Defect Properties and Photoelectrochemical Performance of BiVO₄ Photoanodes

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INTRODUCTION

With a bandgap of 2.4 eV, BiVO₄ is an interesting material for photoelectrochemical and photocatalytic applications in the visible part of the spectrum. However, reported photo-activities for BiVO₄ photoanodes show large variations, ranging from a few hundred nA/cm² up to a few mA/cm². Poor control over surface and/or bulk defects appears to be the main reason for these variations, since they are too large to be explained by differences in specific surface areas and/or illumination intensities. Clearly, a better understanding of the influence and origin of these defects is essential for the further development of BiVO₄-based photoanodes.

RESULTS

We report on the defect properties of commercially produced BiVO₄ powders and on the photo-electrochemical properties of spray-deposited BiVO₄ thin films. The BiVO₄ powders, consisting of ~0.5 µm particles, were pressed into pellets by cold uni-axial compression. After firing at 700°C in air and subsequent cooling to room temperature, significant shrinkage of the pellets was observed due to sintering. Moreover, the color of the material had changed from bright yellow to reddish/pink. Since the material still showed the original monoclinic Scheelite structure, the color change cannot be attributed to the ferroelastic properties of BiVO₄.¹ Instead, we attribute the color change to the formation of sub-bandgap states by oxygen vacancies. These vacancies are formed during the evaporation of Bi from the lattice. Support for this model is provided by the high temperature conductivity measurements shown in Figure 1. This figure shows the resistivity changes during a step change in the p(O₂) from 0.2 to 0.02 bar. First, a decrease in the resistance is observed, which is due to the loss of oxygen from the lattice and the concomitant charge-compensation by free electrons. At the same time, but on a much slower time scale, an overall increase in the resistivity is observed. We attribute this increase to the evaporation of metallic bismuth. This results in the creation of Bi vacancies, which are charge-compensated by a decrease in the concentration of free electrons present in the (n-type) BiVO₄.

The evaporation of Bi metal is a well known phenomenon in solid state chemistry, and is supported by XPS data. The overall slope of σ vs. $\log(p(\text{O}_2))$ is virtually zero, indicating that overall charge-compensation of the oxygen vacancies is provided by the bismuth vacancies. Therefore, the observed changes in electronic conductivity are only temporary (cf. Figure 1), and can only be observed because the diffusion of oxygen vacancies occurs on a faster time scale than the evaporation of Bi. Thin dense films of BiVO₄ have been prepared by spray pyrolysis for the first time. SEM images reveal a layered structure, consisting of a compact underlayer of ~0.1 µm particles and a more porous, open top layer of ~0.2-0.8 µm particles. The film thickness was ~300 nm to ensure that most of the incident light at wavelengths below 450 nm is absorbed. Front- and back-side illumination

experiments show an IPCE of 10% for undoped BiVO₄, with electron transport being the rate-limiting factor. By doping the BiVO₄ with tungsten (1% W in spray solution), the electron transport properties could be significantly improved. When the W-doped BiVO₄ films were deposited onto a thin spray-deposited SnO₂ film on TCO glass, IPCE values of 50% are reached (Figure 2). The SnO₂ interfacial layer is thought to act as a barrier that prevents photo-generated holes to reach surface recombination centers (electron traps) that appear to be intrinsic to the TCO glass. This model will be explained in more detail and its implications will be discussed.

Figure 1. Resistivity change of a BiVO₄ pellet at 700°C after a step-change in the p(O₂) from 0.2 to 0.02 bar at $t=0$. The impedance data were recorded at various frequencies.

Figure 2. Incident photon-to-current conversion efficiency (IPCE) of spray-deposited BiVO₄ at 1.63 V vs. RHE.

CONCLUSIONS

The results indicate that oxygen vacancies and bismuth vacancies are the main defects present in BiVO₄ photoanodes fired at high temperatures. Since these defects may act as recombination centers, their formation should be avoided. This limits the processing temperature BiVO₄ photoanodes to ~550°C. The photo-electrochemical properties of BiVO₄ could be significantly improved by doping with tungsten, and by depositing a thin interfacial layer of SnO₂ onto the TCO substrate. IPCE values of 50% can be reached, indicating that BiVO₄ is a promising photoanode material.

REFERENCES

1. A.K. Bhattacharya, K.K. Mallick and A. Hartridge, *Mater. Lett.* **30**, 7 (1997).