Data-driven Sensitivity Analysis in Surface Structure Determination by Total-Reflection High-Energy Positron Diffraction (TRHEPD)

A new data-analysis method for total-reflection high-energy positron diffraction (TRHEPD) experiments to determine the surface and near-surface crystal structure (atomic positions) is proposed. This method consists of an optimization procedure and data-driven sensitivity analysis by solving the eigenvalue equation for the variance-covariance matrix. Applying the method to a novel sub-nanometer-thick semiconductor $Si_4O_5N_3$/6H-SiC(0001)-($\sqrt{3}\times\sqrt{3}$)R30° (SION) structure, it is found that the directional variances differ among the structural deformation directions. This confirms the surface selectivity of TRHEPD. The combination of the TRHEPD experiment and the present data analysis method is promising to accelerate structural analysis research of two-dimensional (2D) materials.

Two-dimensional (2D) materials have attracted much attention in the field of materials science. Recently, total-reflection high-energy positron diffraction (TRHEPD) [1] has emerged as a novel experimental measurement technique for structure determination of 2D materials on a surface. This technique has rapidly progressed in the last decade at the Slow Positron Facility of the Institute of Materials Structure Science, KEK [1]. The experimental setup of TRHEPD is shown schematically in **Fig. 1(a)**; TRHEPD is a positron counterpart of reflection high-energy electron diffraction (RHEED). Unlike electrons, which penetrate deep into the bulk owing to the negative crystal potential energy inside the material, positrons are repelled by the positive crystal potential energy due to the positive charge and are sensitive to the topmost and subsurface layers, making TRHEPD an ideal method for analyzing surface structures at an atomic scale within sub-nanometer depth [2].

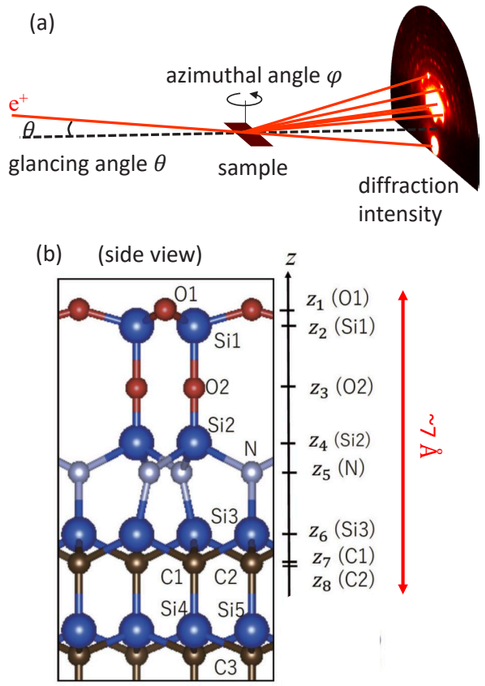

Figure 1: (a) Schematic diagram of the TRHEPD experiment. **(b)** Example of 2D material; $Si_4O_5N_3$/6H-SiC(0001)-($\sqrt{3}\times\sqrt{3}$)R30° (SiON) structure [3].

The present article reports a new data-analysis method for TRHEPD experiments. This method consists of an optimization procedure and data-driven sensitivity analysis [3] and was applied to the structural analysis of $Si_4O_5N_3$/6H-SiC(0001)-($\sqrt{3}\times\sqrt{3}$)R30° [4-6], which is a novel sub-nanometer-thick semiconductor material, SION, fabricated on a silicon carbide (SiC) surface. A side view of SiON is shown in **Fig. 1(b)**. The z axis is chosen to be perpendicular to the surface. We performed the analysis of the TRHEPD data in the one-beam condition, which is sensitive only to the atomic coordinates perpendicular to the surface, z. The dependence of the 00-spot diffraction intensity on the glancing angle (θ) of incidence, called the rocking curve, was extracted from the series of TRHEPD patterns acquired. The variables to be determined were set to be the z-coordinates of the eight atomic surface layers ($X \equiv (z_1,z_2,\ldots,z_8)$). With a trial set of the atomic positions X, the rocking curve is calculated by the fully-dynamical quantum diffraction theory; the norm of the residual difference between the experimental and calculated rocking curves is called the reliability factor or R-factor ($R = R(X)$).

First, the optimization procedure was carried out to obtain the optimal structure $X^* = \mathrm{argmin}_X R(X)$. **Figure 2(a)** shows the comparison between the experimental rocking curve and the calculated rocking curves before and after the optimization. The calculated rocking curve before the optimization was given by the structure data determined from a LEED experiment [5].

Figure 2(a) indicates that the rocking curve after the optimization achieves a better agreement with the experimental one than that before the optimization.

Second, a data-driven sensitivity analysis was carried out, where the variance-covariance matrix S is calculated among the eight variables $(z_1,z_2,\ldots,z_8)$ centered on the optimal point $X^* \equiv (z_1^*,z_2^*,\ldots,z_8^*)$ and the matrix eigen-value equation of S is solved. As a result, the eigenvectors indicate the structural deformation directions to which the R-factor is sensitive. For example, **Fig. 2(b)** visualizes the R-factor in the (z_1,z_2) data subspace. Here, the direction of the arrow is almost parallel to the eigenvector with the lowest eigenvalue and, therefore, is the deformation direction with the highest sensitivity. In other words, the value of the R-factor is quite sensitive to the interlayer distance between the first and second layers (z_1–z_2), meaning that the interaction of the positron waves scattered from the two atomic layers contributes significantly to the diffraction signal. **Figure 2(c)**, on the other hand, visualizes the R-factor function in the (z_1,z_8) data subspace, showing that the deformation direction on the z_1-axis indicated by the arrow is more sensitive than that on the z_8-axis. Similar analysis for combinations of eight variables led to the important conclusion that the rocking curve is not affected by z_7 and z_8 but is dominated by the six variables $(z_1,z_2,\cdots,z_6)$. The sensitivity analysis validated the selectivity of TRHEPD for the depth. The sensitivity analysis also provides objective guidance on the range of atomic coordinates that should be used as variables in optimization.

The combination of the TRHEPD experiment and the present data analysis method promises to accelerate structural analysis research of 2D materials.

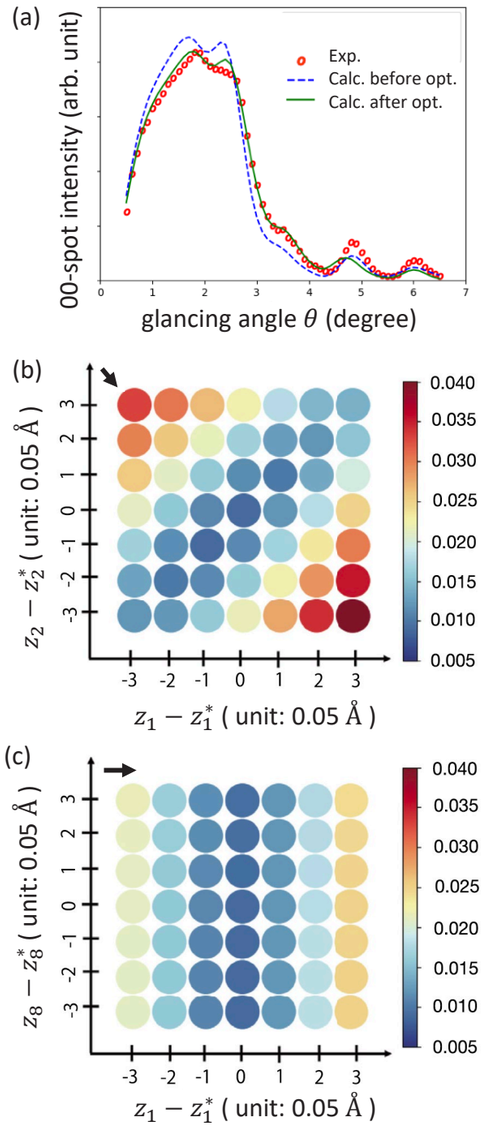

Figure 2: (a) Comparison of the rocking curves in the experiment (open circles), the calculation before the optimization (dashed line), and the calculation after the optimization (solid line) [3]. **(b) (c)** The color-coded isovalue plots of the R-factor in **(b)** the (z_1,z_2) and **(c)** (z_1,z_8) subspaces [3]. The arrows in **(b)** and **(c)** indicate the directions with high sensitivity in **(b)** the (z_1,z_2) and **(c)** (z_1,z_8) subspaces, respectively.

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