



JOURNAL OF  
APPLIED  
CRYSTALLOGRAPHY

**Volume 51 (2018)**

**Supporting information for article:**

**Direct determination of one-dimensional interphase structures  
using normalized crystal truncation rod analysis**

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## Supplemental Materials

### Direct determination of the one-dimensional interphase structure by crystal truncation rod analysis

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#### Lattice strain

The top layers of Pt(111) surface relax or contract depending on the applied potentials. Even though the overall strain is much less than 1%, it modifies the crystal truncation rods (CTR) intensity. However, it affects mainly the intensities near Bragg peaks and has little influence on the intensities near anti-braggs. The intensities near anti-bragg are determining factors for the electrochemical double layers.

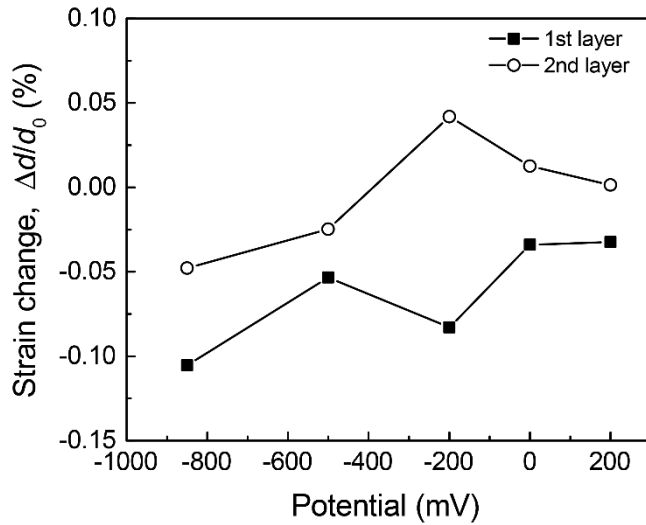


Figure S1 The relative strain change of the first two layers of the Pt (111) substrate determined by the inversion method described in the main text. The applied potentials are vs. Ag/AgCl reference electrode in 3 M KCl.

#### Property of Hilbert transformation for $z < 0$

Let us define  $f_+ = f'_+ + if''_+$  and  $f_- = f'_- + if''_-$  to be the Fourier transformations of  $\rho_+(z)$  and  $\rho_-(z)$ , respectively. The real part of  $f_{\text{ana}} = f_+ + f_-$  is different from  $f'_+ + f'_-$  because  $-H[f''_+ + f''_-] = f'_+ - f'_-$  when the electron density also exists in the negative coordinate. This relation is clear from the following transformation:  $H[f''_-] = -H[\text{Im}[f''_-]] = -(-\text{Re}[f''_-]) = f'_-$

where a star denotes the complex conjugate. The conversion is based on the fact that  $\rho_-(-z)$ , whose Fourier transform is  $f_-^*$ , has the value only in the positive coordinate and Eq. (2) can be applied.

### Numerical inversion of an interphase structure with lattice strain

A numerical inversion was performed for a structure of the interphase with the lattice strain in the substrate. The parameters for the interphase structure and strain were same as those used in the individual numerical simulations as in the main text. A normalized CTR intensity was calculated using the model electron density (see blue broken line in Fig. S2). Otherwise, it was analyzed in the same manner as mentioned in the main article. In the reconstructed electron density distribution, the interphase structure includes the lattice strain inverted to the positive coordinate (see arrows in Fig. S2) and there is no electron densities for the negative coordinate. The final electron density distribution of the interphase structure was obtained by subtracting the sharp features from the strain (orange solid line in Fig. S2). While the lattice strain causes a small discrepancy between the model and reconstructed electron densities, the reconstructed electron density is still in excellent agreement with that of the model. The determined strain values were 0.0095, 0.0058 and 0.00067 for 1st, 2nd and 3rd substrate layers, respectively, while the assumed strain values were 0.01, 0.05 and 0.001.

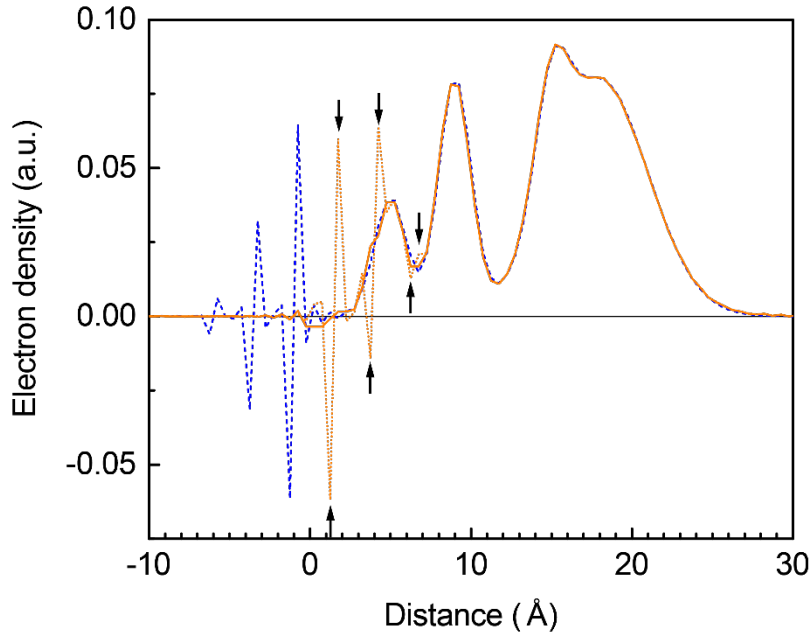


Figure S2. A model electron density distribution including lattice strain in the substrate (blue broken line), the reconstructed distribution by analyzing the scattering data (orange dotted line), and that after the sharp lattice strain is subtracted (orange solid line). Arrows indicate the

contribution from the lattice strain that was inverted through the analysis.

### **Codes for analyses**

The code used in the present analysis was developed with R2014a with *Optimization Toolbox* and *Signal Processing Toolbox*. The main program is “main\_ctr\_anal\_for...”, where analysis parameters such as a lattice spacing and some options should be set in advance to execute. The typical parameters for corresponding sample data have been already entered. Thus, using this prepared script will reproduce a part of the analysis performed in this study. Just after executing the main script, a user interface appears in order to choose a data file. The current code accepts a set of text data that has no header and three columns delimited by tabs. The first, second, and third columns are  $l$ , normalized intensity, and error, respectively. The errors are only used for the error propagation calculation for the result. It can be therefore zero when using a simulated scattering data. The other parameters for the analysis are input interactively during the analysis. The first question is about the absorption factor used for calculating the structure factor of a substrate. In the present analysis, the effect of the absorption was negligible because of a relatively high photon energy. The second question is for the forward Fourier transform calculation, i.e., the Fourier transform from the reconstructed electron density to the scattering factors. It was implemented in order to estimate the contribution from a certain electron density to the scattering. By limiting the range of the Fourier transform, the structure factors only from the region are compared with the original experimental data. This comparison can be skipped by inputting Return. The graphs for the results appearing at the end of the analysis are saved if the saving option is selected. The saved result is stored in a new folder whose name is same as that of the input data, in the same directory of the input data. If the older result folder exists, the program will rename to avoid overwriting.

### **Application for X-ray reflectivity**

The reflectivity of X-ray and neutron scattering within the Born approximation is described as follows (Als-Nielsen & McMorrow, 2011):

$$R(Q) = R_F(Q)|\Phi(Q)|^2, \quad (S1)$$

where  $Q$  is length of a scattering vector defined as  $Q \equiv 4\pi \sin \theta / \lambda$ ,  $R_F$  is the Fresnel reflectivity, and  $\Phi$  is the Fourier transform of the derivative of the electron density distribution. This is given by

$$\Phi(Q) = \int_{-\infty}^{\infty} \frac{d\rho}{dz} \exp(iQz) dz, \quad (\text{S2})$$

where  $z$  is the distance from the substrate surface,  $\rho$  is the electron density distribution along  $z$  direction. Since  $\rho$  is a sum of the electron densities of the substrate,  $\rho_s$ , and interphase layers,  $\rho_l$ ,  $\Phi$  is further expanded to  $\Phi = iQ(F + f)$ , where  $F$  and  $f$  is the Fourier transform of  $\rho_s$  and  $\rho_l$ , respectively. Thus, the normalized XRR spectrum is further described as follows:

$$\frac{|F|}{2} \left( \frac{|\Phi|^2}{Q^2|F|^2} - 1 \right) = \frac{F'}{|F|} f' + \frac{F''}{|F|} f'' + \frac{f'^2 + f''^2}{2|F|}. \quad (\text{S3})$$

This equation is similar to Eq. (1) in the main text for CTR and can be solved with known structure factor of  $F$ , the Hilbert transform given in Eq. (2) and (3) in the main text and experimentally obtained XRR profile. The structure factor of the substrate is given by the Fourier transform of the step function as follows:

$$F = \int_{-\infty}^{\infty} \theta(-z) \exp(iQz) dz = \pi\delta(Q) - iP\left\{\frac{1}{Q}\right\}. \quad (\text{S4})$$

where  $\theta(-z)$  is the step function,  $\delta$  is the Dirac's delta function and  $P\{\}$  denotes the Cauchy principal value. In the practical analysis, the first term on the right-hand side of Eq. (S4) is neglected because one can only measure the region of  $Q > 0$ . Thus, the first term on the right-hand side of Eq. (S3) vanishes, and the third term can be neglected when the density of the interphase layer is much smaller than that of the substrate, which gives an initial solution of

$$f'' \sim \frac{1}{2Q} (|\Phi|^2 - 1) \quad (\text{S5})$$

for the subsequent numerical solver.

Numerical simulation was performed to demonstrate the present analysis method for XRR. A normalized XRR profile of a three-layer film (see Fig. S3(b)) was calculated based on Eq. (S2) (see Fig. S3(a)). Then, the structure factor of the film was determined by numerically solving Eq. (S3) with the Hilbert transform, and the electron density distribution was reconstructed from the determined structure factor through the Fourier transform. The originally assumed normalized reflectivity profile was almost identical to that obtained from the reconstructed electron density distribution (see Fig. S3(a)), which indicates the formulas of the

structure factors were successfully solved numerically. The reconstructed electron density distribution was also in excellent agreement with that originally assumed, where the small discrepancy is mainly derived from the numerical derivation in Eq. (S2). Thus, the direct inversion method using the Hilbert transform in the present study is also applicable to XRR within the kinematical limit.

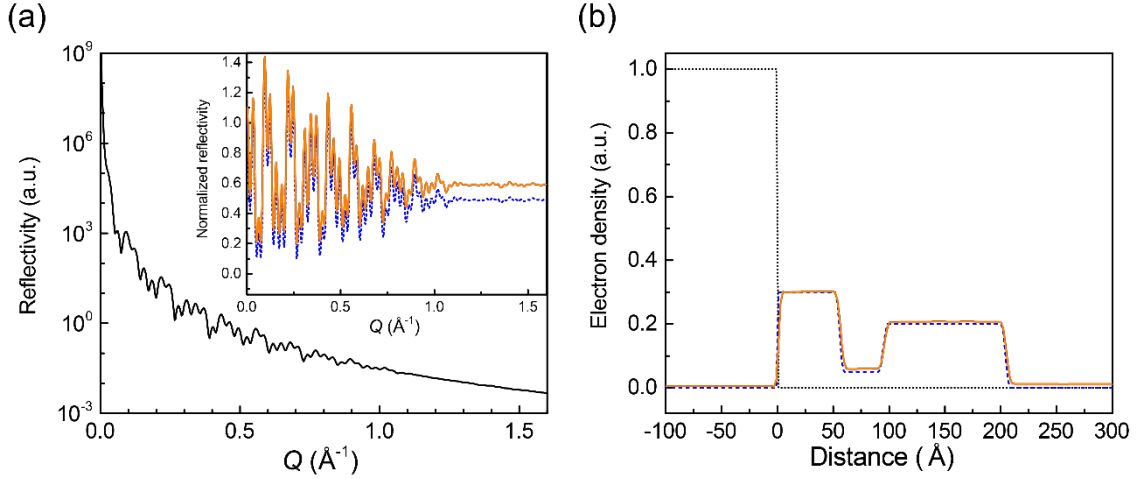


Figure S3. (a) A simulated X-ray reflectivity profile. The inset exhibits the normalized spectrum from the simulation (blue broken) and that obtained from the reconstructed electron density (orange solid) with offset of 0.1. (b) Electron density profiles of the original object (blue broken), the reconstructed object (orange solid) and the substrate (black dot).

### Multiple solutions in the scattering formula

Multiple solutions may simultaneously satisfy the scattering formulas. In this case, it is impossible to determine uniquely the original electron density distribution without additional information or a priori knowledge. When  $f$  is a solution of the scattering formulas such as Eq. (1) in the body text or Eq. (S3),  $\hat{f} = \alpha(Q)f$  is also a solution of these formulas, where  $\alpha(k)$  is a complex function of  $k$  holding the following relation

$$|f|^2(|\alpha|^2 - 1) + 2(\alpha' - 1)f''F'' + 2\alpha''f'F'' = 0. \quad (\text{S6})$$

$\alpha'$  and  $\alpha''$  are the real and imaginary part of  $\alpha$ , respectively. Real values of  $\alpha$  other than a trivial solution, i.e.,  $\alpha = 1$ , can be solved as  $\alpha = -(|f|^2 + 2f''F'')/|f|^2$  and it gives multiple solutions of  $f$  in the scattering formula. Notably this is not a specific problem of the present

analysis method but a general problem in the whole CTR and XRR analyses.

This multiple solution is more critical in the XRR analysis. For example, when a single layer with relative electron density of  $r$  to the substrate whose thickness is  $2w$  exists on the substrate, the structure factors are as follows:  $f = 2r \sin(wQ) \exp(iwQ) / Q$  and  $F = -i/Q$ . Then,  $\alpha = (1 - r)/r$  is a solution of Eq. (S6) and it gives another structure factor of  $\hat{f} = \alpha f = 2(1 - r) \sin(wQ) \exp(iwQ) / Q$ , which simultaneously satisfies the scattering formula. It shows that it is impossible to distinguish the layer with relative density of  $r$  from that with  $1 - r$  only from the experimental data. When the interphase structure is known to be much lighter than the substrate, initial solutions given in Eqs. (4) or (S5) can be used and the numerically solved structure factor must reflect the actual structure. Otherwise, an appropriate a priori constraint is required to determine uniquely the structure.

## Reference

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- You, H. (1992). Surface X-ray and Neutron Scattering, Eds.: H. Zabel and I.K. Robinson, pp. 47–50. Springer, Berlin, Heidelberg.