doi: 10.1017/S1431927609093775
Microsc Microanal 15(Suppl 2), 2009

Direct observation of TiO_2 (110) surfaces by HVEM and HAADF STEM

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Titania (TiO_2) is used in many technological applications, such as heterogeneous catalysts, photocatalysts, gas sensors, and coatings. These applications strongly depend on its surface properties, so an understanding of the atomic as well as the electronic structure of the surfaces has been sought for many years [1]. However, the atomic-scale structure of TiO_2 surfaces is still controversial, even for low-index, stable surfaces such as (110), which have long been studied as a model oxide surface. Particularly, when the (110) surfaces are reduced, the expected (1×1) bulk termination evolves into several atomic-scale surface reconstructions and there has been growing speculation that these surface reconstructions involve Ti atoms in the interstitial sites of rutile structure. Recently, Park *et al.* proposed a new structural candidate for the (1×2) reconstruction, based on scanning tunneling microscopy observations combined with DFT calculations [2]. In this model, Ti atoms occupy interstitial sites on the surface, similar to the commonly accepted added Ti_2O_3 row model proposed by Onishi and Iwasawa [3,4]. However, the critical difference between these two models is the occupation of different Ti interstitial sites on the surface. In each (110) layer, there are two Ti interstitial sites surrounded by distorted O octahedra in rutile TiO_2. Here we adopt the standard notation for these two Ti interstitial sites as *ih* and *iv* sites [5], whose octahedra have parallel (horizontal) and perpendicular (vertical) equatorial planes to the (110) surface, respectively. In the Park *et al.* model, Ti interstitials are proposed to occupy *ih* sites, while in the Onishi-Iwasawa model, they occupy *iv* sites. Thus, while Ti interstitials have been suggested as the fundamental building block of surface reconstructions in reduced TiO_2 (110) surfaces, their presence and positioning has not yet been established.

In the present study, we use atomic-resolution TEM to directly observe surface structures of TiO_2 (110) from directions parallel to the surface. Combining the advanced TEM techniques of high-voltage electron microscopy (HVEM), aberration-corrected, high-angle annular dark-field (HAADF), scanning transmission electron microscopy (STEM), and their observations from orthogonal directions, we show definitive evidence of the presence and positioning of Ti interstitials in the reconstructed surface structure under reducing atmosphere. Fig. 1 shows a HVEM image of the (110) surface observed from the [001] direction [6]. The (110) surfaces are atomically flat over extended regions up to several tens of nanometers along the $[\bar{1}10]$ direction but it is also clear that structural reconstruction has occurred at the top surface layer. These reconstructions are thought to be caused by the high-voltage electron irradiation that occurs in HVEM [6]. Figs. 2A and B show magnified HVEM and HAADF STEM images of the TiO_2 (110) surfaces viewed from the [001]

direction, respectively. As indicated by the arrows, the positions of Ti atoms at the top surface layer are shifted from the expected positions in the rutile structure. These Ti sites correspond to the interstitial sites as referred to the bulk rutile structure, and, combining with the observations from the [1$\bar{1}$0] direction, we could determine that these Ti interstitials occupy *ih* sites, which is consistent with the Park *et al.* model [6].

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[7] This work was supported in part by the Grant-in-Aid for Scientific Research on Priority Areas "Nano Materials Science for Atomic-scale Modification" (no. 19053001) from the Ministry of Education, Culture, Sports and Technology (MEXT). N.S. acknowledges supports from PRESTO, Japan Science and Technology Agency, and from Industrial Technology Research Grant program in 2007, New Energy and Industrial Technology Development Organization (NEDO) of Japan. S.D.F. is supported as a Japanese Society for the Promotion of Science (JSPS) fellow.

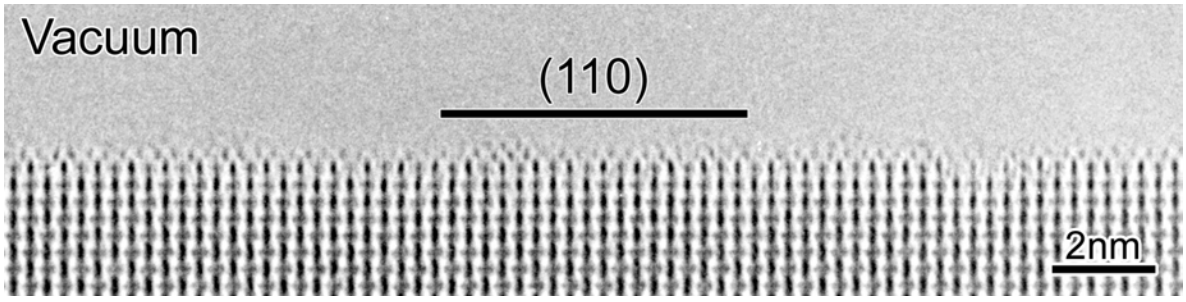

FIG.1: HVEM image of TiO_2 (110) surface.

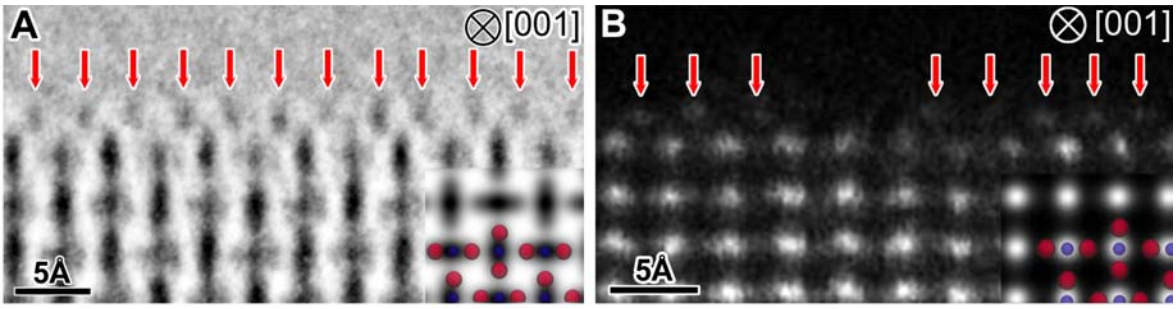

FIG.2: Magnified (A) HVEM and (B) HAADF STEM images of the TiO_2 (110) surfaces. The arrows indicate the positions of reconstructed Ti atoms on the top surfaces.

https://doi.org/10.1017/S1431927609093775 Published online by Cambridge University Press