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Adsorption-controlled growth of BiVO$_4$ by molecular-beam epitaxy

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Single-phase epitaxial films of the monoclinic polymorph of BiVO$_4$ were synthesized by reactive molecular-beam epitaxy under adsorption-controlled conditions. The BiVO$_4$ films were grown on (001) yttria-stabilized cubic zirconia (YSZ) substrates. Four-circle x-ray diffraction, scanning transmission electron microscopy (STEM), and Raman spectroscopy confirm the epitaxial growth of monoclinic BiVO$_4$ with an atomically abrupt interface and orientation relationship (001)$_{\text{BiVO}_4}$$\parallel$(001)$_{\text{YSZ}}$ with [100]$_{\text{BiVO}_4}$$\parallel$[100]$_{\text{YSZ}}$. Spectroscopic ellipsometry, STEM electron energy loss spectroscopy (STEM-EELS), and x-ray absorption spectroscopy indicate that the films have a direct band gap of 2.5 ± 0.1 eV. © 2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4824041]

Water splitting by photocatalytic materials is relevant for clean fuel generation using sunlight, i.e., artificial photosynthesis. For this application, it is critical that the band gap and band lineup are correct and also that the material does not corrode in water.$^{1,2}$ Additionally, photocatalysts that work in the visible light range are needed in order to make efficient use of solar radiation.$^{2,3}$ Recently, bismuth vanadate (BiVO$_4$) has attracted much attention as a promising photocatalyst due to its favorable band structure$^{4-12}$ and, with surface additives, reasonable stability in water.$^{15}$ BiVO$_4$ is known to exist in four different crystal structures at atmospheric pressure, though one of these (the mineral pucherite, an orthorhombic polymorph with the CrUO$_4$ structure) is only found in nature.$^{14}$ The remaining polymorphs, two with tetragonal and one with monoclinic symmetries, have all been synthesized artificially. The tetragonal polymorphs include one with the zircon structure and a band gap of $\sim$2.8 eV,$^{4,6,7}$ and one with the CaWO$_4$ structure and bandgap $\sim$2.3 eV,$^6$ the latter phase is the stable polymorph of BiVO$_4$ above 255$^\circ$C.$^{14}$ It is the monoclinic polymorph of BiVO$_4$ with the YNbO$_4$ structure, however, that has been found to have the best photocatalytic properties in powder form, exhibiting high activity for oxygen evolution under visible light irradiation.$^{4,5,7,13}$ This monoclinic polymorph is the stable polymorph of BiVO$_4$ at room temperature and has a band gap of $\sim$2.4 eV.$^{4-12}$

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To date BiVO₄ has been produced in the form of powder,4–7,10–12 polycrystalline thin films,8,11,15–17 and single crystals.14,18 If epitaxial thin films could be produced, BiVO₄ could be modified and studied in ways heretofore infeasible. For example, in epitaxial films it is possible to impose a doping profile or biaxial strain, techniques often used in the growth of epitaxial materials to manipulate the band structure. Similar strategies may make it possible to improve the photocatalytic activity of BiVO₄. For instance, theoretical studies have indicated that the (100) surface of monoclinic BiVO₄ is likely to have the greatest photocatalytic activity.19 A prerequisite for employing the above concepts, however, is the ability to grow phase-pure epitaxial BiVO₄ films of good quality.

In this Letter, we report the growth of epitaxial films of the monoclinic polymorph of BiVO₄. These films were grown by reactive molecular-beam epitaxy (MBE) in a Veeco GEN 10 oxide MBE system under adsorption-controlled conditions in which a large excess of bismuth is supplied during growth. Within a certain temperature range, BiVO₄ is the only thermodynamically stable condensed phase, and excess bismuth oxide evaporates from the film surface leaving behind phase-pure BiVO₄. Molecular beams of bismuth and ozone, the volatile components, were supplied continuously during growth, while vanadium, the non-volatile component, was supplied in shuttered doses corresponding to individual BiVO₄ monolayers. This procedure is analogous to the growth conditions reported for the adsorption-controlled growth of other bismuth containing oxides by MBE including Bi₂Sr₂CuO₆,20 Bi₄Ti₃O₁₂,21 and BiFeO₃.22

The films were deposited onto 10 × 10 mm², (001)-oriented, single crystalline, cubic yttria-stabilized zirconia (YSZ) substrates containing 9.5 mol. % Y₂O₃. A substrate temperature of 700°C and a Bi:V flux ratio of 7.5 were used to produce the highest-quality film. Distilled ozone was supplied continuously at a background partial pressure of 1.0 × 10⁻⁶ Torr. Prior to film deposition, a quartz crystal microbalance was used to calibrate the fluxes such that the vanadium flux was 1.6 × 10¹³ atoms/(cm²·s) and the bismuth flux was 1.2 × 10¹⁴ atoms/(cm²·s). Although the amount of bismuth supplied was many times that required for the BiVO₄ structure, the excess bismuth was not incorporated into the film. As expected, for optimized growth conditions, higher Bi:V ratios were needed at higher substrate temperatures in order to compensate for the increased bismuth desorption. For the optimum film the vanadium shutter was held open for 10 s at 32 s intervals, while the bismuth and ozone were supplied continuously. These conditions correspond to an average Bi:V atomic ratio of 31.5 (Bi flux × time/V flux × time), and to a growth rate of about 2.5 Å/min. In situ reflection high-energy electron diffraction (RHEED) was limited to the beginning and end of growth because the 10 keV electron beam adversely affected the phase of the film.

In order to encourage epitaxial growth of monoclinic BiVO₄, a substrate was chosen to match both the lattice parameters and the location of ions within the structure (see the supplementary material).23 The in-plane lattice parameters of (001) monoclinic BiVO₄ are a = 5.1956 Å and b = 5.0935 Å with γ = 90.383°,18 whereas cubic YSZ with 9.5 mol. % Y₂O₃ has lattice parameter a = 5.145 Å.24 This substrate provides a lattice match, (a_{film}/a_{YSZ}) of −1.0% along [100]YST and +1.0% along [010]YST to the monoclinic polymorph of BiVO₄ oriented (001)[100]BiVO₄ || (001)[100]YST. At growth temperature, the substrate is well above the 255°C phase transition of monoclinic BiVO₄,14 so if we instead consider the lattice match to the tetragonal polymorph of BiVO₄ with the CaWO₄ structure and in-plane lattice parameter at 293°C, a = 5.147 Å,18 then the lattice match to YSZ at this same temperature (where YSZ has lattice parameter a = 5.160 Å)25 would be +0.3%. It can be seen that the lattice match of (001) BiVO₄ to (001) YSZ is quite good. An additional reason to anticipate epitaxial growth of BiVO₄ on (001) YSZ is the texture observed in polycrystalline BiVO₄ films grown on textured polycrystalline indium tin oxide (ITO) coated glass substrates, where local epitaxy with orientation relationship (001)[100]BiVO₄ || (001)[100]ITO has been inferred.15,16 YSZ has a similar structure to ITO (isostructural if oxygen vacancy ordering is ignored) and has a superior lattice match to BiVO₄ than does ITO.

After growth, to assess the phase purity, epitaxy, and crystalline perfection of the BiVO₄ films, four-circle x-ray diffraction (XRD) was performed on a Rigaku SmartLab x-ray diffractometer using Cu-Kα radiation and a 220 Ge two-bounce incident-beam monochromator. In addition, cross-sectional, high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) images were recorded on a 200kV FEI Tecnai F-20-ST equipped with a monochromator.
Figure 1(a) shows a $\theta-2\theta$ XRD scan of a BiVO$_4$ film grown under optimized conditions. The presence of a peak at $2\theta = 15.16^\circ$ is indicative of the presence of monoclinic BiVO$_4$ in the film as only the 002 peak of monoclinic BiVO$_4$ can occur there; the 002 peak of tetragonal BiVO$_4$ with the CaWO$_4$ structure is forbidden. The $\theta-2\theta$ XRD pattern is consistent with a single-phase monoclinic BiVO$_4$ film oriented with its (001) plane parallel to the (001) plane of the YSZ substrate. Thickness fringes around the 004 peak of monoclinic BiVO$_4$ in the $\theta-2\theta$ XRD scan give an average film thickness of 44 $\pm$ 1 nm. Additional XRD scans were performed to check for the presence of other BiVO$_4$ polymorphs; none were detected.

The crystalline perfection of the monoclinic BiVO$_4$ film was assessed by measuring the full width at half maximum (FWHM) of the rocking curve in $\omega$ and comparing it to the rocking curve of the underlying substrate. Figure 1(b) shows that the FWHM in $\omega$ of the 004 film peak is 58 arc sec (0.016'), while that of the 002 YSZ substrate peak is 40 arc sec (0.011').

To check for epitaxy and establish the epitaxial orientation relationship, a $\phi$-scan of the {301} family of planes of monoclinic BiVO$_4$ was made (Fig. 1(c)). This family of planes was chosen because the peaks are intense and unambiguous. In other words, the 301-type peaks are sufficiently far from other film and substrate peaks in $\chi$ or $2\theta$ to avoid overlap. The $\phi$-scan indicates that the BiVO$_4$ film is epitaxial with orientation relationship (001)$_{\text{BiVO}_4}$ $\parallel$ (001)$_{\text{YSZ}}$ with [100]$_{\text{BiVO}_4}$ $\parallel$ [100]$_{\text{YSZ}}$. If the monoclinic BiVO$_4$ were an untwinned single crystal, only two 301-type peaks would be observed in the $\phi$-scan. The fact that instead four peaks appear in the scan implies that the sample contains 90° in-plane rotational twinning, which is expected considering the 4-fold symmetry of the (001) YSZ substrate.

The epitaxial orientation relationship and the film thickness were corroborated by HAADF STEM imaging. In addition, STEM elucidated the film microstructure. The HAADF STEM images in Fig. 2 reveal the film/substrate interface to be abrupt and the film to be free of amorphous content, with island thicknesses in the range of 40–50 nm. Additional XRD scans were performed to check for the presence of other BiVO$_4$ polymorphs; none were detected.

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FIG. 1. (a) $\theta - 2\theta$ x-ray diffraction scan of BiVO$_4$ grown on a (001) YSZ substrate. The peak labeled with * in (a) corresponds to the 002 YSZ substrate peak. (b) Rocking curve ($\omega$ scan) of the 004 BiVO$_4$ film peak overlaid on the 002 YSZ substrate peak. The FWHM of the BiVO$_4$ peak is 0.016$^\circ$ and that of the substrate is 0.011$^\circ$. (c) $\phi$-scan of the 301 BiVO$_4$ reflection at $2\theta = 54.36^\circ$ and $\chi = 8.42^\circ$. $\chi = 90^\circ$ is defined as perpendicular to the plane of the substrate. $\phi = 0^\circ$ is aligned to be parallel to the 202 in-plane direction of YSZ. These scans show that the film is the monoclinic polymorph of BiVO$_4$ and is epitaxially oriented to the YSZ substrate with 90$^\circ$ in-plane twinning.
FIG. 2. Cross-sectional HAADF-STEM images of the same monoclinic BiVO₄ film analyzed in Fig. 1. The bright positions in the BiVO₄ layer correspond to the projected positions of the Bi ions, and the bright positions in the YSZ layer are the Y/Zr ions. The model of the expected epitaxial alignment between (001) BiVO₄ and (001) YSZ is shown in (c), which corresponds to the region enclosed within the yellow-rectangle in (b). (d) Low magnification image showing the islanded film.

FIG. 3. Raman spectra of the same BiVO₄ film analyzed in Fig. 1 at 10 K and 300 K. Notations (yy) and (xy) indicate parallel and perpendicular polarizations of incident and scattered light, respectively. The peak labeled YSZ can be attributed to Raman scattering from the YSZ substrate.
V5+ charge state throughout the film (see the supplementary material). Room temperature ellipsometric spectra (in $\Delta, \psi$) were collected after growth using a variable-angle rotating-compensator multichannel spectroscopic ellipsometer. Multiple sample orientations were studied at angles of incidence of $\psi = 60^\circ$ and $70^\circ$ over a spectral range from 0.75 to 6.0 eV. The complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) and microstructural parameters (film thickness, $d_b$, and surface roughness thickness, $d_s$) were extracted using a least squares regression analysis and an unweighted error function, to fit the experimental ellipsometric spectra to an optical model. The system was modeled as semi-infinite YSZ substrate / BiVO$_4$ film/surface roughness/air ambient, where free parameters correspond to the BiVO$_4$ film and surface roughness and a parameterization of $\varepsilon$ for BiVO$_4$. The optical properties of the BiVO$_4$ film and surface roughness layers are represented using the Bruggeman effective medium approximation with fixed fractions of "dense" BiVO$_4$ material ($f_{\text{BiVO}_4}$) and void in order to account for fractional coverage. $f_{\text{BiVO}_4}$ was fixed at 0.65, 0.70, and 0.75 to evaluate the impact of the $\pm 5\%$ uncertainty in the 70% surface coverage. The void fraction in the surface roughness was fixed at 0.675, 0.65, and 0.625, respectively, so that the properties of this layer represented equal contributions from void and the film itself containing some fraction of voids.

The optical model assumed average fractional coverage, which is valid when the spacing between transition-metal cation sites is small compared to the wavelength of the probing light. Larger features can result in scattering, which may lead to the artificially high values of absorption below the band gap that were observed. To determine the band gap independently of the morphology, an electron energy loss spectrum (EELS) of the same BiVO$_4$ film was recorded from a spot with $\pm 0.05$ eV ($\alpha_f = \alpha_{0.05}$), $\pm 0.1$ nm) and surface layer thickness ($0.3 \pm 0.1$ nm) for each fixed $f_{\text{BiVO}_4}$ in the film layer were obtained using this approach; the results were found to correlate with XRD and STEM observations. Then, the thicknesses were fixed and $\varepsilon$ was extracted by numerical inversion over the full spectral range. The results for $f_{\text{BiVO}_4} = 0.70$ are shown in Fig. 4(a). $\varepsilon$ obtained assuming $f_{\text{BiVO}_4} = 0.65$ and 0.75 yielded similar line shapes, but approximately 10% higher or lower amplitudes, respectively. It should be noted that although BiVO$_4$ is anisotropic, an isotropic approximation for $\varepsilon$ was used to maintain the highest signal-to-noise ratio in the extracted values. Parameterization of $\varepsilon_2$ shows the lowest energy critical point at 2.74 $\pm$ 0.01 eV with an additional point slightly higher at 2.93 $\pm$ 0.02 eV. Theoretical calculations suggest that these features may be attributed to transitions between the V 3$d$ and O 2$p$ electrons.

After $\varepsilon$ was obtained, the absorption coefficient, $\alpha$, was determined for each assumed $f_{\text{BiVO}_4}$ with results for $f_{\text{BiVO}_4} = 0.70$ shown in Fig. 4(b). $\alpha^{1/2}$ and $\sigma^2$ were plotted as functions of photon energy and extrapolated using a linear relationship to $\alpha^{1/2} \sigma^2 = 0$ in order to identify the indirect (direct) band gap. The direct gap is determined from a single slope of $\alpha^2 = 0$, as shown in the inset of Fig. 4(b). Linearity in the spectral region near $\alpha \sim 10^4 - 10^5$ cm$^{-1}$ yields direct band gap values of 2.52 $\pm$ 0.05 eV ($f_{\text{BiVO}_4} = 0.65$), 2.54 $\pm$ 0.05 eV ($f_{\text{BiVO}_4} = 0.70$), and 2.56 $\pm$ 0.05 eV ($f_{\text{BiVO}_4} = 0.75$). The lowest energy critical point at 2.74 eV may be considered the upper limit for band gap extrapolation. The significant absorption observed below the band gap obtained from spectroscopic ellipsometry measurements may be attributed to transitions between the V 3$d$ and O 2$p$ electrons.

The optical model assumed average fractional coverage, which is valid when the spacing between BiVO$_4$ regions is small compared to the wavelength of the probing light. Larger features can result in scattering, which may lead to the artificially high values of absorption below the band gap that were observed. To determine the band gap independently of the morphology, an electron energy loss spectrum (EELS) of the same BiVO$_4$ film was recorded from a spot with $\pm 4$ nm diameter in the interior of the monoclinic BiVO$_4$ layer, as indicated in the cross-sectional STEM image (inset of Fig. 4(c)). EELS measures $\text{Im} \left( -1/\varepsilon \right) = \varepsilon_2 / (\varepsilon_1^2 + \varepsilon_2^2)$, and the resulting spectrum is shown in
FIG. 4. (a) Complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) and (b) absorption coefficient of the same monoclinic BiVO$_4$ film studied in Fig. 1 extracted assuming a film coverage of 70% (i.e., 70% BiVO$_4$, 30% void). The inset to (b) shows the direct band gap, $E_g$, obtained by linearizing $\alpha^2 = 0$ eV. (c) Spatially resolved monochromated EELS from the interior of the same BiVO$_4$ film, viewed in cross-section (inset). The background was corrected with a power-law fit from 1.5 to 2 eV, with the flat region in the band gap from 2 to 2.4 eV showing the precision of the fit. The energy resolution, as determined from the FWHM of the zero loss peak, was 0.14 eV.

Fig. 4(c). After fitting a power law background to the tails of the unscattered beam, the band gap could be resolved and estimated using linear extrapolation. Depending on the extrapolation, the gap would be $2.43 \pm 0.05$ eV for the small knee or $2.56 \pm 0.015$ eV for the main peak. The absorption giving rise to the lower band gap ($2.43$ eV) could arise from a small concentration of point defects such as oxygen vacancies in the BiVO$_4$ film or it could be due to surface damage that occurs during STEM sample preparation.

In summary, epitaxial thin films of monoclinic BiVO$_4$ have been grown on cubic (001) YSZ substrates using adsorption-controlled MBE. XRD, STEM, and Raman spectroscopy confirm that the sample is epitaxial, phase-pure monoclinic BiVO$_4$. Global and localized spectroscopic probes indicate that the epitaxial monoclinic BiVO$_4$ film has a direct band gap of $2.5 \pm 0.1$ eV.

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23. See supplementary material at http://dx.doi.org/10.1063/1.4824041 for depictions of the crystal structure of the film and substrate, air SEM analysis from which fractional coverage was estimated, and x-ray spectroscopy results confirming bonding states of film atoms.
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