論文審査の結果の要旨

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The Doctoral thesis defense for Seiji Kawasaki took place on January 18, 2016 at 11 am in Kashiwa. The defense committee members were professors Kawai, Ohtomo, Matsumoto, Matsuura, and Lippmaa.

The topic of the thesis is the development of model photocatalysts and the analysis of the rate-liming factors in solar-driven photocatalytic and photoelectrochemical water splitting reactions. The thesis starts with an overview of photocatalyst design principles and the current state of the art in photocatalyst design. Based on the review of prior results, several open questions are identified. Most of the earlier work has been done on powder materials that do not have crystallographically well defined surfaces. It is thus difficult to assess the role of the photocatalyst surface in determining the water splitting reaction efficiency. It was also recognized that the electronic structures of some of the best oxide photocathode materials are not well understood. The thesis work thus set out several targets: developing thin film model catalysts with well-defined crystal surfaces, analysis of the electronic structure of Rh- and Ir-doped $SrTiO_3$ and linking the photocatalytic performance with the electronic structure, search for possible light-induced metastable electronic surface reconstructions, and attempt to improve the efficiency of collecting photogenerated charge in water-stable oxide semiconductors.

Chapter 2 covers the methods and techniques. The materials used in this work were fabricated mostly in form of thin films, the film growth by pulsed laser deposition and the basic thin film characterization tools were described. The most important experiments for electronic structure analysis were done by various soft x-ray spectroscopies, including XPS, XES, and XAS. The possibility of electronic reconstructions was considered and measurements were attempted by observing the water contact angle and by in-situ atomic force microscopy in water.

The hydrophilicity of oxide surfaces are described in Chapter 3. The main conclusion from the work is that the appearance of photoinduced hydrophilicity is mainly due to the cleaning effect of ultraviolet light ex-

posure in water. The stability of the $SrTiO_3$ crystal surface was verified by AFM observations, showing that an atomically ordered surface reconstruction remained stable in water. It thus appeared that no metastable electronic states appear at the oxide photocatalyst surfaces. It is thus unlikely that any such changes would have a significant effect on the water splitting reaction efficiency. The attention thus changed to bulk semiconductor analysis.

In Chapter 4, the analysis of the electronic structure of Rh- and Ir-doped $SrTiO_3$ is presented. The work involved bulk and thin film sample synthesis and characterization by x-ray photoelectron, absorption, and emission spectroscopies. The spectroscopic results were compared with first-principles density-functional calculations, and all detected spectral features could be assigned to dopant-related in-gap states forming in the host $SrTiO_3$ lattice.

It was found that the main difference between the Rh and Ir dopings is a slight shift in the dopant level distance from the top of the valence band. The effect of the dopant level position on the photocarrier lifetime was studied in terms of classical semiconductor physics. It was shown that there is an inherent competition between the need to improve light absorption by shifting the dopant level deeper into the gap, while increasing the energy separation between the dopant level and the top the valence band, reduces the mobility of photoinduced carriers. The works showed that Rh:$SrTiO_3$ and possibly Cr:$SrTiO_3$ should have close to optimal doping configurations.

It is also known that dopants in $SrTiO_3$ can assume different valence states. Experimental electrochemical measurements have shown that the water splitting efficiency is very different for Rh^{4+} and Rh^{3+} dopants in $SrTiO_3$. This behavior was analyzed from the point of view of the electronic structure and it was found that Rh^{4+}:$SrTiO_3$ has a Rh-related, unoccupied mid-gap state that works as a very rapid trap center for photogenerated carriers, reducing the energy conversion efficiency to nearly zero.

The limited diffusivity of photocarriers in an oxide semiconductor was identified as the main cause of the limited efficiency of oxide photocatalysts. A new nanoscale design was therefore developed to improve the charge collection efficiency. This part of the work is described in Chapter 5.

It was found that several noble metals that have been used as dopants in $SrTiO_3$ have certain solubility limits. If thin films are grown under suitable kinetic conditions, it is possible to intentionally segregate the

noble metals in nanostructure form. This technique was developed for Ir to nucleate Ir metal nanoparticles at the substrate interface, followed by gradual formation of nanoscale pillars inside the oxide semiconductor matrix. Since Ir metal has a high workfunction, it forms Schottky junctions with the surrounding Ir-doped $SrTiO_3$ film and the n-type Nb:$SrTiO_3$ substrate. Due to this, the embedded Ir nanopillars can work as efficient charge collection electrodes, expanding the electronically active space-charge region from the film surface deep into the bulk of the semiconductor.

Indeed, the nanopillar composite thin films were shown in electrochemical measurements to have far superior efficiencies over homogeneous thin films. The best results were obtained with embedded Ir nanopillars, reaching nearly 100% absorbed photon to current efficiency in the visible part of the solar spectrum.

Besides Ir doping and Ir nanopillar growth, the general aspects of metal nanostructure segregation in $SrTiO_3$ were studied. Nanopillar growth was achieved for several noble metals, including Ir, Pt, Pd, and Rh.

The thesis work made a significant contribution to the field of photocatalyst development in showing how systematic electronic analysis can help with the materials design process. Several open questions regarding the role of photogenerated surface effects were successfully clarified. Finally a beautiful demonstration of nanoscale material design was demonstrated.

The thesis work has been published in three full papers and one proceeding. The thesis defense committee members presented many detailed questions regarding the experimental details and the interpretation of the experimental results. The judges identified no major faults and made no further correction requests.

The work described in Ch. 3 was conducted in collaboration with Prof. Onishi and Prof. Foster. Access to experimental equipment for collecting the data presented in Ch. 4 was provided by Profs. Kudo, Harada, Yoshinobu, Komori, and Kumigashira. Calculation help was provided by prof. Akagi. The TEM data in Ch. 5 was acquired by prof. Yamamoto. The committee found that the role of the author of the thesis in the synthesis, characterization experiments, and data analysis was sufficient for granting the doctoral degree.

By unanimous decision, the defense committee agreed that the candidate, Mr. Seiji Kawasaki, should be awarded the PhD degree.