Supporting Information

Orientation domains in vacancy-ordered titanium monoxide

Cong Guo,[†] *Shuangfeng Jia,*[†] *Weiwei Meng, He Zheng, Lei Jin, Yong Liu, Jing Shi, Jianbo Wang*[*]

School of Physics and Technology, Center for Electron Microscopy and MOE Key Laboratory of Artificial Micro- and Nano-structures, Wuhan University, Wuhan 430072, China

[†] The first two authors contributed equally to this work.
[*] Corresponding author. Fax: +86 27 6875 2569. E-mail address: wang@whu.edu.cn (J. Wang).

Part 1

Here $\mathbf{a_m}$, $\mathbf{b_m}$, and $\mathbf{c_m}$ are also represent basis vectors of the domain variant 1 (D1, here D*i* denote domain variant *i*, *i* ranges from 1 to 12). The general orientation relationship between ordered and disordered TiO_x can be deduced relying on the choice of basic vectors for further systematic comparison:

$$\begin{pmatrix} \boldsymbol{a}_m & \boldsymbol{b}_m & \boldsymbol{c}_m \end{pmatrix} = \begin{pmatrix} \boldsymbol{a}_c & \boldsymbol{b}_c & \boldsymbol{c}_c \end{pmatrix} \begin{pmatrix} 1 & 1 & 0 \\ \bar{1} & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{S1}$$

Mathematically, the basis vectors $\mathbf{a}_i$, $\mathbf{b}_i$, and $\mathbf{c}_i$ of the twelve domain variants *i* can be related to those of $\mathbf{a}_c$, $\mathbf{b}_c$, and $\mathbf{c}_c$ of the cubic by

$$\begin{pmatrix} \boldsymbol{a}_i & \boldsymbol{b}_i & \boldsymbol{c}_i \end{pmatrix} = \begin{pmatrix} \boldsymbol{a}_c & \boldsymbol{b}_c & \boldsymbol{c}_c \end{pmatrix} M_i \tag{S2}$$

where M_i is a transformation matrix for domain variant *i* (*i*=1…12).

With this formulation, we can easily index the diffraction patterns for each domain variant and understand the relationship between domain variants. Base on crystallography, both the relationship of the plane indices and that of the zone axes indices can be derived as

$$\begin{pmatrix} h_i & k_i & l_i \end{pmatrix} = \begin{pmatrix} h_c & k_c & l_c \end{pmatrix} M_i \tag{S3}$$

$$\begin{pmatrix} u_i & v_i & w_i \end{pmatrix} = \begin{pmatrix} u_c & v_c & w_c \end{pmatrix} (M_i^{-1})^T \tag{S4}$$

In the formulations, h_i, k_i and l_i are the plane indices of the twelve domain variants *i*, while h_c, k_c and l_c are the plane indices of the cubic TiO_x; u_i, v_i and w_i denote the zone axes indices of the twelve domain variants *i*, while u_c, v_c and w_c denote the zone axes indices of the cubic phase. M_i^{-1} is the inverse matrix of M_i, and $(M_i^{-1})^T$ means transpose matrix of M_i^{-1}. Hence, with the above transformation formulas, all zone axes for disordered TiO_x and twelve domain variants *i* can be compared conveniently.

Table S1 lists all essential symmetry operations in the cosets for these twelve domain variants. A complete set of operations of each coset can be obtained by multiplying the essential symmetry operations with the translation operations of the subgroup under the space group of *A*2*/m*.

Subsequently, Table S2 shows the relevant twelve transformation matrix which can be obtained by multiplying the corresponding symmetry operation matrix with the transformation matrix of domain variant 1.

Part 2

In Figure S1 and Figure S2, a series of SAED patterns recorded and the corresponding simulated composite patterns of twelve monoclinic domain variants are listed for detail. The reflections in diffraction patterns are consistent with simulated patterns, besides the occurrence of theoretically forbidden spots due to double diffraction, confirming the existence of ordered monoclinic domain variants.

Table S1

Orientation domain variants and the essential operations in cosets corresponding to these 12 domains

Domain	Coset	Essential operations in coset			
1	$A2/m$	1	$2[001]$	$\bar{1}$	$m[001]$
2	$3^{+}[111]A2/m$	$3^{+}[111]$	$3^{+}[\bar{1}1\bar{1}]$	$\bar{3}^{+}[111]$	$\bar{3}^{+}[\bar{1}1\bar{1}]$
3	$3^{+}[\bar{1}\bar{1}1]A2/m$	$3^{+}[\bar{1}\bar{1}1]$	$3^{+}[1\bar{1}\bar{1}]$	$\bar{3}^{+}[\bar{1}\bar{1}1]$	$\bar{3}^{+}[1\bar{1}\bar{1}]$
4	$3^{-}[111]A2/m$	$3^{-}[111]$	$3^{-}[1\bar{1}\bar{1}]$	$\bar{3}^{-}[111]$	$\bar{3}^{-}[1\bar{1}\bar{1}]$
5	$3^{-}[\bar{1}1\bar{1}]A2/m$	$3^{-}[\bar{1}1\bar{1}]$	$3^{-}[\bar{1}\bar{1}1]$	$\bar{3}^{-}[\bar{1}1\bar{1}]$	$\bar{3}^{-}[\bar{1}\bar{1}1]$
6	$4^{+}[001]A2/m$	$4^{+}[001]$	$4^{-}[001]$	$\bar{4}^{+}[001]$	$\bar{4}^{-}[001]$
7	$4^{-}[100]A2/m$	$4^{-}[100]$	$2[011]$	$\bar{4}^{-}[100]$	$m[011]$
8	$2[100]A2/m$	$2[100]$	$2[010]$	$m[100]$	$m[010]$
9	$2[101]A2/m$	$2[101]$	$4^{+}[010]$	$m[101]$	$\bar{4}^{+}[010]$
10	$2[1\bar{1}0]A2/m$	$2[1\bar{1}0]$	$2[110]$	$m[1\bar{1}0]$	$m[110]$
11	$2[01\bar{1}]A2/m$	$2[01\bar{1}]$	$4^{+}[100]$	$m[01\bar{1}]$	$\bar{4}^{+}[100]$
12	$2[\bar{1}01]A2/m$	$2[\bar{1}01]$	$4^{-}[010]$	$m[\bar{1}01]$	$\bar{4}^{-}[010]$

Table S2

Transformation matrices of the 12 orientation domain variants

type	matrix	type	matrix
M_1	$\begin{pmatrix} 1 & 1 & 0 \\ \bar{1} & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	M_7=4$^-$[100]M_1	$\begin{pmatrix} 1 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & \bar{2} & 0 \end{pmatrix}$
M_2=3$^+$[111]M_1	$\begin{pmatrix} 0 & 0 & 1 \\ 1 & 1 & 0 \\ \bar{1} & 2 & 0 \end{pmatrix}$	M_8=2[100]M_1	$\begin{pmatrix} 1 & 1 & 0 \\ 1 & \bar{2} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}$
M_3=3$^+$[$\bar{1}\bar{1}$1]M_1	$\begin{pmatrix} 0 & 0 & \bar{1} \\ 1 & 1 & 0 \\ 1 & \bar{2} & 0 \end{pmatrix}$	M_9=2[101]M_1	$\begin{pmatrix} 0 & 0 & 1 \\ 1 & \bar{2} & 0 \\ 1 & 1 & 0 \end{pmatrix}$
M_4=3$^-$[111]M_1	$\begin{pmatrix} \bar{1} & 2 & 0 \\ 0 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}$	M_{10}=2[1$\bar{1}$0]M_1	$\begin{pmatrix} 1 & \bar{2} & 0 \\ \bar{1} & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}$
M_5=3$^-$[$\bar{1}$1$\bar{1}$]M_1	$\begin{pmatrix} 1 & \bar{2} & 0 \\ 0 & 0 & \bar{1} \\ 1 & 1 & 0 \end{pmatrix}$	M_{11}=2[01$\bar{1}$]M_1	$\begin{pmatrix} \bar{1} & \bar{1} & 0 \\ 0 & 0 & \bar{1} \\ 1 & \bar{2} & 0 \end{pmatrix}$
M_6=4$^+$[001]M_1	$\begin{pmatrix} 1 & \bar{2} & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	M_{12}=2[$\bar{1}$01]M_1	$\begin{pmatrix} 0 & 0 & \bar{1} \\ 1 & \bar{2} & 0 \\ \bar{1} & \bar{1} & 0 \end{pmatrix}$

Figure S1

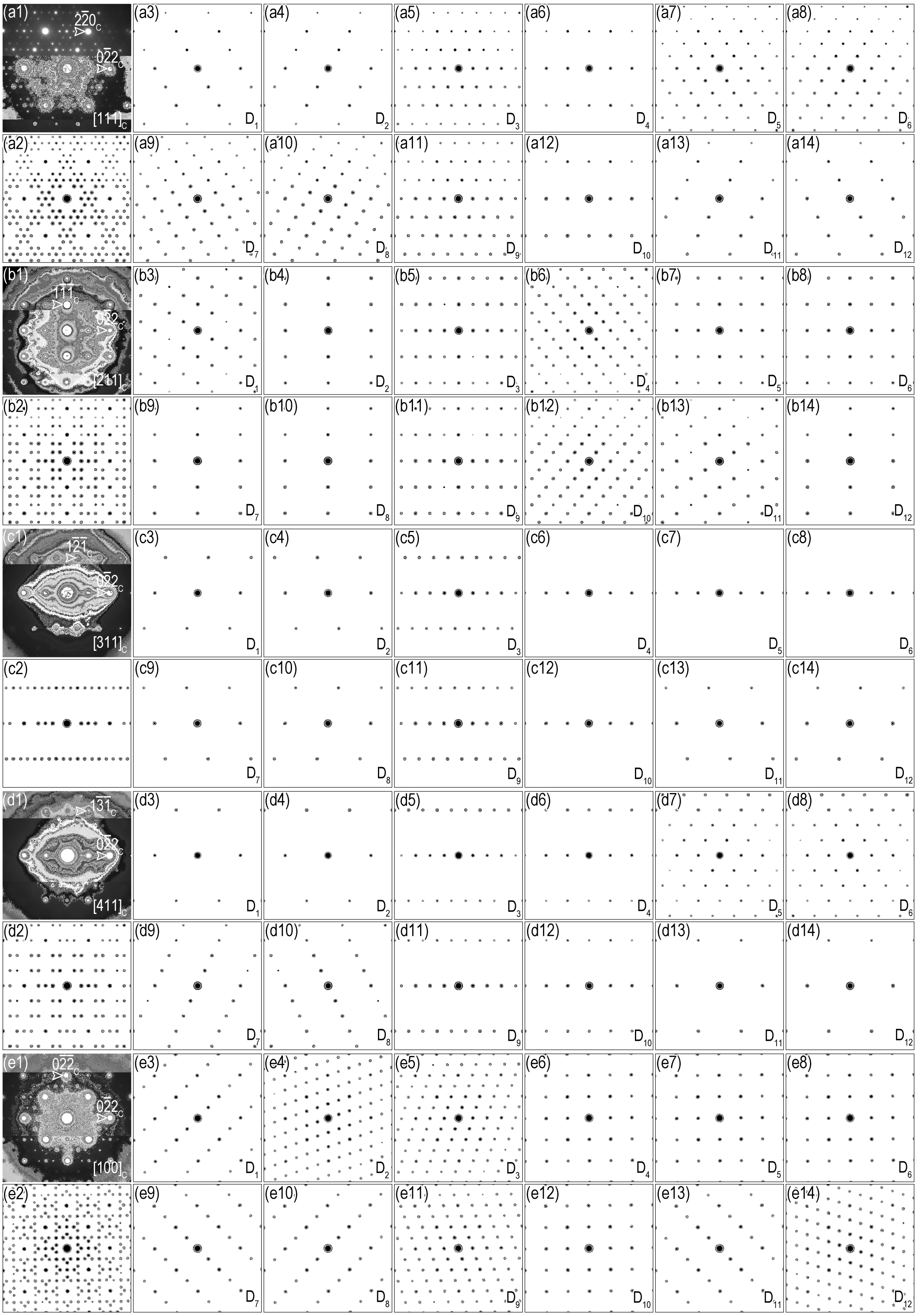

Figure S2

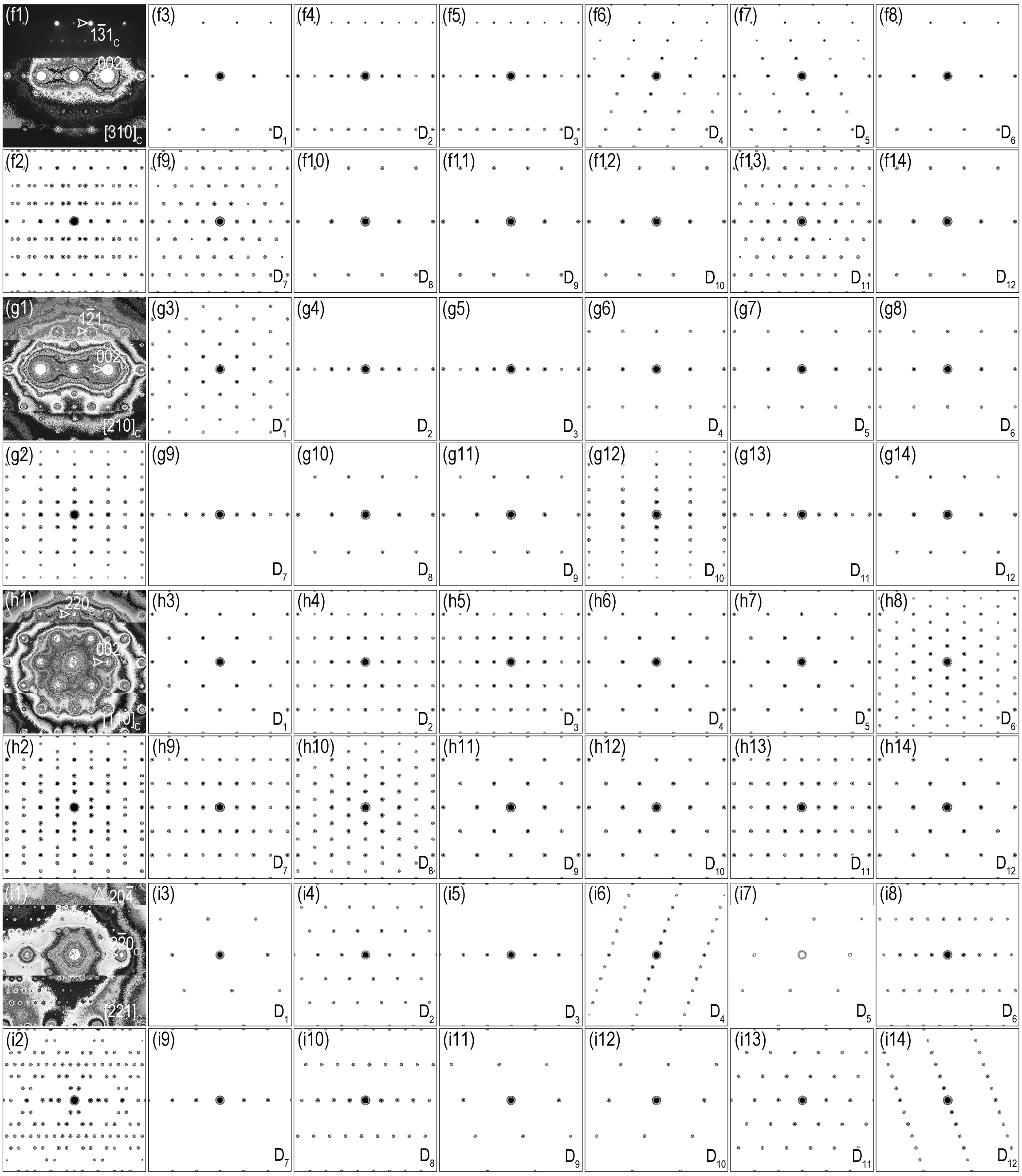

Figure S1 and Figure S2 Experimental SAED pattern and simulated patterns. (a1) Experimental SAED patterns viewed along the cubic $[111]_c$ direction and (a2) simulated composite pattern of the twelve monoclinic domain variants. (a3)-(a14) Simulated patterns of all twelve monoclinic domain variants, respectively. (b)-(i) Corresponding experimental SAED patterns and simulated patterns viewed along the $[211]_c$, $[311]_c$, $[411]_c$, $[100]_c$, $[310]_c$, $[210]_c$, $[110]_c$ and $[221]_c$ directions.