Comment on "Oxygen Vacancy Origin of the Surface Band-Gap State of TiO_2(110)"

Recently, increasing research efforts have been dedicated to unravel the nature of the band-gap state of reduced titania (TiO_2) [1–4]. In a recent Letter, Yim *et al.* [5] address this seminally important question and claim to present direct evidence that the band-gap state measured on bulk-reduced rutile TiO_2(110)-(1 × 1) originates mainly from oxygen vacancies (O_b vac) rather than from Ti interstitials, as we proposed in Ref. [1]. In this Comment, we reveal that the data analysis by Yim *et al.* [5] is based on an erroneous assumption and that their conclusions are consequently incorrect.

Yim *et al.* [5] started with four differently prepared samples: i.e., (i) a mildly reduced TiO_2(110) sample [red dot in Fig. 4(a) of [5]], (ii) a more reduced sample [dark blue dot in Fig. 4(a) of [5]], (iii) a hydroxylated sample [filled square in Fig. 4(b) of [5]], and (iv) an oxidized sample [filled circle in Fig. 4(b) of [5]]. To disentangle surface and near-surface contributions to the gap state, Yim *et al.* irradiated two of the samples [(i) and (iv)] with low-energy electrons (75 eV, ~1 mA, current density ~0.2 mA/cm^2) for total durations of up to 20 s to reduce the samples while monitoring the intensity of the gap state. From a linear extrapolation of the gap-state intensity into the region of low surface defect [O_b vac or hydroxyl (OH_b)] density, Yim *et al.* concluded that the gap state stems mainly from O_b vac. The basis of this conclusion is the assumption that electron (e^-) irradiation leads to an increase in the O_b vac density only, while the near-surface region is anticipated to be unaffected.

However, this crucial assumption made by Yim *et al.* is incorrect as documented by the authors' very own experimental data. In Figs. 1(a) and 1(b) we replotted the evolution of the gap-state intensity and the O_b vac density, respectively, with e^--irradiation time for the experiment performed by Yim *et al.* on the mildly reduced sample (i) [see Fig. 4(a) of [5]]. While the gap-state area is found to increase linearly in time, the O_b vac density shows a highly nonlinear dependence. Note, in particular, the results by Yim *et al.* obtained after 10 and 20 s of e^- irradiation: the O_b vac density decreases, whereas the gap-state intensity increases. This shows clearly that the measured gap-state intensity is not a single-valued function of the measured O_b vac density. Thus, indisputably, near-surface defects other than O_b vac are introduced to the sample by e^- irradiation. Apparently, these additional defects are not surface defects since the only new species observed by Yim *et al.* are "pitlike structures" that were found to be in very minute abundance even after 20 s irradiation. Hence, the additional defects are near-surface defects that are not directly visible in the STM images. The occurrence of unintended additional changes to the near-surface region implies that Yim *et al.* cannot disentangle the contributions from the various defect species to the gap state.

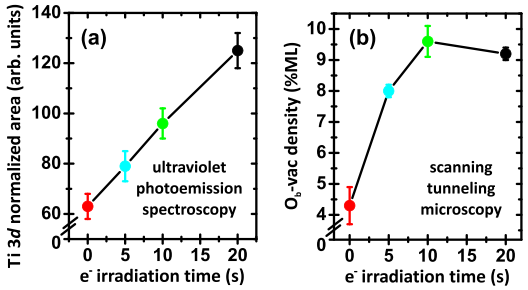

FIG. 1 (color online). (a) Gap-state intensity and (b) O_b vac density as function of e^--irradiation time. The data were taken from the experiment by Yim *et al.* on the mildly reduced sample (i) [labels and symbols as in Fig. 4(a) of [5]]. The underlying experimental techniques are written directly in the plots.

The situation is even more complicated in the experiment by Yim *et al.* on the oxidized sample (iv) [see Fig. 4(b) of [5]]. Here, three parameters were changed simultaneously upon e^- irradiation: removal of adsorbates such as O adatoms, creation of O_b vac, and the creation of defects in the near-surface region (see above), all of which influence the gap state. It is not possible to disentangle the various contributions to the gap state from this complex experiment.

On the contrary, in our own experiment [1], the surface defect concentration was varied in a much gentler manner. Our starting point was a hydroxylated TiO_2(110); i.e., all the O_b vac on a sputter-annealed TiO_2(110) sample were replaced by OH_b. Subsequently, we successively removed the OH_b through a reaction with O_2 while monitoring the gap-state intensity. Since the gap state retained ~70% of its original intensity when the surface was nearly defect-free, we concluded that the gap state originates mainly from defects in the near-surface region, e.g., Ti interstitials [1]. This experiment allowed us to clearly identify the contribution of O_b vac to the gap state to be of minor importance.

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