiles. The symbols and the blue curves show those of the answer structure and the initial model. After millions of steps of MC calculations, the cost function was minimized, yielding the intensity profile shown by the red curve in panel **(b)**. The atomic displacements are converged to the red plots presented in panel **(a)**, which fall on the answer structure. This result shows that the surface diffraction data contain sufficient information to uniquely reproduce the interfacial structure of metal oxides. MC sampling provides the probability density, whose distribution shows the accuracy of the structural parameters. Typical accuracy of the cation position was 0.02Å. The method was also applied to real experimental results measured at BL-3A, and successfully derived a reasonable interfacial structure. This method can be used to examine various interfacial structures to develop better physical insights into transition metal oxides.

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BL-3A

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