Optical and photocatalytic properties of BiVO$_4$ thin films

Why BiVO$_4$?

Polymorph

- orthorombic (pucherite)
- monoclinic (clinobisvanite)
- tetragonal (zircon-like)
- (sheelite like)

- Ferro-elastics
- Pigments replacing toxic ones containing lead/cadmium

Still increasing industrial demand to meet EU chemicals regulation REACH

News Release

BASF to increase production capacities for bismuth vanadate pigments in Besigheim

Investments due to increasing demand for alternatives to lead chromate pigments

February 4, 2015
P130/15e
Dispersions & Pigments
Philipp Schnorbus
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Photocatalytic elimination of organic pollutants

Photocatalytic degradation of rhodamine B

Photodegradation of ibuprofen with pure BiVO₄ and metal-loaded BiVO₄ powders under visible-light irradiation

Z. Zhang et al., Catalysis Communications 11 (2010) 982–986

**Efficient photo-electrochemical cells:** BiVO$_4$ has been proposed as an possible photo-anode for water oxidation.

**Review Article**

*Progress in bismuth vanadate photoanodes for use in solar water oxidation*


**Incorporation of Mo and W into nanostructured BiVO$_4$ films for efficient photoelectrochemical water oxidation**

Drawbacks for BiOV$_4$

- excessive electron-hole recombination,
- poor charge transport properties,
- inefficient water oxidation kinetics

Approaches to overcome the issues:

- doping
- morphology control,
- formation of composite structures,
- addition of oxygen evolution catalysts
Interest of novel deposition methods for the BiVO$_4$

**Sputtering from m-BiVO$_4$ targets**

Solid State Sciences 33 (2014) 58e66
International journal of hydrogen energy 40 (2015) 4311

**PLD**


**CVD**

**Dual sputtering**


**Phys.Chem.Chem.Phys.**, 2014, 16, 1651
Dual sputtering: an appealing technique for tuning the BiVO$_4$ stoechiometry

After annealing at 500 °C for 2 h.

Le Chen et al. J. Phys. Chem. C 2013, 117, 21635–21642,
PHASE EQUILIBRIUM IN THE SYSTEM SnO$_2$-V$_2$O$_5$-Bi$_2$O$_3$

Y. Ivanova, A. Staneva

Journal of the University of Chemical Technology and Metallurgy, 41, 4, 2006, 423-426
Our studies

$\text{BiVO}_4$ synthesized by dual sputtering

- wateroxidation
- dye degradation
Our film growth: experimental setup

RF power source (30-50 W)

DC power source (100-300 W)

Bi$_2$O$_3$ Target

V target

Atmosphere: Ar/O$_2$ (sccm/sccm) = 18/2
Base Pressure: 5x10$^{-6}$ Torr
Working Pressure: 5 mTorr
Deposition Time: 15-30 min
<table>
<thead>
<tr>
<th>V target DC power</th>
<th>Bi$_2$O$_3$ target RF power</th>
<th>Grown at RT</th>
<th>Grown at 100...300°C</th>
<th>Grown at RT postannealed (2h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>50</td>
<td>amorphous</td>
<td>mainly Bi$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>50</td>
<td>amorphous</td>
<td>predominantly Bi$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td>200,300</td>
<td>50</td>
<td>amorphous</td>
<td>Bi + VO$_x$</td>
<td></td>
</tr>
<tr>
<td>175</td>
<td>50</td>
<td>amorphous</td>
<td></td>
<td>100-200°C: amorph. 300°C unstable 400°C: mc-BVO + Bi$_2$O$_3$ excess</td>
</tr>
<tr>
<td>175</td>
<td>30</td>
<td>amorphous</td>
<td></td>
<td>mc-BVO + excess of V</td>
</tr>
<tr>
<td>155-165</td>
<td>30</td>
<td>amorphous</td>
<td></td>
<td>400°C: mc-BVO (+ VO$_x$)</td>
</tr>
</tbody>
</table>

165W + 2h annealing ("as grown") : water oxidation
160W + 2h annealing ("as grown") : dye degradation
KOH bath
- Film immersion in 1 M KOH solution (40 min)
- Rinse of the samples with distilled water (a few minutes),
- Application of N$_2$ to dry the samples.

Published results: M. Thalluri et al., Physical Chemistry Chemical Physics 2015, 17, 17821-17827
KOH treatment improves the charge transfer. Much better kinetics of the photocatalytic water oxidation.

Published results: M. Thalluri et al., Physical Chemistry Chemical Physics 2015 p. 17821

Possible explanations:
- Removing of the impurities on the grain boundaries reduces e-h recombination
- Change of the surface topology

Results obtained without doping or catalysts

V 165W-Bi$_2$O$_3$ 30W

Photocurrent Density (mA/cm$^2$)

Voltage (V) vs RHE

Before KOH

After KOH

1.10 mA/cm$^2$

0.105 mA/cm$^2$

Before KOH

After KOH

Voltage (V) vs RHE

Voltage (V) vs RHE

Photocurrent Density (mA/cm$^2$)

t(nm) = 250 nm

t(nm) = 500 nm
BiOV$_4$ for photocatalytic dye degradation:

Can the KOH treatment improve the photocatalytic response?
**KOH:** removal of V rich phases

**As grown:**
- Quasi pure monoclinic
- Some traces of tetragonal phase/V rich phases

<table>
<thead>
<tr>
<th>020</th>
<th>110</th>
<th>011</th>
</tr>
</thead>
<tbody>
<tr>
<td>(130)</td>
<td>(121)</td>
<td>(121)</td>
</tr>
<tr>
<td>(200)</td>
<td>(002)</td>
<td>(141)</td>
</tr>
<tr>
<td>(211)</td>
<td>(112)</td>
<td>(150)</td>
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<tr>
<td>(240)</td>
<td>(042)</td>
<td>(220)</td>
</tr>
<tr>
<td>(202)</td>
<td>(161)</td>
<td><strong>Vanadium rich phases</strong></td>
</tr>
</tbody>
</table>

Monoclinic BiVO$_4$, JCPDS 01-075-1866

Tetragonal BiVO$_4$, JCPDS 14-0133
Raman spectroscopy

Excitation: 532 nm, at room temperature

KOH treatment leads to better defined modes, converging towards mc-like behaviour.

As grown: the shift of the stretching V-O mode above 800 cm\(^{-1}\) suggests a longer V-O bond length.

The asymmetric and symmetric deformation modes of VO\(_4^{3-}\) tetrahedron are not well resolved.
Experimental set-up of the PC

% Degradation = (1 – C/C₀) * 100

Dye absorption

Lamp Emission (a. u.)

Methyl Orange Absorbance (A.U.)

Wavelength (nm)

Degradation
Acid blue and Methyl Orange are degraded but quite slowly (but without any added catalysts).

KOH treatment deteriorates the PC activity!
Photoluminescence

Excitation: Kimmon IK3201R-F He-Cd laser (325 nm) at 19.2 mW excitation power

PL detection: spectra Pro 2500i Princeton Instruments spectrometer coupled to a photomultiplier

- Shift of the emission peak for KOH films
- Inhomogeneous behavior for the "as grown" film
Optical properties

Jasco V670 spectrophotometer (360-1800 nm)
- Specular transmittance and reflectance
- Diffusive transmittance

Cary 5E Varian (360 – 1500 nm)
- Total reflectance
- Diffusive reflectance

Smart Materials and Structures
5th International Workshop 2015, Marrakech
Transmission

- Specular transmission
- Total transmission

160W as grown
160V30B_KOH

Tt-Ts

as grown
KOH

Rayleigh-like (1/λ^x)

x = 4.1...4.2

Much stronger scattering in the non treated film.

Scattering Rayleigh-like
Scattering is also higher at the surface for the "as grown" sample.

Specular reflection is almost completely suppressed in the blue-UV range.
Models

Specular transmittance/reflectance data

Total transmittance/reflectance data

Rough scattering interface (loss function)

Porous surface layer
Homogenous layer

Porous surface layer
Homogenous layer

Tauc-Lorentz model verifying Kramers-Kronig relations
Oscillators for subbandgap regions
- Adequate fitting with both models converging towards the same properties
- Total film layer thickness compatible with profilometry and growth rates
- Surface roughness is higher for the as grown sample explaining higher scattering
KOH: refractive index close to literature values for mc-BiVO₄, lower for the "as grown" film

Subband gap absorption is significantly higher in the as grown sample than in the KOH treated

Impurities? Defects due to poor phase quality?
Gaps

Direct gap of 2.64 eV

This value is slightly higher than the values reported in literature around 2.45-2.55 eV for mc-BiVO$_4$.

Possible influence of minor phases compatible with Raman and XRD results

Two slopes indicating respective gaps of 2.56 eV / 2.65 eV

A lower gap, close to the value expected for mc-BiVO$_4$ appears.
Surface roughness decreases after KOH treatment.
BiVO4 as grown

BiVO4 after KOH treatment

RMS 42.68 nm
Ra 32.76 nm

RMS 26.65 nm
Ra 21.032 nm
The variation of the roughness at microscale (AFM) is confirmed at higher scale.

There is less surface available.
Conclusions

Dual sputtering sources provide a large panel of phase tuning for Bismuth vanadates.

BiVO$_4$ films show interesting water oxidation and dye degradation properties.

KOH treatment leads to a better defined crystallinity providing a much more efficient water oxidation current.

For photocatalytic dye decoloration the better crystallinity provided by KOH cannot compensate the surface loss.
Effect of the KOH chemical treatment on the optical and photocatalytic properties of BiVO₄ thin films

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The research leading to these results has received funding from the European Community Seven Framework Program (FP7-NMP-2010-EU-MEXICO), CONACYT and Phocsclleen under grant agreements No 263878, 125141 and 318977, respectively.