

Wet chemically prepared rutile TiO₂(110) and TiO₂(011): Substrate preparation for surface studies under non-UHV conditions



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ABSTRACT

A procedure for *wet chemical* preparation of TiO₂ single crystal surfaces is detailed. The potential of this procedure is demonstrated through application to rutile-TiO₂(110) and rutile-TiO₂(011) substrates. Characterisation with atomic force microscopy, low energy electron diffraction, auger electron spectroscopy, and vibrational sum frequency spectroscopy indicates that flat, well-ordered, carbon-free surfaces can be generated. Notably, in contrast to the (2 × 1) low energy electron diffraction pattern observed for TiO₂(011) prepared in ultra-high vacuum, *wet chemical* preparation results in a (4 × 1) unit cell; *wet chemically* prepared TiO₂(110) displays an unreconstructed (1 × 1) surface.

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1. Introduction

A recent special issue of Surface Science was devoted to the topic of 'Surface science under environmental conditions'. In the introductory editorial it was indicated that researchers in fundamental surface science are becoming increasingly concerned with more complex systems and conditions [1]. Focussing on the latter area, greater complexity largely involves a move away from ultra-high vacuum (UHV) work to studies in more technologically pertinent environments, i.e. measurements performed with samples immersed in fluids (gases or liquids). An issue of interest associated with such effort is the reliable preparation of well-defined substrate surfaces. One route is simply to prepare the sample under UHV conditions, and then introduce the fluid. Alternatively, a non-UHV recipe may be adopted. This second option is attractive as it potentially eliminates the requirement for UHV facilities, although substrate characterisation is still required to adhere strictly to a rigorous 'surface science approach'. Furthermore, the use of non-UHV processing may reveal previously unknown substrate terminations, which could have more 'real world' relevance. Here, we contribute to this topic through presenting a non-UHV recipe for the prototypical metal oxide

surface for fundamental surface science, rutile-TiO₂(110), as well as for the rutile-TiO₂(011) surface [2].

To date, a number of non-UHV approaches for preparation of low Miller index single-crystal TiO₂ surfaces have been implemented [3–12]. Despite varying in detail, almost all of these recipes can be labelled as so-called *wet chemical* procedures, involving a combination of chemical cleaning/etching and high temperature annealing [3–6, 8–12]. Hydrofluoric acid (HF) [4–6,9–12], as well as other acidic reagents [3,8], has been successfully employed for the first step. Concerning such preparation of TiO₂(110), substrate characterisation subsequent to processing has shown the feasibility of forming a relatively clean, well-ordered (1 × 1) surface termination with significant terrace sizes (widths can be >100 nm) [5,6,8–10]. A similar positive outcome has been achieved for the (011) surface of rutile-TiO₂ [4,6, 10], with both (1 × 1) [6] and (2 × 1) [10] surface unit cells being observed; typically, a (2 × 1) reconstruction is found following preparation in UHV [2].

Motivated by the desire to develop a relatively straightforward and HF-free *wet chemical* procedure for preparation of single crystal surfaces of TiO₂, a modified recipe is described in this paper. It is applied to both rutile-TiO₂(110) and rutile-TiO₂(011), with its success being evaluated through detailed surface characterisation. Atomic force microscopy (AFM) was employed to assess surface topography, with low energy electron diffraction (LEED) probing surface order. Auger electron spectroscopy (AES) and vibrational sum frequency spectroscopy (VSFS)

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are applied to determine surface composition/cleanliness; further details of the latter technique, an interface specific, non-linear, optical vibrational spectroscopy, can be found in Refs. [13,14]. It should be noted that in some other studies concerned with wet chemical preparation of single crystal TiO_2 substrates, surface characterisation has been somewhat less complete, e.g. no spectroscopy was applied to evaluate surface cleanliness [3,5,7–11]. Besides demonstrating the potential of our procedure for production of well-defined TiO_2 surfaces, a previously unreported LEED pattern is reported for $\text{TiO}_2(011)$.

2. Materials and methods

Experimental work was undertaken with single crystal samples of (110) and (011) oriented rutile- TiO_2 sourced from PI-KEM. Typically, samples measured $10\text{ mm} \times 10\text{ mm} \times 1\text{ mm}$, with an off-cut accuracy of $\leq 1^\circ$. *Wet chemical* preparation of these substrates involved 4 steps (STEPS 1–4), beginning with sonication (~ 15 min duration) in a sequence of solvents: acetone, ethanol, and deionised water. Samples were then dried in a stream of nitrogen. The purpose of this first stage (STEP 1) is to remove any adhered debris and grease from the surfaces of the substrates.

Following STEP 1, preparation continued with annealing in air in a tube furnace at 973 K for ~ 90 min; identical annealing conditions were adopted for both the (110) and (011) surfaces on the basis of empirical trials (i.e. varying anneal temperature and duration). The objective of this heat treatment (STEP 2), which is analogous to the same procedure in UHV, is to form flat, well-ordered surfaces. Following cooling, samples were immersed in aqua regia (a 3:1 by volume mixture of concentrated HCl and HNO_3) at room temperature for ~ 45 min, and then rinsed thoroughly with deionised water. Surface contamination removal is the objective of this procedure (STEP 3).

Finally, samples were inserted into a UV-ozone cleaner (Novascan). Substrates were exposed to UV-light for 20 min, and left immersed in the locally generated ozone atmosphere for another 30 min. This ultimate step (STEP 4) is intended to eliminate adventitious carbon from the substrate surface [15]. To ascertain that the UV treatment is having an impact on the substrate, water droplet contact angle data were acquired with a contact angle and surface tension analyser (FTÅ188 instrument from First Ten Ångströms Inc.). These measurements were undertaken with deionised water, using the static sessile drop approach [16]. On the basis of previous work [9], a hydrophobic to hydrophilic transition is expected to occur following effective UV-exposure.

For surface characterisation, data were acquired at various points in the preparation sequence (STEPS 1–4). AFM images were recorded in air at room temperature with a Nanoscope IIIa Multimode AFM (Digital Instruments) in tapping mode. For AES and LEED measurements, samples were inserted through a load-lock into an appropriately equipped UHV chamber; a four-grid rear view LEED optics (VG) was employed to collect both spectroscopy and diffraction data. Sample charging was an issue during acquisition of both AES and LEED data, due to the insulating nature of the *wet chemically* prepared samples. To compensate for such charging effects in AES spectra, the kinetic energy (KE) scale was calibrated using the location of the O *KLL* feature reported previously for TiO_2 [15]. Regarding acquisition of LEED data, patterns were obtained prior to degradation due to sample charging, which occurred over a period of approximately 1 min at the beam energies employed. We note that standard UHV preparation involving cycles of argon ion bombardment and annealing (typically ≥ 973 K) leads to bulk reduction of TiO_2 , eliminating charging.

Complementing AES data, VSFS data were acquired to assess the extent of surface carbon contamination, using a custom-built broadband VSFS instrument located at the University of Manchester. It should be noted that in contrast to the AES measurements, VSFS data were acquired with the sample exposed to the ambient laboratory atmosphere i.e. in a non-UHV environment. Concerning the latter technique, the signal results from the interaction of spatially and temporally overlapped

infrared and visible laser pulses at the substrate surface leading to sum-frequency generation (SFG) photons; vibrational resonances occur due to a coherent combination of infrared and Raman excitation [13,14]. To produce the required laser pulses, a Ti:Sapphire amplifier (Coherent Legend Elite F-HE), seeded by a Broadband Mai Tai (Spectra Physics), generates ~ 120 fs pulses at a wavelength of 803 nm (visible) and a repetition rate of 1 kHz. A portion of this output was then up-converted by an Optical Parametric Amplifier, OPerA Solo (Coherent), into tunable infrared pulses with a duration of ~ 150 fs. Prior to impinging on the substrate, the remainder of the 803 nm light was time-stretched (3–4 ps pulses) by a Fabry–Perot etalon [17]; this optical element produces a time-asymmetric pulse, allowing the typically broad non-resonant (non-vibrational) background to be suppressed by introducing a time delay (τ) between the visible and infrared pulses [18]. Emerging SFG photons are detected by a combination of a Shamrock 163 Czerny–Turner spectrograph (Andor Technology) and an iStar ICCD DH734 intensified-CCD camera (Andor Technology). VSFS spectra displayed in this paper were acquired with IR pulses centred at $\sim 3000\text{ cm}^{-1}$ at both $\tau \sim 0$ fs and $\tau \sim 900$ fs, using a *ppp* polarization combination, i.e. only p-polarized SFG, visible and infrared photons were detected/impinging.

3. Results and discussion

Fig. 1(a) and (b) shows typical AFM images of $\text{TiO}_2(110)$ and $\text{TiO}_2(011)$, respectively, acquired subsequent to UV treatment (STEP 4). In agreement with previous work [4–6,9,10], both surfaces exhibit relatively large, flat terraces, separated by well-defined steps; terraces are somewhat larger on the (110) surface, which is most likely a result of a smaller off-cut angle for this substrate. It should be noted that we attribute the small variations in intensity within terraces in Fig. 1 to instrumental noise, rather than any significant topographical features. Concerning step heights, the smallest and most prevalent measures ~ 0.3 nm on $\text{TiO}_2(110)$ (see line profile in Fig. 1(c)), which is consistent with the value expected for a monatomic step (0.33 nm) separating equivalent terraces [10]. Monatomic steps (~ 0.25 nm) [10] are also observed on the (011) surface (see line profile in Fig. 1(e)). Larger step heights apparent on both surfaces can be simply reconciled with multiple atomic steps, e.g. the ~ 1.5 nm step height in the line profile from $\text{TiO}_2(110)$ (Fig. 1(d)) is consistent with six monatomic steps. It should be emphasised, given the limited lateral resolution, that it is not possible to determine the precise morphology of these deeper steps, e.g. they may consist of a series of closely spaced single monatomic steps with narrow intervening terraces.

AFM images (not shown) recorded following aqua regia immersion (STEP 3) are essentially identical to those displayed in Fig. 1. These data indicate that UV treatment (STEP 4) does not have any significant impact on surface topography. Images acquired post-annealing (STEP 2), but before aqua regia immersion (STEP 3), typically display a significantly greater degree of undulation within terraces, as demonstrated by the image of $\text{TiO}_2(110)$ in Fig. 2(a) and the corresponding line profile (Fig. 2(b)). We suggest that the origin of this morphology is most likely surface contamination, which is removed by the acid cleaning. Prior to annealing (STEP 2), AFM revealed very rough surfaces, with no clear terraces or steps apparent.

Turning to surface composition, AES spectra are displayed in Fig. 3 of (a) $\text{TiO}_2(110)$ and (b) $\text{TiO}_2(011)$. In each panel there are two spectra, one acquired following aqua regia immersion (STEP 3), and the other following UV treatment (STEP 4). All of the spectra exhibit features expected of the substrate, i.e. Ti *LMM* and O *KLL* Auger peaks. Additionally, a feature assigned to the C *KLL* Auger peak is apparent in the two spectra acquired after aqua regia immersion (STEP 3). This signal is attributed to surface adsorbed adventitious carbon. As indicated by the corresponding spectra, UV treatment (STEP 4) essentially quenches this carbon peak, i.e. this step removes adventitious carbon from the substrate surface, as intended.

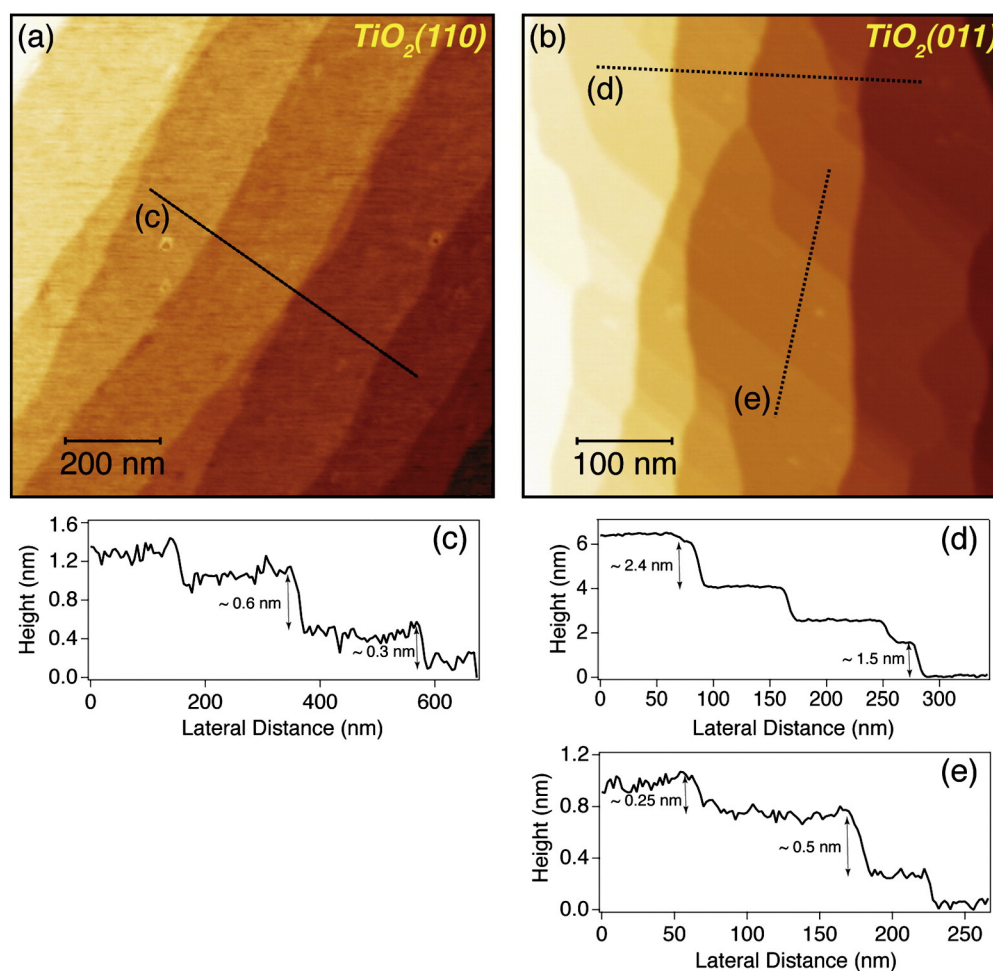


Fig. 1. AFM images of (a) $\text{TiO}_2(110)$ and (b) $\text{TiO}_2(011)$ acquired subsequent to STEP 4 (UV treatment) of the *wet chemical* preparation procedure. (c), (d), and (e) display line profiles from along the lines indicated in (a) and (b). Example step heights are indicated on these profiles, with the smallest being associated with monatomic steps, i.e. ~0.3 nm for $\text{TiO}_2(110)$ and ~0.25 nm for $\text{TiO}_2(011)$ [10]. The uncertainty in the smallest (monatomic) step heights is estimated to be approximately ± 0.05 nm.

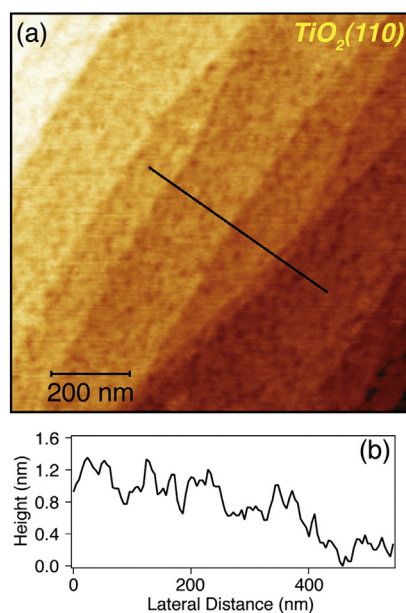


Fig. 2. AFM image of $\text{TiO}_2(110)$ acquired subsequent to STEP 2 (annealing) of the *wet chemical* preparation procedure. (b) displays a line profile from along the line indicated in (a).

Removal of adventitious carbon by UV treatment (STEP 4) is also apparent in VSFS data acquired from both TiO_2 substrates. Fig. 4 shows VSFS spectra of the C–H stretching region acquired from $\text{TiO}_2(110)$ ((a) and (c)) and $\text{TiO}_2(011)$ ((b) and (d)), both following immersion

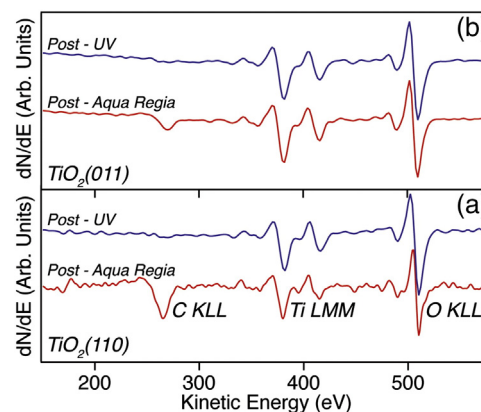


Fig. 3. AES spectra of (a) $\text{TiO}_2(110)$ and (b) $\text{TiO}_2(011)$. In each panel one spectrum (red line) has been acquired subsequent to STEP 3 (aqua regia immersion), and the other (blue line) following STEP 4 (UV treatment) of the *wet chemical* preparation procedure. It should be noted that once a sample was inserted into the UHV chamber, no further preparation (e.g. thermal annealing) was undertaken prior to the acquisition of these spectra. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

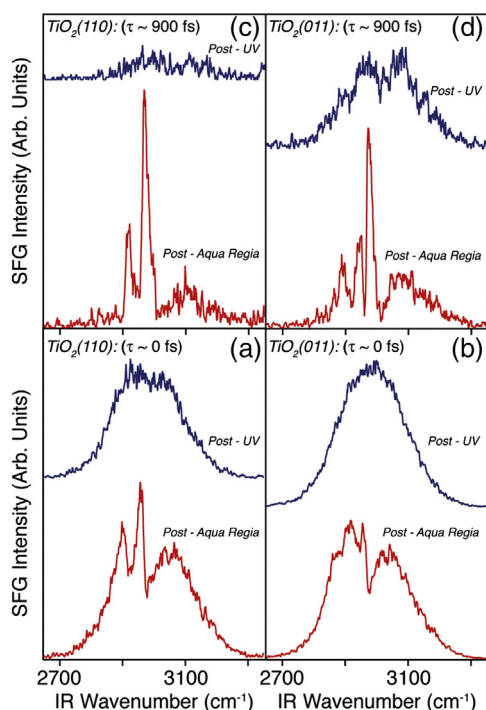


Fig. 4. VSFS spectra (C–H stretching region) acquired from $\text{TiO}_2(110)$ ((a) and (c)) and $\text{TiO}_2(011)$ ((b) and (d)). In each panel one spectrum (red line) has been acquired subsequent to STEP 3 (aqua regia immersion), the other (blue line) following STEP 4 (UV treatment) of the wet chemical preparation procedure. All data were acquired with IR pulses centred at $\sim 3000 \text{ cm}^{-1}$, using a *ppp* polarization combination. Spectra in panels (a) and (b) ((c) and (d)) were recorded with $\tau \sim 0 \text{ fs}$ ($\tau \sim 900 \text{ fs}$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in aqua regia (STEP 3) and post-UV treatment (STEP 4); background non-suppressed ($\tau \sim 0 \text{ fs}$ in panels (a) and (b)) and background suppressed ($\tau \sim 900 \text{ fs}$ in panels (c) and (d)) data are displayed. It is evident that there are sharp features present in the spectra acquired after chemical cleaning with aqua regia, and that they are clearly effectively eliminated by the UV exposure. These data are consistent with previous VSFS studies of TiO_2 substrates, which also show a complete loss of resonant (vibrational) signal in the C–H stretching region subsequent to UV exposure [19,20]. In accord with the Auger data, these results suggest that UV treatment removes adventitious carbon from the two TiO_2 substrates. We note that the broad feature remaining after UV treatment in the $\tau \sim 0 \text{ fs}$ spectra (panels (a) and (b)) is attributed to non-resonant (non-vibrational) contributions [14,18]. Concerning the significantly greater intensity of the signal from $\text{TiO}_2(011)$ than $\text{TiO}_2(110)$ following UV treatment in the background suppressed ($\tau \sim 900 \text{ fs}$) spectra (panels (c) and (d)), its breadth strongly suggests that again it almost certainly arises from non-resonant processes rather than any adsorbate-related vibrational resonances [14,18]; the reason for this difference between the two substrates is not currently clear, but may be related to differences in surface electronic structure.

Besides removing adventitious carbon, the UV treatment (STEP 4) also effects a step change in the hydrophilic nature of both $\text{TiO}_2(110)$ and $\text{TiO}_2(011)$. This phenomenon is demonstrated by the data Table 1, which lists the water droplet contact angles recorded before and after UV treatment. In accord with previously published data for $\text{TiO}_2(110)$ [9], the surfaces become highly hydrophilic subsequent to the UV treatment. Such a clear increase in wettability has the potential to be useful as a simple test to ascertain the effectiveness of the UV treatment; a quick, semi-quantitative assessment can be achieved by visual inspection of the shape of a water droplet delivered to the surface through a hypodermic syringe.

Table 1

Water (deionised) droplet contact angles acquired from wet chemically prepared rutile $\text{TiO}_2(110)$ and $\text{TiO}_2(011)$ substrates. Data were acquired subsequent to both STEP 3 (aqua regia immersion) and STEP 4 (UV treatment) of the preparation procedure, i.e. before and after UV treatment. The static sessile drop approach was adopted for these measurements [16].

| | Contact angle ($^\circ$) | |
|---------------------|----------------------------|------------------|
| | Post-aqua regia (STEP 3) | Post-UV (STEP 4) |
| $\text{TiO}_2(110)$ | ~ 80 | ~ 0 |
| $\text{TiO}_2(011)$ | ~ 78 | ~ 0 |

Regarding surface order, Fig. 5 shows LEED patterns from (a) $\text{TiO}_2(110)$ and (b) $\text{TiO}_2(011)$ after UV treatment (STEP 4). Distinct diffraction spots can be observed in each of the images, indicating that both surfaces possess significant translational order. Surface unit cells are indicated. For $\text{TiO}_2(110)$ (Fig. 5(a)), the relative dimensions of the unit cell are those expected for an unreconstructed (1×1) surface; all other wet chemical preparations of $\text{TiO}_2(110)$ used to date have also produced a (1×1) termination [5,6,9]. Hence, wet chemical preparation replicates typical UHV preparation (Ar^+ bombardment and anneal cycles) of $\text{TiO}_2(110)$ in that both result in a (1×1) termination, at least for lower degrees of bulk reduction in UHV [2]. More notably, given that preparation of $\text{TiO}_2(011)$ in UHV typically results in a (2×1) unit cell [2], a (4×1) surface reconstruction is found for our wet chemical preparation of $\text{TiO}_2(011)$. For clarity, both the (4×1) and (1×1) surface

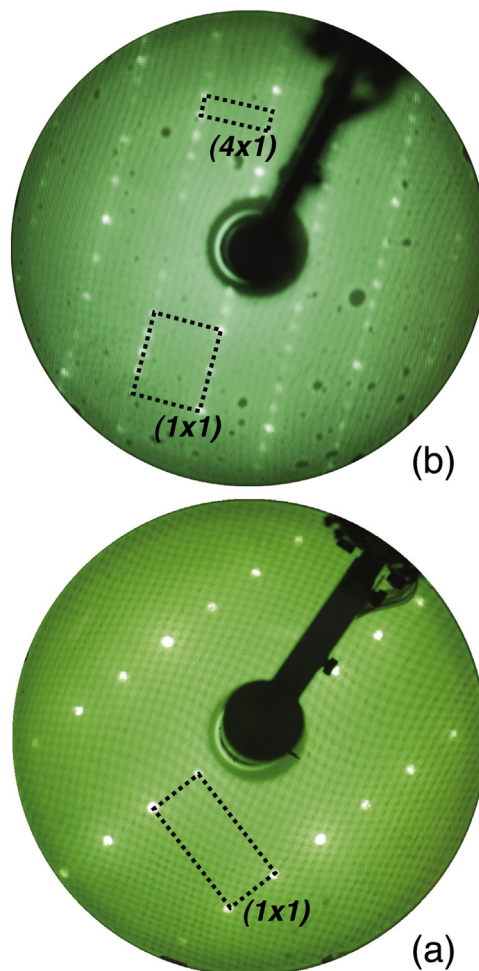


Fig. 5. LEED patterns of (a) $\text{TiO}_2(110)$ (beam energy $\sim 100 \text{ eV}$) and (b) $\text{TiO}_2(011)$ (beam energy $\sim 90 \text{ eV}$) acquired subsequent to STEP 4 (UV treatment) of the wet chemical preparation procedure. Surface unit cells are indicated. It should be noted that once a sample was inserted into the UHV chamber, no further preparation (e.g. thermal annealing) was undertaken prior to the acquisition of these data.

unit cells are highlighted in Fig. 5(b). Additionally, as expected [21], the (0, 2n-1) diffraction spots are absent from the $\text{TiO}_2(011)$ LEED patterns, due to the presence of a glide plane. We note that, previously, Kobo et al. [22] have reported AFM images showing areas of (4×1) termination, alongside (2×1) domains on a $\text{TiO}_2(011)$ substrate prepared in UHV; no LEED patterns were apparently acquired. Annealing of the (4×1) phase in UHV at a series of increasing temperatures (steps of 50 K) resulted in a change in the surface termination to a (2×1) unit cell following annealing at 873 K for 20 min, as demonstrated by Fig. 6.

Given that rutile- $\text{TiO}_2(011)$ is reported to exhibit enhanced photocatalytic activity [2,21], the observation of a (4×1) termination following *wet chemical* preparation has potentially significant implications. It may be that this non-UHV (4×1) phase underpins such increased photo-activity, and that previous studies (see [2] and Refs. therein) of the UHV (2×1) reconstruction are not particularly relevant in this regard. On this basis, a fully quantitative structure determination of the *wet chemically* prepared $\text{TiO}_2(011)$ (4×1) surface is clearly of significant interest; the (1×1) [6] and (2×1) [10] surface terminations formed following other *wet chemical* preparations of $\text{TiO}_2(011)$ also require further study. Similar effort to elucidate surface structure is required for the (110) surface, as a (1×1) surface unit cell does not guarantee that the surface termination is identical to that found in UHV (see [2] and Refs. therein). Indeed, it seems plausible that *wet chemically* prepared TiO_2 surfaces may be decorated to some extent with surface hydroxyls.

Finally, comparing our *wet chemical* preparation procedure with previously described similar procedures [3–6,8–12], it appears to be at least as effective as those procedures in terms of producing well-defined surfaces suitable for surface science type studies under non-UHV conditions. In particular, the employment of UV treatment as a final step enables carbon-free surfaces to be generated. Additionally, replacing HF with aqua regia in the chemical cleaning step eases safety concerns, increasing flexibility.

4. Conclusions

In summary, a *wet chemical* (non-UHV) procedure, involving thermal annealing, immersion in aqua regia, and exposure to UV-light, for preparation of single crystal TiO_2 surfaces is described. Comparing this recipe to others in the literature [3–12], it is relatively straightforward and avoids the need for HF, about which there are significant health and safety issues. The success of the method is demonstrated through characterisation of rutile- $\text{TiO}_2(110)$ and rutile- $\text{TiO}_2(011)$ samples subjected to such preparation. Well-defined substrates, displaying

relatively large terraces, are produced. Surface adsorbed adventitious carbon is depleted by a final processing step of exposure to UV-light. Such a procedure is not an integral component of other *wet chemical* preparation TiO_2 recipes in the literature [3–13], although UV illumination was employed in Ref. [11] prior to chemical cleaning and thermal annealing. Furthermore, and perhaps of greatest potential interest, a (4×1) LEED pattern is observed for $\text{TiO}_2(011)$; UHV preparation of the same surface typically leads to a (2×1) unit cell.

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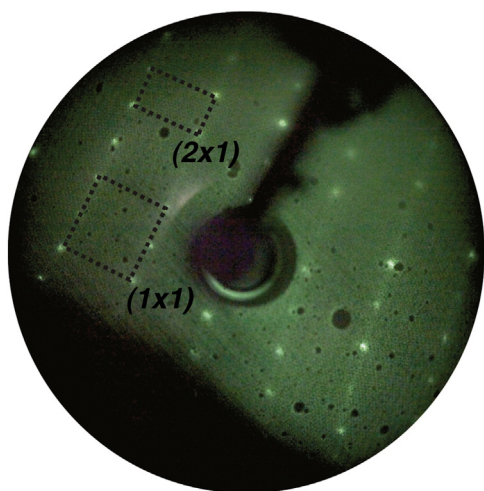


Fig. 6. LEED pattern of *wet chemically* prepared $\text{TiO}_2(011)$ (beam energy ~ 90 eV) acquired subsequent to annealing (873 K for 20 min) in UHV. Surface unit cells are indicated.