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High resolution X-ray photoemission study of nitrogen doped TiO_2 rutile single crystals

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Abstract

The electronic structure of nitrogen doped TiO_2 prepared by annealing single crystal rutile (1 1 0) substrates in NH_3 at elevated temperatures was investigated using high resolution X-ray photoelectron spectroscopy. NH_3 treatment at 600 °C introduced N into the TiO_2 lattice without concomitant surface reduction of the rutile phase. This doping leads to bandgap narrowing associated with the appearance of new N 2p electronic states above the O 2p band in valence region photoemission spectra. Surface modification at the higher temperature of 700 °C also produced bandgap narrowing but at the same time led to pronounced surface reduction.

The two main polymorphs of TiO_2 are rutile and anatase, with bandgaps of 3.06 eV and 3.20 eV, respectively. Both polymorphs can act as photocatalysts with the ability to degrade adsorbed organic pollutants under irradiation with photons whose energy is bigger than the energy of the bulk bandgap [1,2]. Anatase is the more active phase and anatase-TiO_2 photocatalysts have been successfully commercialised [3]. However interest in fundamental research in this area has remained strong. Recent work has focussed on sensitizing TiO_2 to radiation with wavelengths longer than 400 nm in order to increase the efficiency of the photocatalyst in sunlight. Visible light absorption in TiO_2 could in principle be achieved by introducing mid band gap donor or acceptor states associated with cation dopants. However, it has been found that such localised states promote electron or hole trapping and recombination, deactivating the catalyst [4,5]. An alternative method is to narrow the band gap of TiO_2 by anion doping. Interest in this idea was aroused by Asahi et al. [6] who reported that visible light photocatalysis could be induced by nitrogen doping. The empirical observation of visible light photocatalysis has been widely replicated in both anatase and rutile phases of N-doped TiO_2 [7–9] but no general consensus has emerged as to the mechanism of visible region activation. Optical measurements have shown a reduction in the energy of the near UV absorption edge with N-doping [10] but this has been variously ascribed to localised N 2p states and localised Ti 3d states as well as true band gap narrowing with mixing of N 2p and O 2p states at the top of the valence band [11,12]. Detailed measurements of the electronic structure are necessary to resolve this issue.

In this Letter we report X-ray photoelectron spectra of N-doped rutile TiO_2 obtained with much higher resolution than in previous work. N-Doping can be achieved during sample preparation by wet chemical procedures using N-containing precursors or growth of TiO_2 films by molecular beam epitaxy (MBE) in the presence of a nitrogen source [12–14]. Alternatively pre-existing powder or thin film samples may be nitrided by N-ion implantation or by treatment with NH_3 at elevated temperatures [7,15–18]. However attempts to achieve high doping levels with these technique have in previous work led to surface reduction of the TiO_2 phase and the appearance of localised Ti 3d states in valence region photoemission spectra and Ti 2p core level structure associated with reduced Ti^{3+} states [19]. In the

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present communication we explore the reaction of NH_3 with $TiO_2(1\,1\,0)$ single crystal surfaces. Of course $TiO_2(1\,1\,0)$ is not an optimal photocatalyst but it is nonetheless the most widely studied oxide surface and serves as an idealised model system in which to explore N-doping. It is shown that by optimal treatment of $TiO_2(1\,1\,0)$ single crystal surfaces with NH_3 at 600 °C it is possible to prepare samples which give the XPS signature of substitutional incorporation of N^{3-} without concurrent reduction of Ti^{4+}. This implies that the charge difference between O^{2-} and N^{3-} is compensated for by the creation of oxygen vacancies. Additionally filled states with significant photoemission intensity were observed above the valence band maximum (VBM) of undoped rutile TiO_2. The XPS spectra thus provide clear evidence of band gap narrowing due to N-doping.

Commercial epipolished rutile single crystals (PiKem Ltd.) were heated in recrystallised alumina boats to temperatures between 600 °C and 700 °C under flowing NH_3 gas for periods of up to three hours. X-ray photoelectron spectroscopy was carried out using a Scienta ESCA 300 spectrometer located at Daresbury Laboratory, UK. This incorporates a rotating anode Al Kα ($h\nu = 1486.6$ eV) X-ray source, a seven crystal monochromator and a 300 mm mean radius spherical sector analyser with parallel electron detection system. The effective instrument resolution was set at 0.35 eV.

The N 1s and O 1s core level X-ray photoelectron spectra of rutile $TiO_2(1\,1\,0)$ samples heated to 600 °C and 700 °C for 3 h under flowing NH_3 are shown in Fig. 1.

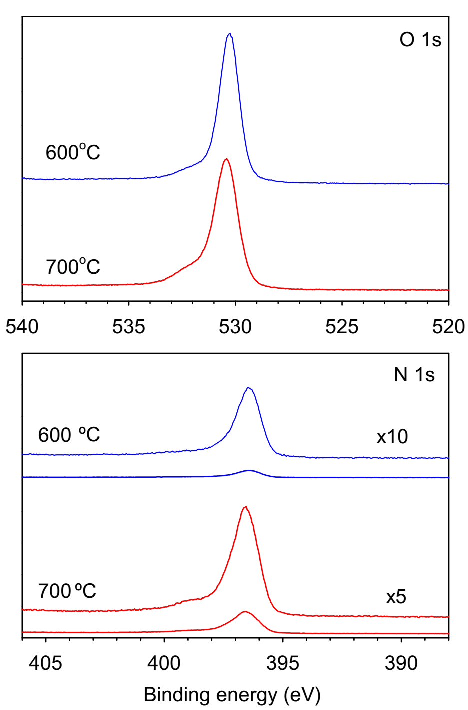

Fig. 1. Al Kα XPS of NH_3 treated rutile TiO_2 single crystals in region of O1s and N 1s core levels. Treatment temperature 600 °C (top) and 700 °C (bottom).

For both samples the most intense N 1s peak appears at 396.5 eV. This binding energy is slightly lower than values between 396.8 eV and 397.4 eV that have been observed for TiN itself but is very close to values previously reported for N-doped TiO_2 [12,15,20]. The peak at 396.5 eV appears to be characteristic of N^{3-} substitutionally incorporated onto O^{2-} sites. For samples annealed at 600 °C this is the only N 1s peak observed but for samples annealed at 700 °C an additional small peak is apparent at a binding energy of 398.7 eV. This is very close to the value of 398.8 eV cited for NH_3 [21,22]. NH_3 may be bound to defect sites or trapped in the subsurface region. We found no evidence of structure at 400.0 eV binding energy assigned to elemental N_2 (400.0 eV) or of core level structure associated with oxides of nitrogen, although both have been observed in previous work [12,23]. The O 1s core line appears at 530.4 eV in samples treated with ammonia at both 600 °C and 700 °C. At the lower temperature, a small shoulder was evident around 532 eV. The nitrogen to oxygen ratio was calculated as 0.10 and 0.27 for the samples prepared at 600 °C and 700 °C, respectively.

The valence region X-ray photoelectron spectra of untreated and NH_3 treated $TiO_2(1\,1\,0)$ samples excited with the Al Kα X-ray source are shown in Fig. 2. Binding energies are referenced to the Fermi energy of a metallic Ag sample which is used regularly to calibrate the spectrometer. In TiO_2 the Fermi level is pinned by donor states very near to the bottom of the conduction band and this level equalises with the position of the Fermi level in metallic Ag. Thus the binding energy of the VBM relative to the Fermi level corresponds to the band gap energy. In the untreated sample, the VBM can be observed at a binding energy of 3.0 ± 0.1 eV, which is consistent with the reported bulk value of the band gap as 3.06 eV [18]. There is a clear difference in the ammonia treated samples. The sample treated at 600 °C shows filled states within the band gap at binding energies from 1 to 3 eV. This feature has

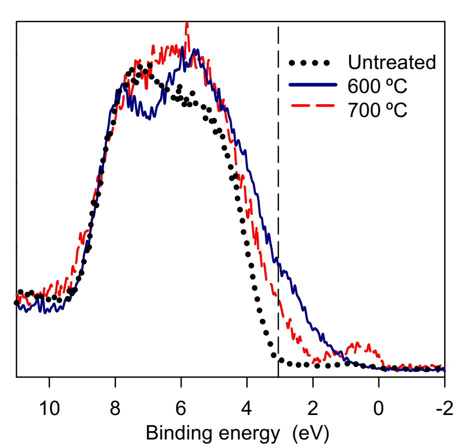

Fig. 2. Al Kα XPS spectra (valence band region) of untreated and NH_3 treated rutile TiO_2 single crystals. The vertical dashed line marks the bandgap of rutile TiO_2.

been observed previously, but with much lower intensity, in similarly nitrided rutile TiO_2 samples [12,15]. This may be interpreted as a shift in the VBM to lower binding energy, representing a narrowing of the band gap. Note that the bottom edge of the valence band, thought to be derived from O 2p states hybridised with Ti 3d states (at a binding energy of 9 eV) is unchanged from the untreated rutile crystal. The sample treated at 700 °C also shows a shift in the top of the valence band, but in addition shows a separate distinct peak at the top of the band gap, centred at a binding energy of 0.5 eV. Diebold et al. recently showed using resonant UPS on similarly treated rutile TiO_2 that the peak at 0.5 eV is derived from Ti 3d orbitals, while the states observed at higher binding energies are not [15]. Thus two inter-band gap features are evident after ammonia treatment at 700 °C: a peak near to the top of the band gap at a binding energy of 0.5 eV, which is assigned to Ti 3d states, present due to reduction of Ti^{4+} to Ti^{3+}, and lower band gap states at binding energies from 1 to 3 eV which are essentially an extension of the valence band and are assigned to N 2p derived states. While these two features have been observed previously [15]. It is apparent from the present results that treatment by ammonia at 600 °C can lead to the introduction of N 2p derived states at the top of the valence band without concurrent reduction of Ti^{4+}. It is known that doping of TiO_2 with N significantly reduces the enthalpy of formation of O vacancies [24,25]. And therefore it is postulated that the charge compensation required by the substitution of O^{2-} for N^{3-} is accounted for by the creation of O vacancies rather than reduction of Ti. As already stated, the core line photoemission spectra confirm that N and O are present in the 3- and 2- oxidation states, respectively. This, coupled with the presence of Ti^{4+} as the sole titanium oxidation state, and the requirement for charge neutrality, implies that the material has a stoichiometry of $TiO_{2-3x}N_{2x}$. Using the nitrogen: oxygen ratio obtained from the intensities of the respective core lines, the stoichiometry can be defined as $x = 0.087$, or $TiO_{1.74}N_{0.17}$. A comparison should be drawn with the work of Diebold et al. and Chambers et al., who studied similarly nitrided rutile TiO_2 systems using photoemission spectroscopy [12,15]. The samples reported in this work are much more heavily doped than previously studied. In the work of Chambers et al. N:O ratios from 2×10^{-3} to 10^{-2} were observed, while Diebold et al. reported N:O ratios of around 3×10^{-2}. In this work the same ratios are 0.10 and 0.27 for samples treated at 600 °C and 700 °C, respectively. Correspondingly, the intensity of photoemission from N 2p states above the VBM was significantly higher than was reported in the two earlier studies, yet despite this, in the film treated at 600 °C, no Ti 3d states were observed, indicating that no reduction of Ti^{4+} had occurred. This may have important consequences for the photocatalytic properties of the material, as localised Ti^{3+} states have been identified as hole traps which deactivate the photocatalyst, and are therefore undesirable [4,5].

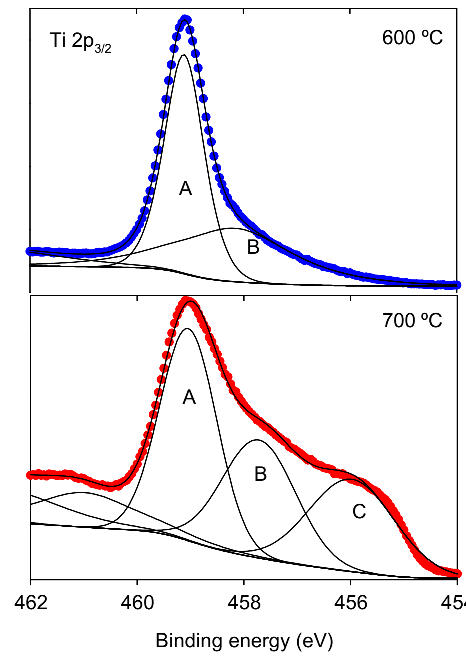

Fig. 3. Al Kα XPS spectra (Ti $2p_{3/2}$ region) of untreated and NH_3 treated rutile TiO_2 single crystals.

Fig. 3 shows the Ti $2p_{3/2}$ core line from samples treated with ammonia at 600 °C and 700 °C. For each Ti $2p_{3/2}$ peak mentioned in the following discussion, a corresponding $2p_{1/2}$ peak was observed at higher binding energy shifted by the spin-orbit splitting of the Ti 2p core level. In samples treated at both temperatures, the most intense Ti $2p_{3/2}$ peak appears at a binding energy of 459.1 eV, corresponding to Ti^{4+} in TiO_2 [26]. In the sample treated at 600 °C, the Ti $2p_{3/2}$ core line shows a small but very broad shoulder on the low binding energy side, which has been fitted with a single Voigt function, centred on 458.1 eV. Several relevant materials have been reported with a matching Ti $2p_{3/2}$ binding energy, such as titanium(III) oxide (Ti_2O_3), titanium oxynitrides (TiN_xO_y), or super stoichiometric TiN_{1+x} produced by ion implantation [27–31]. We believe that the absence of Ti 3d states in the valence region precludes assignment of this environment to Ti^{3+}, and instead points to an oxynitride environment where Ti^{4+} is coordinated with N and O to give a $TiO_{6-x}N_x$ coordination sphere [12]. Such an environment would be expected to give a lower Ti $2p_{3/2}$ binding energy than TiO_2 due to the lower electronegativity of N compared to O, and thus a higher electron density on Ti. Moreover the binding energy of such an environment would depend principally on the number of N ions in the coordination sphere of Ti, which will be a statistical distribution of values of x between 1 and 6, and perhaps accounts for the rather broad nature of the observed photoelectron peak. In the sample treated at 700 °C, the Ti $2p_{3/2}$ core line shows a much broader shoulder, which is shown in Fig. 3 fitted with two Voigt functions, centred at binding energies of 457.8 eV and 456.0 eV. The former appears to be in common with the oxynitride environment observed in the sample treated at 600 °C. The latter matches the binding energy of Ti^{3+} in TiN [27,32], and this assignment is corroborated by the presence of Ti 3d states within the band gap. However, no bulk TiN phase was observed by X-ray diffraction.

In summary, the results presented here indicate that the doping of rutile TiO_2 with nitrogen to a high degree is possible without creation of Ti^{3+} defect states, which act as traps for photogenerated holes. The obvious advantage of the NH_3 route for nitridation of TiO_2 is that it can be applied to powders and thin film material with well defined nanostructures, irrespective of the phase under investigation. The anatase to rutile phase transition requires temperatures of around 800 °C [33], which is well above that required for optimal nitrogen incorporation. We are therefore currently exploring the surface doping of highly porous anatase thin films by NH_3 treatment. In addition we have already shown that anatase powders doped by this technique show excellent catalytic activity in the photodestruction of methylene blue [6].

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