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Abstract

Titanium dioxide (TiO_2) is undoubtedly one of the most studied materials for photocatalytical applications. It comes with no surprise that many different crystallographic forms of TiO_2 have been studied in various shapes and sizes, modified using multiple methods [1]. However, in order to better develop these applications, the processes which underline photocatalysis first must be studied and understood. Powders, nanocrystalites, and nanostructures show promising results, but due to their complexity they are not best suited for investigations into the basic processes. On the other hand, studying monocrystal surfaces in ultra-high vacuum comes with many advantages – great control of the experimental conditions, easier to understand system. This is why these investigations are performed in such conditions.

In order to begin such an investigation, the sample must first be prepared, so that it is free of impurities, adsorbates and is crystalline. The typical way of achieving it is to repeatedly sputter the surface with an ion beam and then to anneal it to high temperatures. Only after multiple cycles the surface is deemed to be fit for experiments. However, the preparation method varies between laboratories – the temperatures, times, fluences and the number of cycles is not set in stone – typically such experimental details are omitted in publications, as they are considered a means to an end and thus not of significant importance. In the presentation we show that this initial step greatly changes the electronic properties of $\text{TiO}_2(110)$ rutile, that is work function and conductivity, the properties important for photocatalysis. Moreover, this presentation shows that by using sputtering and annealing the electronic properties of TiO_2 crystal can be modified and even tuned to reach desired values [2]. Using local conductivity (LC-AFM) and Kelvin (KPFM) modes of atomic force microscopy we show that the rutile surface undergoes substantial changes in properties due to the sputtering and annealing, even though scanning tunneling microscopy and low energy electron diffraction methods confirm its crystallinity. These changes are accompanied by the stoichiometry change, as proved by means of XPS x-ray photoelectron spectroscopy and secondary ions mass spectrometry, where we measured the tracer diffusion of oxygen inside the reduced TiO_2 .

References

[1] M. Humayun, F. Raziq, A. Khan, W. Luo, *Modification strategies of TiO_2 for potential applications in photocatalysis: a critical review*, Green Chem. Lett. Rev. 11 (2018) 86

[2] K. Cieslik, D. Wrana, K. Szajna, W. Bełza, M. Rogala, C. Rodenbacher, J. Rysz, P. Dąbczyński, K. Szot, F. Krok, *Tuning the electronic properties by repeated sputtering and annealing of clean $\text{TiO}_2(110)$ surface: a KPFM and LC-AFM study*, Appl. Surf. Sci. 571(2022)151303