V-doped TiO$_2$(110): Quantitative structure determination using energy scanned photoelectron diffraction

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Abstract

The surface structure of a novel vanadium-titanium dioxide epitaxial film (Ti$_{1-x}$V$_x$O$_2$, x ~ 0.2) has been explored using V^{4+} 2p and Ti^{4+} 2p energy-scanned photoelectron diffraction (PhD). The determined structure is a rutile TiO$_2$(110)-like surface, with V atoms substitutionally replacing some Ti atoms. The results show no evidence for significant preferential occupation by V atoms of any specific surface or sub-surface sites. LEED shows a (1x2) reconstruction to be present on the surface, and the PhD simulations do favour this being the dominant surface termination, although the reliability factor for simulations for a (1x1) termination falls just within the variance of the value for the preferred (1x2) structure. The V^{3+} and Ti^{3+} species were observed to occupy the same sites as the V^{4+} and Ti^{4+} species; V^{5+} species do not appear to occupy a single well-defined structural site.

Keywords: TiO$_2$; vanadium oxides; surface structure

1. Introduction

Titanium dioxide is one of the most studied oxides in surface science [1], in part due to its importance in catalysis [2] and photocatalysis (particularly its potential for water cracking to produce hydrogen [3]). The influence of vanadium both on and in the surface has also been studied extensively [e.g. 4, 5, 6, 7]. VO_x (specifically including V_2O_5) particles on TiO_2 are known to be particularly catalytically active [8], while doping bulk TiO_2 with transition metals [9], and particularly with vanadium [10, 11, 12, 13], offers a route to lowering the band gap of the pure oxide (~3 eV), thus allowing photoactivation to occur with light in the visible spectral range [14].

Of course, heterogeneous catalysis occurs at the surface of the catalyst, so understanding the structural and electronic properties of the surface are crucial to understanding the surface chemistry. With this in mind we present here the results of a quantitative local structure determination of the near-surface region of the (110) surface of vanadium-doped TiO_2 using scanned-energy mode photoelectron diffraction (PhD) [15, 16] to identify the V site within the surface and the underlying subsurface region. The PhD technique exploits the coherent interference of the directly emitted component of a photoelectron wavefield from a near-surface atom with that of the components scattered by atoms in the local environment of the emitter. By varying the incident photon energy, the photoelectron kinetic energy (and therefore the photoelectron wavelength) is varied, and the scattered components of the photoelectron wavefield switch in and out of phase with the directly emitted component. The resulting modulations in the photoemission intensity in a specific direction, as a function of photon energy, provide structural information on the local environment of the emitter. This technique is best-suited to determine the structure of adsorbate layers on surfaces, because in this case one can measure the PhD modulation spectra arising from atomic species that occur only within the adsorbate, ensuring that the structural information is specific to the adsorbate atoms alone. In the present case, in which the photoemission from V (or Ti) atoms in the surface and subsurface cannot be distinguished by their photoelectron binding energies, the technique is less

incisive in determining the surface structure. Nevertheless, this approach has been used successfully in the past to provide quantitative information on the structure of the clean rutile $TiO_2(110)$ surface [17]. Of course, the difference in 2p photoelectron binding energies of V and Ti do allow us to distinguish the local geometries of these two species, and indeed chemical shifts in these states associated with different nominal charge states of the emitter atoms provide further atomic specificity.

2. Experimental details and surface characterisation

The experiments were conducted in an ultra-high vacuum surface science end-station equipped with typical facilities for sample cleaning, heating and cooling. This instrument was installed on the UE52-PGM-PES beamline of the BESSY-II synchrotron radiation source and the associated UHV surface science end-station, described more fully elsewhere [18].

The growth of the epitaxial $Ti_xV_{1-x}O_2(110)$ films on $TiO_2(110)$ was performed in two steps. After cleaning of the $TiO_2(110)$ sample by standard sputtering and annealing techniques, a Ti+Ta mixed oxide layer was first prepared by co-deposition of tantalum and titanium in an oxygen ambient atmosphere (10^{-6} mbar) at a sample temperature of 800-850 K, followed by annealing at the same temperature and oxygen partial pressure for 5 min. This layer, with a typical thickness of ~30 Å and a tantalum/titanium ratio of ~0.25, was found [19] to act as a barrier to diffusion of vanadium atoms into underlying $TiO_2(110)$ substrate from the Ti+V mixed oxide layer that was then grown on top. An epitaxial $Ti_xV_{1-x}O_2(110)$ film of thickness ~ 40-45 Å was then deposited by co-evaporation of vanadium and titanium, also in an oxygen partial pressure of 10^{-6} mbar at a sample temperature of 800-850 K, followed by annealing in vacuum at the same temperature. The vanadium concentration in the layers studied here were in the range of approximately 18-28% and the film surfaces showed a clear (1x2) low energy electron diffraction (LEED) pattern consistent (together with the PhD data presented below) with good epitaxy (Fig. 1). Full details of the development

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and characterisation of this film preparation methodology are presented elsewhere [19].

The Ti 2p, V 2p and O 1s SXP spectra, measured at 220 K from the $Ti_xV_{1-x}O_2$ surface, are shown in Fig 2. Each of the two spin-orbit split peaks of the V 2p SXP spectrum can be resolved into three chemically-shifted components separated by ~1 eV, which are attributed to V^{3+}, V^{4+} and V^{5+} species in order of increasing binding energy. The dominant component is the V^{4+} species, but there are significant amounts of the other species also present (3+, 4+ and 5+ states are in a ~2:5:2 ratio, respectively). Angle-resolved XPS measurements from these films have shown that the V^{5+} species are localised at the surface, but the V^{3+} and V^{4+} components are located in both surface and subsurface sites [19]. The Ti 2p SXP spectrum is dominated by the main Ti^{4+} peak, but a small ($1/10^{th}$ intensity) shoulder attributable to Ti^{3+} is present; on clean TiO_2(110) surfaces such a component is generally attributed to oxygen vacancies in both the surface and subsurface regions. In the present case, though, an alternative possibility is that this shoulder (and the V^{3+} peak) could be associated with the (1x2) reconstruction that must be present on at least some fraction of the surface. The existence of a (1x2) reconstruction on the reduced TiO_2(110) surface is well known and has been determined, by quantitative LEED, to involve Ti_2O_3 "quasi-1D metallic chains" [20, 21] (see figure 3). However, it is possible that the metal ions in these "chains" could be in Ti^{4+}, rather than in the Ti^{3+} state that the stoichiometry would imply.

The O 1s SXP spectrum shows three distinct features which are nominally assigned to adsorbed intact water, surface hydroxyl species and the bulk oxide (in order of decreasing binding energy), the first two associated with some degree of water contamination. There is no evidence of any significant binding energy difference between oxygen atoms bonded to V and Ti atoms.

PhD modulation spectra were obtained by measuring photoelectron energy distribution curves (EDCs) of the Ti 2p and V 2p peaks, at 4 eV steps in photon

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energy, over the photoelectron kinetic energy range of 50-250 eV, for a number of different polar emission angles in the [001] and [11̄0] azimuths. The data from the electron spectrometer were integrated over an angular range of $\pm 3.5°$, and then processed following our general PhD methodology (e.g. [16, 17]) in which the individual EDCs are fitted by one or more Gaussian peaks, a Gauss error function (step), and a template background obtained from the wings of the EDCs. The integrated areas of each of the individual peaks were then plotted as a function of photoelectron kinetic energy, $I(E)$, and used to define a stiff spline, $I_0(E)$, through $I(E)$, that represents the non-diffractive intensity and instrumental factors. The spline was then subtracted from, and used to normalise, the integrated areas, to provide the final PhD modulation spectrum, $\chi(E)=(I(E)-I_0(E))/I_0(E)$.

3. Results

3.1. PhD results and qualitative evaluation

Although a full quantitative analysis of PhD requires an extensive trial and error process, comparing theoretically calculated modulations against those that were measured experimentally, it is often possible to gain qualitative information from inspection of the experimental data alone. Specifically, chemical species that present similar PhD spectra are likely to be found in similar structural sites. The measured PhD 2p spectra from the V^{3+}, V^{4+} and V^{5+} species, and the Ti^{3+} and Ti^{4+} species, are shown in figure 4. Clearly, not only are the dominant modulations essentially the same in the spectra from the Ti^{4+} and V^{4+} 2p species, but they are also the same as those in the spectra from the Ti^{3+} and V^{3+} species. The clear implication is that not only do the V^{4+} atoms and Ti^{4+} ion occupy similar, if not identical sites, but so do the V^{3+} and Ti^{3+} ions. This would be consistent with both the V^{3+} and Ti^{3+} ions being localised near oxygen defects, but otherwise in essentially the same sites as the V^{4+} and Ti^{4+} ions; in particular, these similarities indicate that the presence of the V^{3+} and Ti^{3+} spectral peaks is not exclusively due to the different local environment of ions in the reconstructed (1x2) surface. The PhD spectra from the V^{5+} ions mostly (with the possible exception of that recorded at normal emission) lack significant long-period modulations

characteristic of reliable PhD data, implying that the V^{5+} ions probably do not occupy a single well-defined structural site.

3.2. PhD results: quantitative evaluation

In order to achieve a more quantitative analysis of the PhD data, multiple scattering simulations for different structural models were performed using the computer codes developed by Fritzsche [22, 23, 24]. These are based on the expansion of the final state wave-function into a sum over all scattering pathways that the electron can take from the emitter atom to the detector outside the sample. The level of agreement between the theoretical and experimental modulation amplitudes is quantified using an objective reliability factor (R-factor) [15, 16] defined in a fashion closely similar to that proposed by Pendry for quantitative LEED studies [25]. The R-factor is defined such that a value of 0 corresponds to perfect agreement, and a value of 1 to uncorrelated data. The lowest value achievable in practice depends on the complexity of the structure and the amplitude of the modulations, but typically falls in the range 0.2-0.4. In order to estimate the uncertainty in the structural parameters of the best structural model, a variance ($Var(R_{min})$) of the lowest value of the R-factor (R_{min}), corresponding to the best-fit structure, is calculated. Any structure having a R-factor less than R_{min} + $Var(R_{min})$ is assumed to lie within one standard deviation of the best-fit model [26].

Application of this approach to the present system is particularly challenging, not only because the calculations must include emitter atoms in several layers of the surface and subsurface (the results for which must be summed incoherently), with a large number of associated structural parameters, but also because the PhD data set is of only modest size due to the particularly time-consuming sample preparation that was performed *in situ* in the limited synchrotron radiation beam-time available. As a result the precision in the structural parameters achievable falls below that which is normally obtained by this technique. Nevertheless, quantitative analysis of the available data can certainly distinguish between

occupation of interstitial or substitutional sites by the V atoms. In addition, if the V atoms do occupy substitutional sites (as clearly implied by the qualitative analysis) then three specific questions can be addressed, namely: (i) whether there is preferential substitution of either the 5-fold-ccordinated or 6-fold-coordinated metal sites in the first layer (labelled '2' and '1' respectively in Fig. 3), (ii) whether there is preferential substitution of sites in the first layer relative to those in lower layers, and (iii) whether or not the (1x2) reconstruction is the dominant termination at the surface.

The first two questions can be resolved by considering only the V^{4+} 2p PhD data, using comparatively simple models. The third question is addressed by utilising both the Ti^{4+} and V^{4+} 2p PhD spectra and investigating two competing models, one of which is a "bulk-like" (1x1) termination using the bulk termination of TiO_2(110) as the starting point, while the other is the clean TiO_2(110)-(1x2) "metallic chain" reconstruction found by Blanco-Rey *et al.* [20, 21] (see also the review of TiO_2(110) surface structures by Pang *et al.* [27])

3.2.1 V: Interstitial v. substitutional sites and surface v. subsurface site occupation

Though the clear indication from the qualitative analysis that the Ti and V atoms occupy similar, if not identical, sites would seem to exclude V atoms predominantly occupying interstitial sites, one possibility that might be consistent with the data is that there is a significant proportion of *both* Ti and V atoms in interstitial sites. To explore this idea it is necessary to perform quantitative simulations of the PhD modulations that would be expected from occupation of this interstitial site, and the results of this calculation are compared to the experimental data in Fig. 5. Clearly not only are the predicted modulations significantly more intense than those observed experimentally, but the periodicity of the modulations is also significantly different; indeed, in some cases the peaks of troughs of the modulation are exactly out of phase, so even modest changes in bondlengths will not significantly change this poor agreement. We may therefore

conclude that no more than a small minority of the V atoms can occupy interstitial sites.

While the earlier angle-resolved XPS studies [19] indicated that the V^{4+} species occupy both surface and subsurface sites, the more detailed PhD data may allow us to address this issue more precisely. Specifically, is there any preference of the substitutional V atoms to occupy the 5-fold-coordinated or 6-fold coordinated surface sites of the outermost atomic layer, or to occupy substitutional sites in either this outermost surface layer or in the first sub-surface layer? A significantly more complex set of multiple scattering calculations was required to address these questions. In these calculations all metal atoms other than the emitter were assumed to be Ti; in the samples studied approximately 20-25% of scatterers must actually be V (presumably distributed randomly on the relevant sites), but the scattering factors for Ti and V are closely similar and a few test calculations confirmed the insensitivity of the results to this difference. In order to determine any preference for V occupation of sites in the two outermost layers a global search algorithm was used, specifically a Particle Swarm Optimisation (PSO – described elsewhere [28]), in which the occupancies of the 6-fold and 5-fold sites (Ti(1) and Ti(2) in Fig. 3) in the first layer, and the occupancies of the two symmetrically distinct 6-fold coordinated sites in the second layer (Ti(7) and Ti(8) in Fig. 3) were set as variables (allowing the sites to be either occupied or not occupied), as well as allowing reasonable relaxation of the atoms in the surface.

These calculations, performed on over 10,000 specific models, showed clearly that acceptable agreement with experiment could only be achieved if V atoms occupy both the 5-fold coordinated and 6-fold coordinated surface metal sites. The evidence for this is shown in the upper panel of figure 6, which displays the *R*-factors obtained for these models grouped according to the occupancy of the Ti(1) and Ti(2) sites as a function of the displacement perpendicular to the surface of the V atom in the Ti(2) 5-fold coordinated surface site. Clearly all the lowest *R*-factor values correspond to structures in which both of these surface layer

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substitutional sites are occupied. The results regarding the occupation of the second-layer substitutional sites are less definitive. The lower panel of Fig. 6 shows a similar map, only including structures with the lowest range of *R*-factors, comparing the results of models that include one or both of the locally-inequivalent second layer V emitters with the results for models in which both are omitted. The lowest *R*-factor models clearly do correspond to those including at least one second-layer emitter, but the improvement in *R*-factor is more marginal. More detailed analysis showed that the agreement between experiment and theory was improved by including emission from V atoms at the Ti(8) sites of Fig. 3, although adding V emitters in the Ti(7) sites had little influence on the level of agreement. While we are therefore formally not able to confirm V occupation of Ti(7) sites on the basis of these data, it is difficult to see how any preference for occupation of the two different 6-fold coordinated subsurface sites should occur. We therefore conclude that the data indicate that V atoms substitute some Ti atoms in both the outermost surface and subsurface layers with no strong site preference.

3.2.2 (1x1) or (1x2) surface models

The (1x2) LEED pattern clearly indicates that some fraction of the surface must have a (1x2) reconstruction, but because the integral order beams are common to both (1x1) and (1x2) phases, the observation of this pattern provides no information on the relative areas of unreconstructed (1x1) and reconstructed (1x2) surface that may coexist on the surface. We have therefore made multiple scattering calculations of models of these two phases in an attempt to identify the dominant surface structure.

The structure of the unreduced, clean $TiO_2(110)(1x1)$ surface has been determined by numerous techniques (e.g. [17, 29, 30, 31, 32]), including PhD (using both Ti 2p and O 1s emission) [17]. Fig. 7 shows a comparison of the Ti^{4+} 2p PhD modulation spectra obtained in the present study with equivalent

spectra obtained by Kröger *et al.* from the clean $TiO_2(110)(1x1)$ surface. The main features of the two sets of spectra are very similar, although the modulation amplitude measured at normal emission in the present study is somewhat weaker than that recorded by Kröger *et al.*; there also appear to be slight differences in the modulation periodicity between the spectra recorded at a polar emission angle of 20°. These differences could be due to the presence of Ti^{4+} emitter ions in the (1x2) reconstruction.

To explore this possibility, calculations were performed for two competing models, namely a "bulk-like" (1x1) surface termination, similar to that found by Kröger *et al.*, and the "metallic chain" (1x2) reconstruction model found by Blanco-Rey *et al.* [20, 21]. These models were explored using the full Ti^{4+} 2p and V^{4+} 2p dataset (i.e. the calculated *R*-factor used to establish the best-fit set of structural parameter values was calculated using the set of three Ti^{4+} PhD spectra and four V^{4+} 2p PhD spectra), utilising the PSO global search algorithm.

Emission from the six outermost layers of the surface was included in these calculations, resulting in 12 different emitter sites for the (1x1) model and 22 different emitter sites for the (1x2) model (7 emitters in the layers under and including the "metallic chain", 5 emitters in the layer not-under the "metallic chain", and 5 emitters that do not lie on an axis that shares the 2-fold symmetry of the surface and must therefore be included in each of two symmetrically equivalent domains). Based on a parameterisation of the 'universal curve' for inelastic scattering mean-free-paths we estimate the contribution to the detected intensity from deeper layers to vary between ~1% and ~10% at the lowest and highest kinetic energies investigated. Emission from these atoms in the six outermost layers in different sites was assumed to sum incoherently. All non-emitting (scattering) metal atoms were assumed to be Ti atoms, and the only structural difference considered for the V emitter sites was a fractional relaxation of the bond length between the V emitter and the nearest neighbour O atoms. In the (1x1) model all atoms in the top three

layers were allowed to relax perpendicular to the surface (z), and the planar O atoms were allowed to relax along the [1$\bar{1}$0] direction (x); in the (1x2) model all atoms in the "metallic chain" and in the next two layers were similarly allowed to relax in z, and the metal atoms and the O atom that bridges them in the "metallic chain", as well as the planar oxygen atoms in the lower two layers, were also allowed to relax in x. It was assumed in both models that the point group symmetry of the substrate was retained at the surface.

The experiment – theory comparison of the best fits are shown in figures 8 and 9 for the (1x1) and (1x2) models respectively. The associated *R*-factor values were 0.37 and 0.32 respectively, but the associated variance of the lowest value is 0.06, which means that the difference is formally not significant: i.e. the value for the (1x1) structure lies just within one standard deviation of the value for the (1x2) structure. Of course, in reality it is likely that the true surface contains at least some fraction of both phases, but this formally near-significant preference for the (1x2) phase, reinforced by the clear superiority of the fit to the V^{4+} 2p PhD spectrum recorded at normal emission, does indicate that it is probable that a significant fraction of the surface does show the (1x2) reconstruction identified by Blanco-Rey *et al.* The structural parameter values associated with the best-fit structure are compared with the values obtained for the pure TiO$_2$ surfaces by Kröger *et al*. and by Blanco-Rey *et al.* in table 1. As the available data set is relatively small, the quantitative structural parameters obtained in this study do show very significant uncertainties; however it is clear that the parameter values for both the (1x1) and (1x2) models are compatible with those found in the earlier TiO$_2$(110) studies.

4. General discussion and conclusions

Our energy scanned photoelectron diffraction investigation of the surface structure of a novel mixed titanium – vanadium oxide, Ti$_{1-x}$V$_x$O$_2$(110) surface clearly indicates that V atoms occupy metal substitutional sites in both the surface

and subsurface, with no evident preference for specific sites (notably 5-fold-coordinated or 6-fold-coordinated) in the surface. LEED shows a (1x2) reconstruction must occur on at least part of the surface, and simulations of the V^{4+} and Ti^4 2p PhD spectra based on the 'metallic chain' model of Blanco-Rey *et al.* do provide a better fit to the data than similar calculations based on a (1x1) relaxed bulk termination, although the difference in the associated *R*-factors just fails to be statistically significant.

Despite the considerable interest in VO_x species in and on $TiO_2(110)$, there are few published theoretical density functional theory calculations that are relevant to our investigation. Several such studies have been performed on mixed Ti-V-O clusters in isolation or on $TiO_2(110)$ (e.g. [33, 7]), but the only calculations of V in crystalline $TiO_2(110)$ appear to be restricted to investigations of a low concentration (~6%) of V in the surface layer alone in which V was *assumed* to substitute Ti sites [34, 35]. The conclusion of this work was that this modified surface showed no substantial reconstruction. There does, however, seem to be significant evidence that at the higher concentrations (in the surface and the underlying bulk) studied here, the presence of the V does favour the formation of the (1x2) surface reconstruction. An earlier study of N-doped $TiO_2(110)$ led to the conclusion that N doping increased the number of O vacancies that in turn triggered the formation of a (1x2) phase [36], so it is interesting to note that, somewhat counter-intuitively, the DFT investigation of Kim *et al.* [34] concluded that V substitution also leads to a reduced activation energy for O vacancy creation. It is therefore possible that there is some commonality in these two systems and the associated reconstruction mechanism.

One possibility that has not been discussed thus far, due to the relatively small available dataset and the large number of additional structural variables that it implies, is whether the (1x2) added chain layer metal atoms are also both V and Ti or only one of these. The fact that the agreement between the V^{4+} 2p PhD spectra and the calculations for the (1x1) structure are significantly worse than for the (1x2) structure certainly indicates that V atoms are involved in the added

chains of the (1x2) structure, but the improvement (albeit less pronounced) for the Ti^{4+} 2p PhD data fit indicates that Ti atoms are also likely to occupy this layer. Indeed, the V^{4+} and Ti^{4+} 2p PhD data measured at 20° off normal emission in the both main crystallographic directions are nearly identical, strongly suggesting that any difference in Ti and V site occupation must be small.

One surprising feature of the detailed structural parameter values obtained in this study is that they favour a slightly longer V-O bond length than the Ti-O bond length although the increases of 2 (+6/-4) % in the (1x1) model and 5±5% in the (1x2) model are not formally significant. As the V(IV) ionic radius is (by ~ 2%) smaller than that of the Ti(IV) ionic radius, and the lattice parameters of rutile-phase VO$_2$ are similarly ~1-2% smaller than those of rutile TiO$_2$ it seems highly unlikely that this result is, indeed, meaningful.

In conclusion, the main result of this study is that V atoms substitutionally replace Ti atoms in TiO$_2$(110) with no strong preference for the 5-fold-coordinated or 6-fold-coordinated sites at the surface, nor a strong preference for surface sites over sub-surface sites. Additionally it is clear that the Ti^{3+} and V^{3+} species occupy closely similar, if not identical sites to the Ti^{4+} and V^{4+} species, implying that the (1x2) reconstructed surface layer does not contain only metal^{3+} ions.

Acknowledgements

Table 1: Structural parameters for the best fitting (1x1) and (1x2) models shown in figures 8 and 9, compared against the structural parameters found by Kröger *et al.* [**Error! Bookmark not defined.**] for the clean $TiO_2(110)$-(1x1) surface and by Blanco-Rey *et al.*[20, 21] for the reduced $TiO_2(110)$-(1x2) surface. Atom labelling is defined in Fig. 3. In the case of the (1x2) models, atoms under the metallic chain, and atoms not under the metallic chain have different relaxations. The relaxation of deeper layer atoms not under the metallic chain are signified with a *. The errors in the final digits are shown in the brackets, if no error is provided for the models presented here, then the uncertainty is too large to be defined.

	$TiO_2(110)$ (1x1) [**Error! Bookmark not defined.**]	$Ti_{1-x}V_xO_2(110)$ (1x1)	$TiO_2(110)$ (1x2) [20, 21]	$Ti_{1-x}V_xO_2(110)$ (1x2)
Ti(a) z(Å)	--	--	0.00(3)	-0.03(8)
Ti(a) y(Å)	--	--	0.0	0.1(2)
O(b) z(Å)	--	--	0.00(24)	0.2(+6 / -4)
O(b) y(Å)	--	--	0.0	-0.4(10)
O(c) z(Å)	--	--	0.00(7)	0.0(3)
Ti(2u) z(Å) Ti(2) z(Å) Ti(2c) z(Å)	-0.26(8)	-0.4(1)	-0.11(7) -- -0.17(5)	0.1(1) -- -0.25(10)
Ti(1) z(Å)	0.19(12)	-0.1(+2 / -3)	0.02(6)	0.1(1)
O(3) z(Å)	0.17(15)	-0.2	0.08(11)	-0.1(2)
O(4) z(Å)	0.15(15)	-0.2	0.05(22)	0.0
O(5) z(Å)	0.00(25)	-0.1(5)	-0.04(12)* / 0.29(6)	-0.1(1)* / -0.3(4)
O(5) y(Å)	--	0.1(+8 / -3)	0.03* / 0.11	0.0(3)* / 0.1(7)
O(6) z(Å)	-0.03(8)	-0.1(2)	0.24(22)* /	-0.1* /

			0.25(12)	0.14(10)
Ti(7) z(Å)	0.15(18)	0.1(+6 / -2)	--	--
Ti(8) z(Å)	-0.21(25)	-0.2(2)	--	--
V-O : Ti-O	--	1.02(+6 / -4)	--	1.05(5)

Figure captions

Fig. 1 (1x2) LEED pattern of the $Ti_{1-x}V_xO_2(110)$ surface recorded at an energy of 100 eV.

Figure 2: V 2p, Ti 2p and O 1s SXP spectra measured in the normal emission direction at 225 K with a photon energy of 630 eV. Absolute binding energies are based on the calibration of the Ti $2p^{4+}$ peak energy of 459.3 eV of Diebold and Madey [37]. Using this calibration leads to an O 1s binding energy that agrees with the value of 530.4 eV given by the same authors.

Fig 3. Schematic representation of the (1x1) and (1x2)-added row [20, 21] models, showing the labelling convention [1] for atoms in the outermost layers of the (1x1) structure and the labelling used in the present paper for added and inequivalent atoms in the (1x2) model.

Fig 4. Experimental PhD modulations from the different chemically-shifted components of the Ti 2p and V 2p SXP spectra the emission directions showing the strongest modulations.

Figure 5: Top and side views of a V atom occupying an interstitial site in $TiO_2(110)$ and a comparison of the theoretical simulation of the PhD modulation spectra expected from this emitter with the experimental V^{4+} 2p PhD data.

Fig. 6: *R*-factor maps showing the results of a structural search of more than 10,000 structures involving different occupancy by V emitter atoms of the Ti substitutional sites in the outermost surface layer and the first sub-surface layer of a $TiO_2(110)(1x1)$ surface.

Figure 7: Comparison of the Ti^{4+} 2p PhD modulation spectra obtained in this study of the mixed oxide surface with equivalent data obtained from a clean $TiO_2(110)(1x1)$ surface by Kröger *et al.* [**Error! Bookmark not defined.**].

Figure 8: Comparison the experimental and simulated PhD modulations spectra for the best-fit (1x1) structural model of the surface. The associated structural parameter values are shown in Table 1.

Figure 9: Comparison the experimental and simulated PhD modulations spectra for the best-fit (1x2) structural model of the surface. The associated structural parameter values are shown in Table 1.

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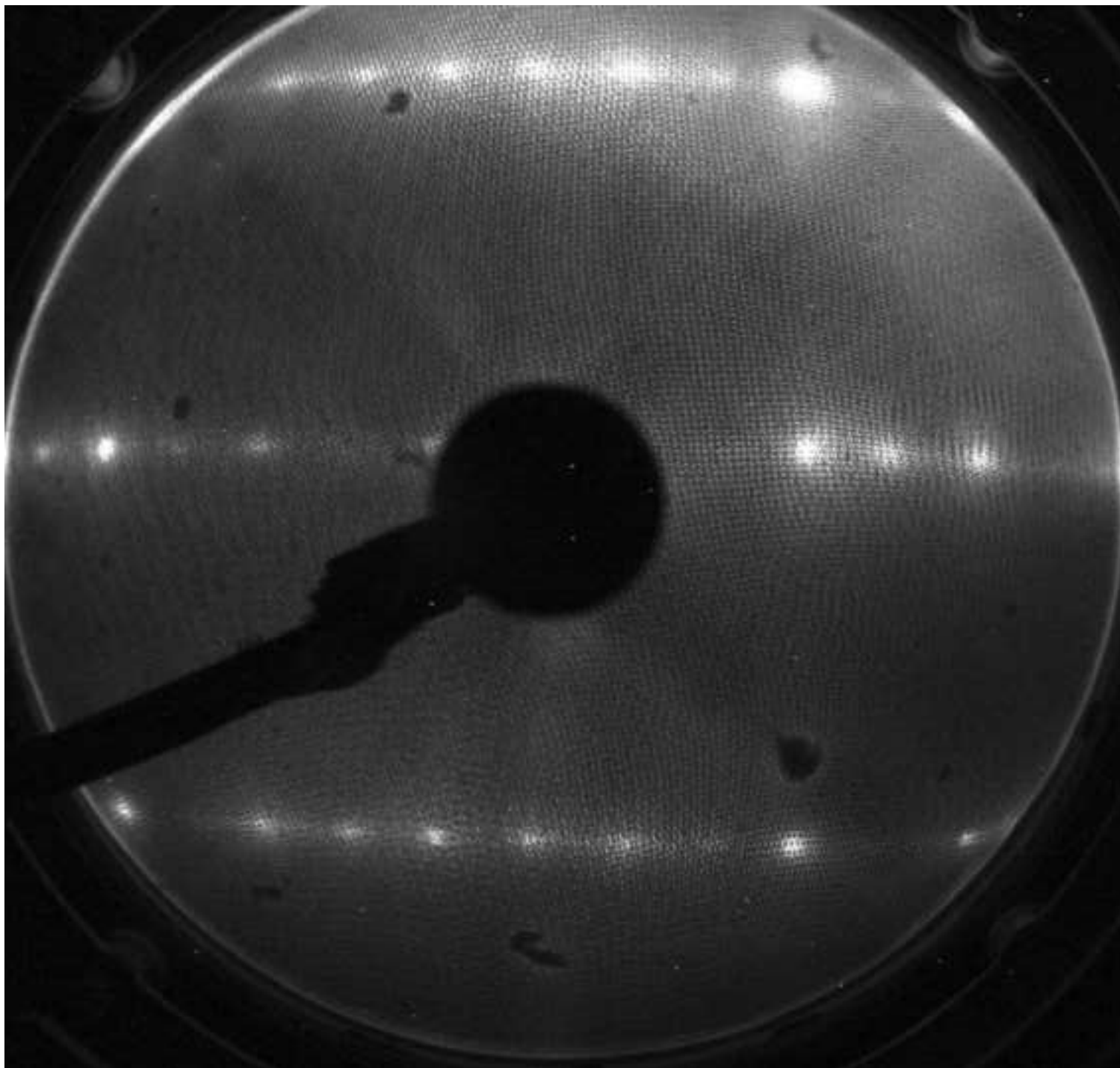**Figure 1**
[Click here to download high resolution image](#)

Figure 2

Figure 3

(1x1)   (1x2)

Figure 4

Figure 5

side

top

theory
experiment

PhD modulation amplitude

30°
[001]

20°
[1$\bar{1}$0]

20°
[001]

0°
[001]

photoelectron kinetic energy (eV)

titanium   vanadium   oxygen

Figure 6

surface site occupation

☆ *V in both Ti(1)* **and** *Ti(2) sites*
+ *V in either Ti(1)* **or** *Ti(2) sites*

sub-surface site occupation

☆ *V in Ti(7) and/or Ti(8) sites*
+ *no V in Ti(7) or Ti(8) sites*

R-factor

z displacement of V in Ti(2) site (Å)
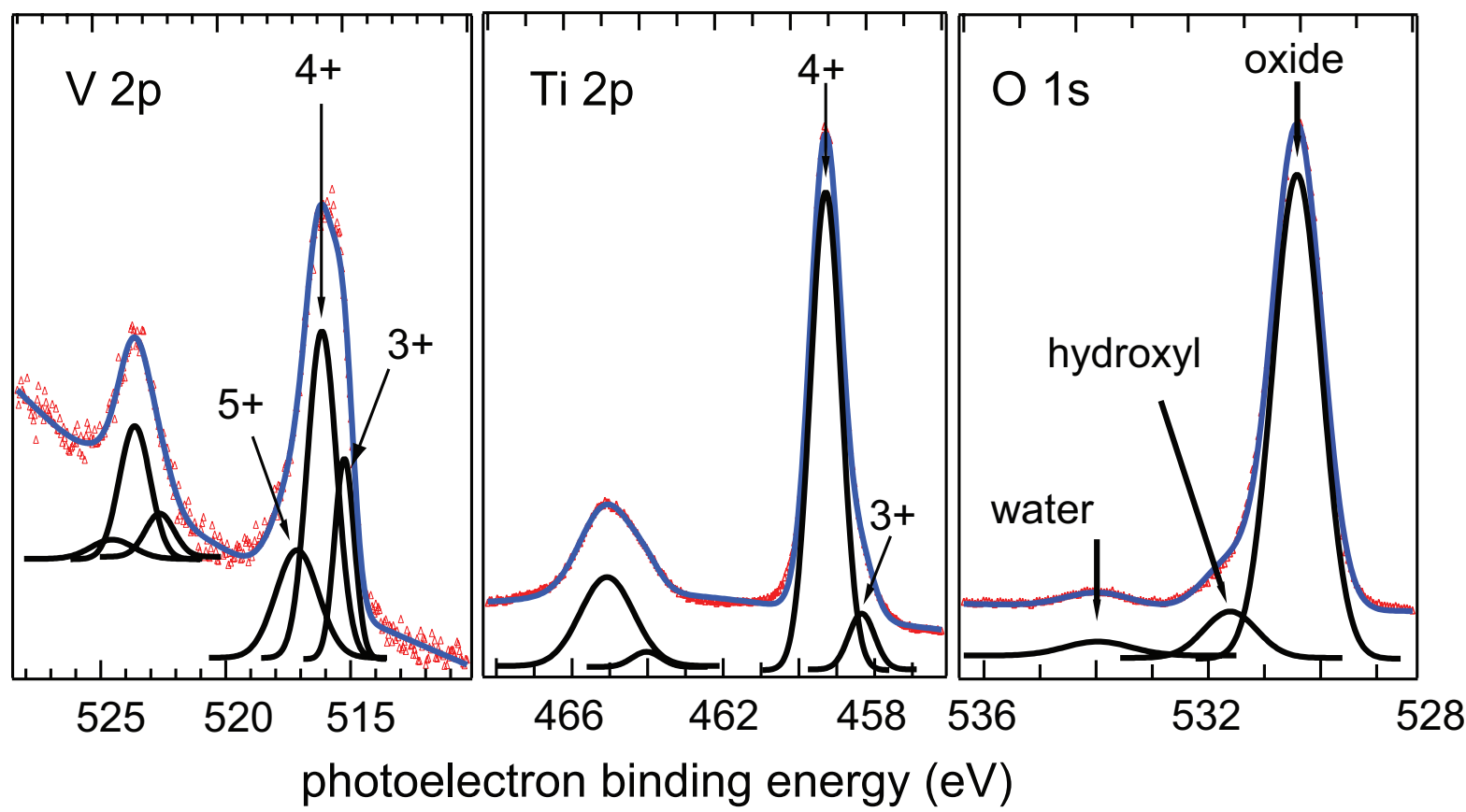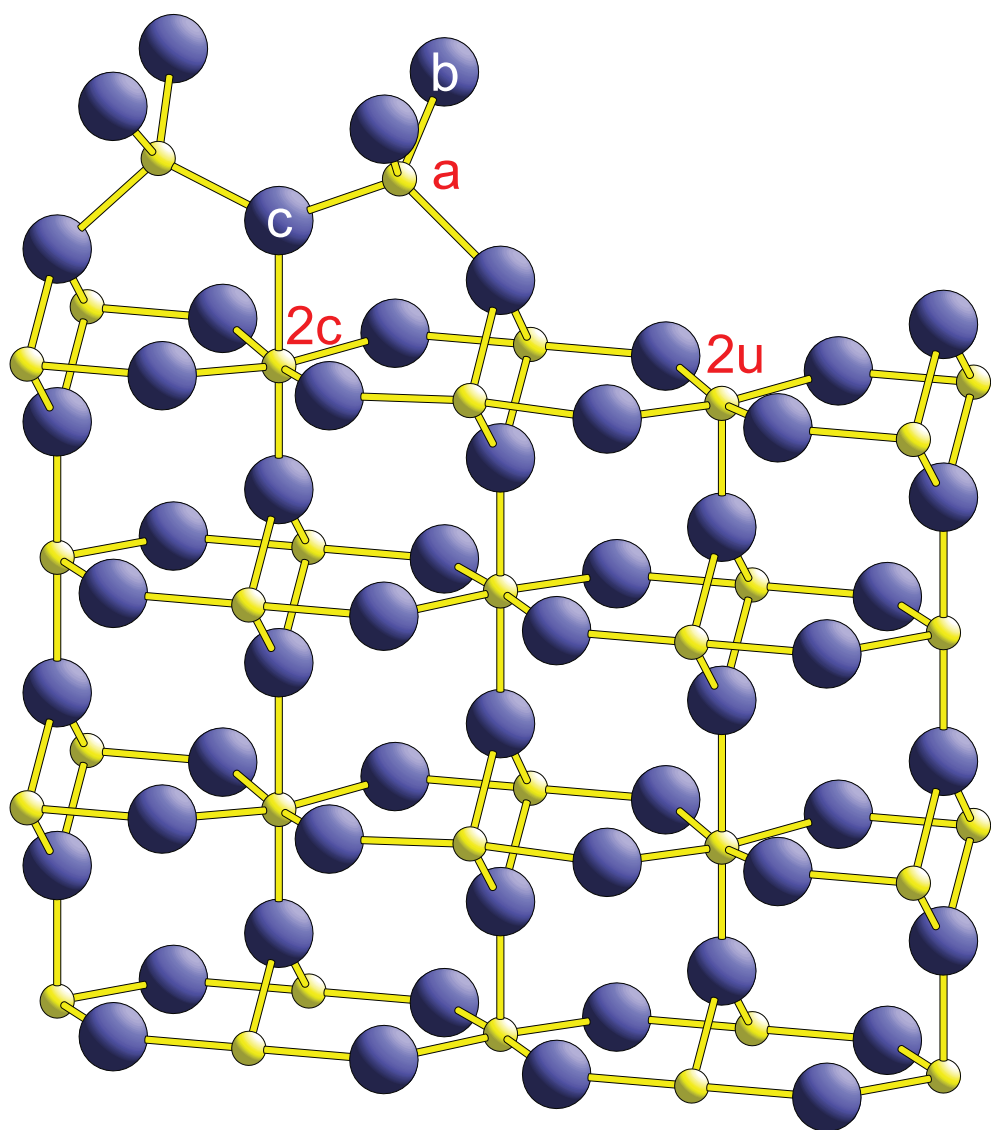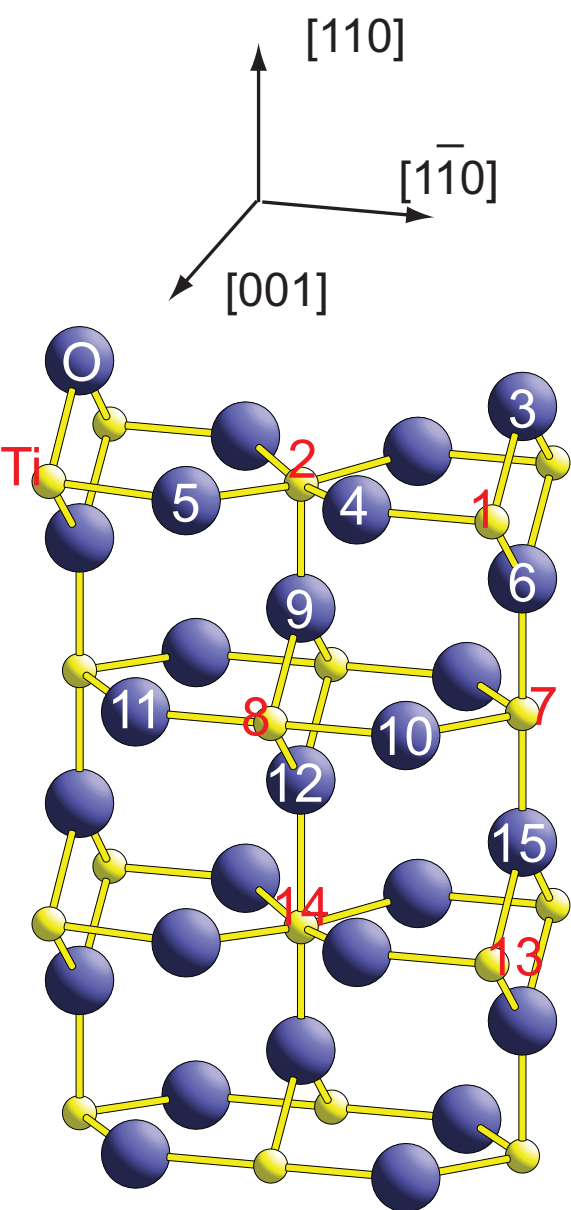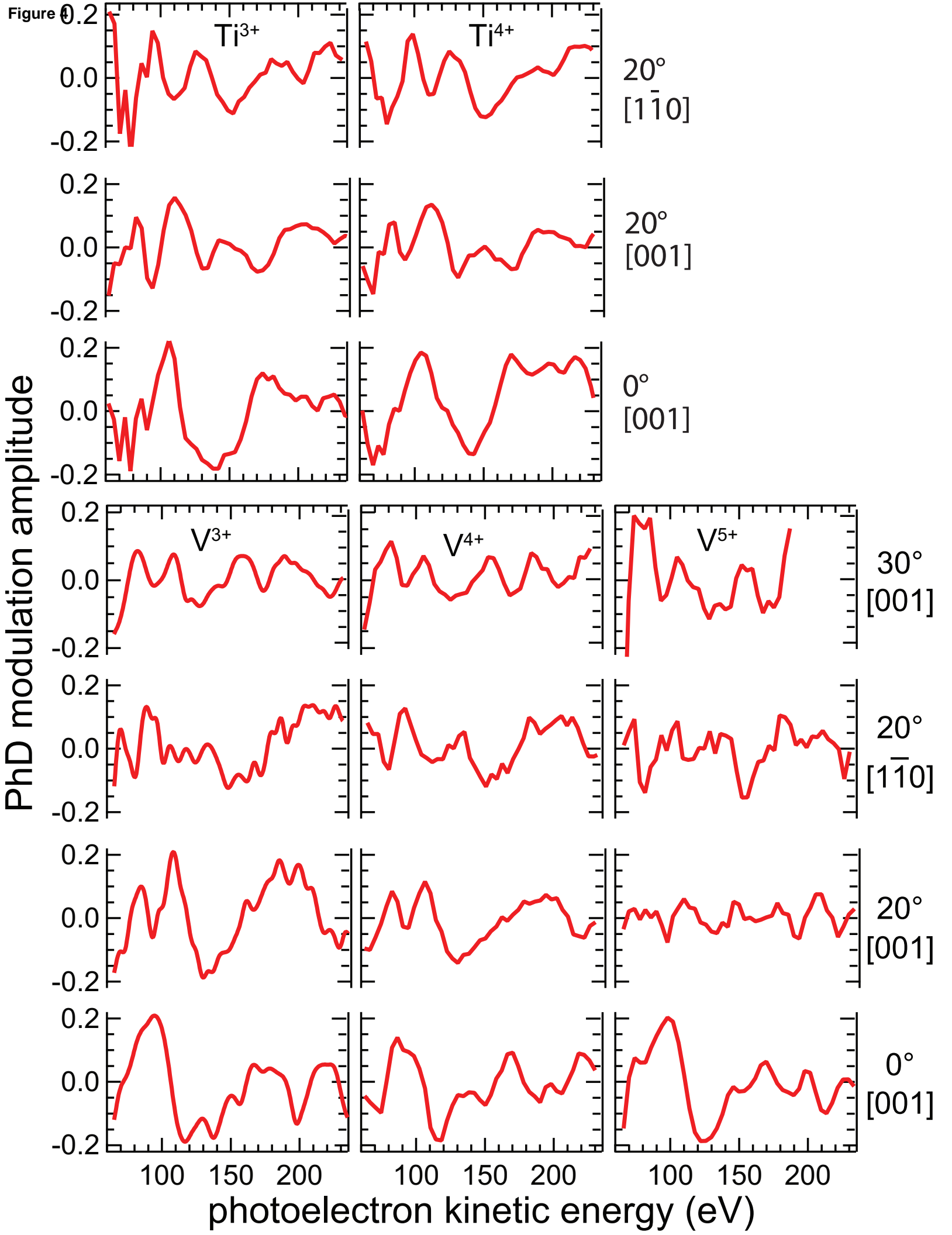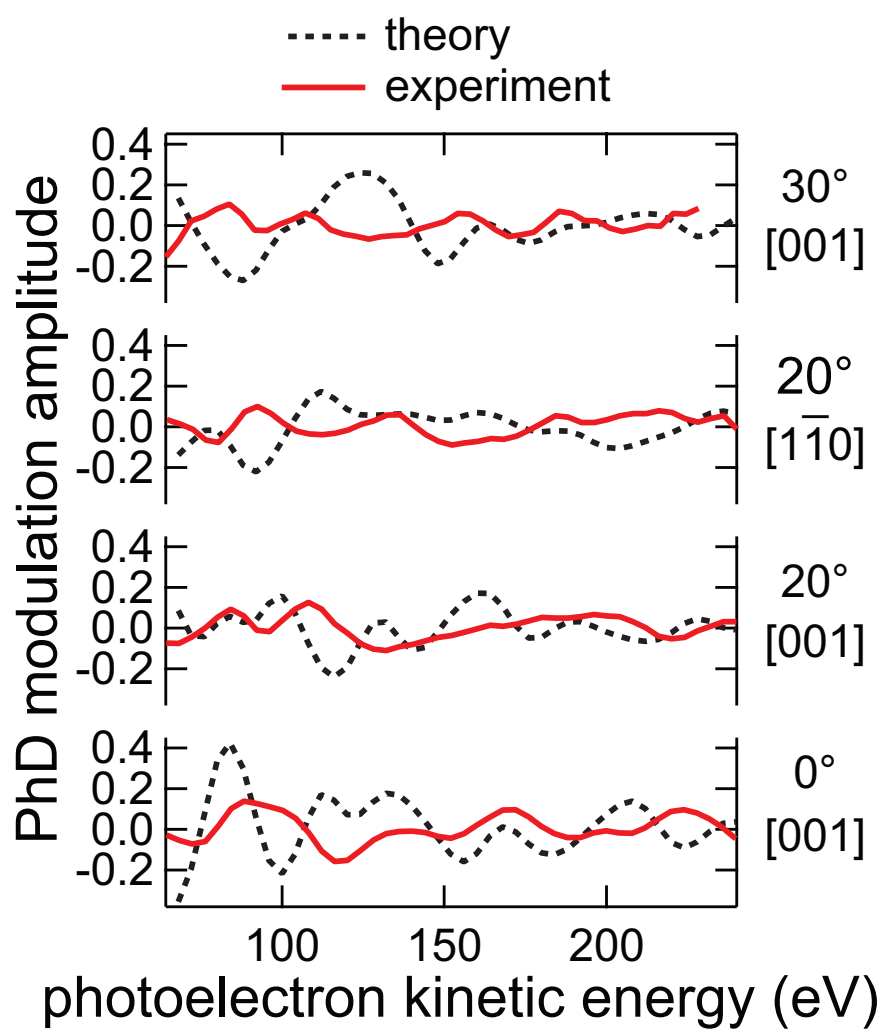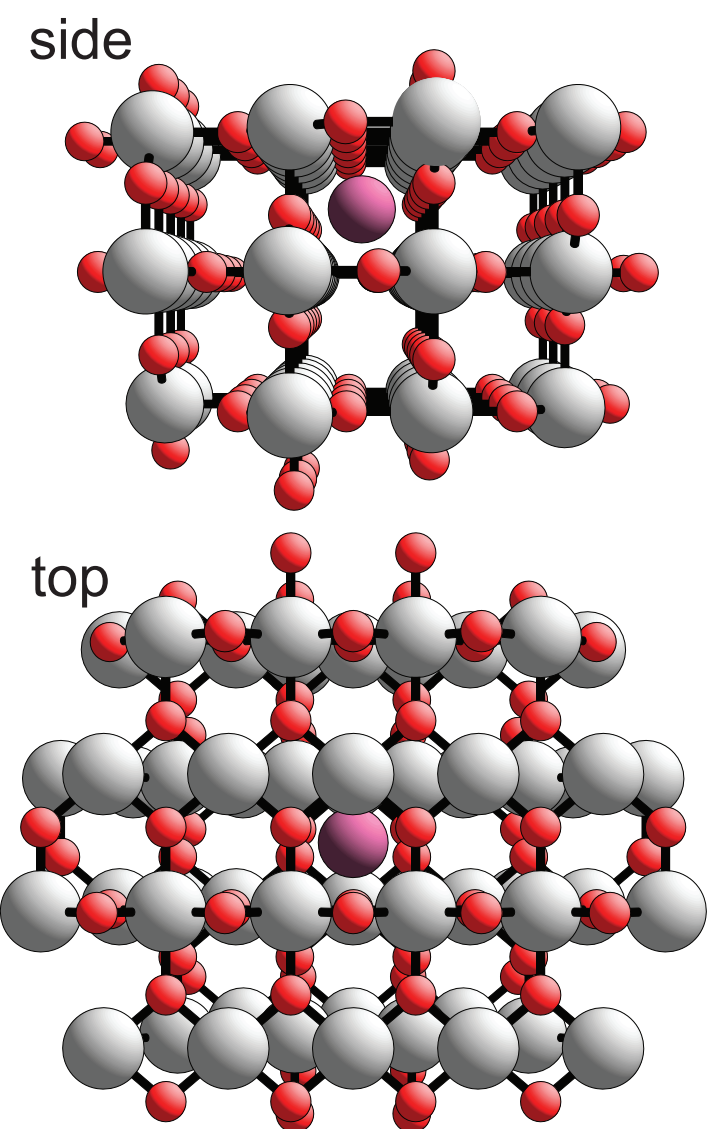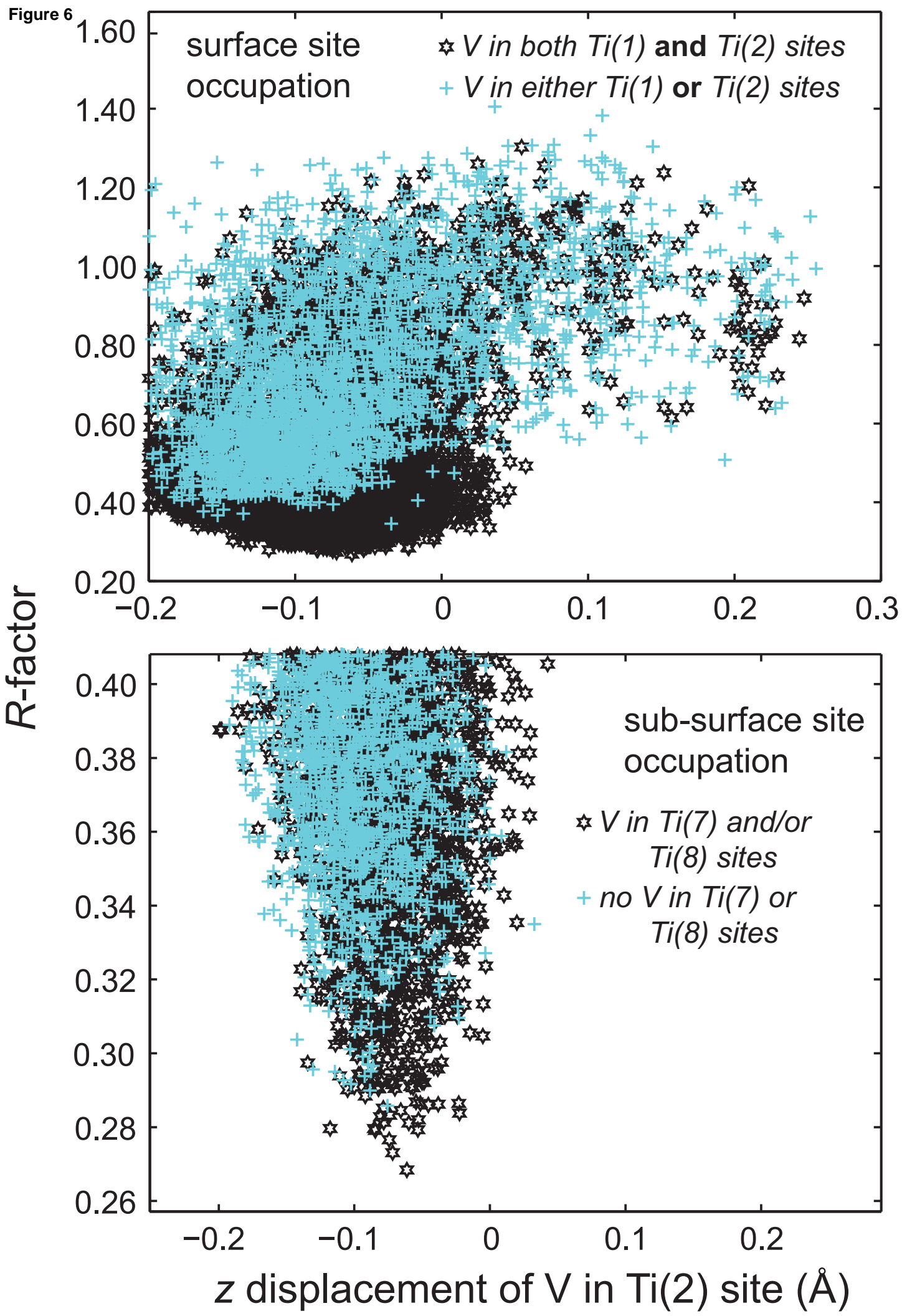
Figure 7

Figure 8

Figure 9