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Reply to comment on Imaging of the hydrogen subsurface site in rutile TiO₂

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Enevoldsen *et al.* Reply: In Ref. [1], from simultaneously recorded atomic force microscopy and STM images and density functional theory (DFT) calculations, we showed that hydrogen species could be atomically resolved in the surface and subsurface of rutile TiO₂. To explain an apparent tip-assisted movement of H atoms between the two sites, we predicted a barrier for hydrogen to diffuse directly from bridging oxygen (O_b) on TiO₂ (110) to a subsurface site (O_{sub}) of 2.4 eV for a H coverage of 1/8 ML using DFT. This barrier is in agreement with the 2.6 eV given in recent calculations for a higher coverage of 1 ML in Ref. [2], but is now questioned in the preceding Comment, Ref. [3]. A number of studies, Refs. [2–4], suggest that a lower energy path via an intermediate in-plane oxygen site (O_{3f}) exists. For a coverage of 2 ML the barrier is predicted to be 1.1 eV [4], and for a coverage of 1 ML it is further reduced to 0.9 eV [2].

To investigate whether the alternative path has the lowest energy for the low coverage case (<0.1 ML) reflecting the experimental conditions in Ref. [1], we calculated it using the same methodology [1,5]. Specifically, DFT calculations were performed using the plane wave VASP code [6] with the local spin density approximation plus Hubbard U [(LSDA) + U] method, which was shown to give better agreement with experiments [5,7]. In order to see if the functional plays a role in the size of the barrier, we also calculated it using the standard generalized gradient approximation (GGA) method.

Our results (see Fig. 1) show that the barrier for O_b to O_{3f} is around 1.0 eV for the GGA functional, but there is no local minimum at the O_{3f} site with LSDA + U . However, in both cases the rate determining barrier is found when passing through the Ti-O plane, and this is about 1.6 eV for GGA and 1.8 eV for LSDA + U . This is lower than the original prediction of Ref. [1], which was likely overestimated due to constraints on the migration path. The barriers remain significantly higher than the predictions of Refs. [2,4], and assuming the barrier for the total path was also considered, the difference must be due to the higher coverages. However, we also speculate that Calatayud *et al.* [3] might have neglected to include the reaction energy from O_b to O_{3f} to the energy barrier from O_{3f} to O_{sub}. In any case, the fact that the barrier is smaller than originally considered actually strengthens the conclusion of our Letter [1] that H is manipulated to a subsurface site.

We disagree with the interpretation of room temperature behavior in the Comment [3]. Regardless of the H coverage, calculations predict a diffusion barrier of at least 1 eV. This value is too high for thermally activated processes to be active at room temperature, and spontaneous diffusion of H should be an extremely rare process. Indeed, the

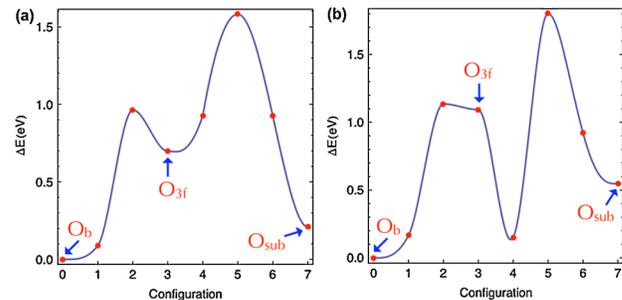


FIG. 1 (color online). Calculated diffusion barriers for hydrogen migration from surface to subsurface site using (a) GGA and (b) LSDA + U .

dynamics of surface H was studied experimentally in high statistical detail in recent fast STM studies (e.g., [8]). Here, the removal or displacement of H adatoms, other than through a surface reaction, was never observed.

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