Yim, Pang, and Thornton Reply: The Comment of Wendt *et al.* [1] on our Letter [2] primarily claims that the electron beam method that we use in our experiment to vary the density of bridging oxygen vacancies (O_b vac) on rutile $TiO_2(110)$ also leads to damage of the near-surface region. Contrary to this assertion, in a two-photon photoemission spectroscopy study of $TiO_2(110)$, Onda *et al.* [3] demonstrate that the defects created on the nearly perfect $TiO_2(110)$ surface after exposure to a ~500 eV electron dose are completely healed by a submonolayer coverage of O_2 at 100 K. This indicates that the defects are located at the surface. In contrast, defects formed by thermal annealing can only be partially quenched by O_2 exposure, suggesting an additional contribution from the subsurface region. The electrons in our experiment are less energetic (~75 eV) than those employed by Onda *et al.* [3]. On this basis, it is clear that we do not expect to induce any significant damage in the near-surface region (as opposed to the surface plane) with our electron beam.

The evidence presented to support the claim of a subsurface change produced by the electron beam is the supposed nonlinearity of the O_b vac density dependence on the electron irradiation time compared with the variation of the band gap photoemission intensity. However, this deviation from a perfect straight line is the scatter that might be expected where there is a small variation in O_b vac density across the surface. This will be reflected in the STM measurement because only a nanoscale area is measured, while the photoemission data are macroscopically averaged.

Measurements on the hydroxylated surface (h-TiO_2) were designed to measure the connection between the band-gap state and O_b vac in a different way. It relies on the known creation of OH_b by the reaction of H_2O with O_b vac [4,5] and the unchanged intensity of the band-gap state when an O_b vac is converted to OH_b [6]. The data, which are shown in Fig. 1, are very clear in showing that the band-gap state scales linearly with the density of OH_b species created by reacting water with the O_b vac [the values are plotted in Fig. 4(b) in Ref. [2]]. Part of this data set shows the effect on the band-gap state of oxidizing h-TiO_2, with a reduction to 15% of its original intensity. Electron beam irradiation for 10 s and rehydroxylation restores the band-gap state and the OH_b density to their original values. This is all consistent with a dominating O_b vac contribution to the band-gap state. It is worth noting that the reduction of the band-gap state to 15% on oxidation compares with a figure of 60%–70% quoted in Refs. [1,7]. The latter values were used to associate Ti interstitials with the band-gap state. A likely cause of this discrepancy is the *ex situ* nature of the earlier measurements, which rely on the repeatability of sample preparation procedures. In contrast, our STM and photoemission measurements were carried out on identical surfaces *in situ*.
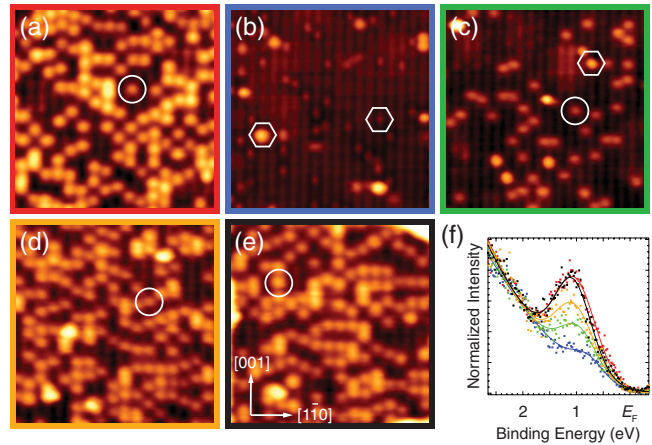

FIG. 1 (color online). STM images (125×125 Å^2) of (a) the hydroxylated $TiO_2(110)$ (h-TiO_2), (b) the oxidized $TiO_2(110)$ (o-TiO_2) surface, and (c)–(e) the surface in (b) after electron bombardment (~75 eV) for 2, 5, and 10 s, respectively. All STM images were collected with a tunneling current ≤ 0.2 nA and a sample bias voltage of 1.3 V at ~78 K. Symbols indicate OH_b (circles) and O_xH_y (hexagons). (f) Corresponding ultraviolet photoemission spectroscopy He I spectra recorded at ~300 K of h-TiO_2 (red), o-TiO_2 (blue), and o-TiO_2 following electron bombardment for 2 s (green), 5 s (orange), and 10 s (black), all recorded under identical conditions. Only the region near the band-gap state [~0.9 eV below the Fermi level (E_F)] is shown in the spectra. The data points are shown as squares, and the curves are the best fit to a Gaussian and polynomial background. The spectra in (f) corresponding to each surface are colored the same as the color borders in (a)–(e). Of the spectra shown, the one showing the second highest peak corresponds to (a), the lowest corresponds to (b), the second lowest corresponds to (c), the median corresponds to (d), and the highest corresponds to (e).

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