Defect-mediated optical bandgap modulation of self-assembled TiO₂ nanorods on chemically etched Si pyramids

C. P. Saini^{1*}, A. Barman¹, B. Satpati², S. R. Bhattacharyya², D. Kanjilal³ and A. Kanjilal¹

¹Department of Physics, School of Natural Sciences, Shiv Nadar University, Gautam Budh Nagar, Uttar Pradesh 201 314, India

²Surface Physics and Materials Science Division, Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata 700064, India

³Inter-University Accelerator Centre, Aruna Asaf Ali Marg, New Delhi 110067, India

*Email: cs810@snu.edu.in

Among various metal oxides, TiO₂ has attracted a considerable interest owing to its potential for photovoltaic, (opto)electronics and photocatalytic applications [1]. Its large bandgap (~3-3.2 eV), however, restricts the performance, even by fabricating nanostructures for engineering bandgap [2]. Ion beam irradiation in this context is known to be a promising and versatile technique to tune the optical bandgap by controlling defects in TiO₂, especially vacancies and interstitials. Here we will discuss how the optical bandgap of self-assembled TiO₂ nanorods on chemically etched Si pyramids can be regulated by 50 keV Ar⁺-ions with fluences in the range of 5×10^{14} to 1×10^{17} ions/cm² at room temperature as shown in Figure 1).

Figure 1: Ar⁺-ion fluence dependent Band gap variation of TiO₂ film on Si pyramids

Although a gradual decrease in optical band gap was evidenced with increasing defect centres in TiO₂ as a function of ion fluence, we will demonstrate a sudden evolution of degenerate states at a critical fluence of 1×10^{17} ions/cm² with the help of ultraviolet-visible spectroscopy. The observed intriguing phenomenon at 1×10^{17} ions/cm² will be addressed in details in the light of *Burstein-Moss* effect due to the gradual increase of oxygen vacancies in TiO₂ as examined by cross-sectional transmission electron microscopy as shown in Figure 2. X-ray photoelectron spectroscopy (XPS) analyses of the Ti 2p_{3/2} and 2p_{1/2} peaks further reveal ion-induced evolution of TiO/Ti₂O₃ phase.

The production of oxygen vacancies has reached its maximum at 1×10^{17} ions/cm² with an atomic concentration of Ti-suboxides up to ~11.43% as clearly evident in Figure 3.

Figure 2: Transmission spectra of TiO₂ film on Si pyramids

Figure 3: XPS spectra of TiO₂ film with different ion fluence

References

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