Crystallization and phase separation of tungsten oxide-bismuth vanadate amorphous film by annealing in air

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Abstract. A WO₃-BiVO₄ amorphous film grown on the (001) yttria-stabilized zirconia (YSZ) substrate was annealed at 600 °C in air. The microstructures evolution was investigated by X-ray diffraction, scanning electron microscopy and high-resolution transmission electron microscopy. After annealed, the amorphous composite film crystalized into monoclinic BiVO₄ and orthorhombic WO₃. BiVO₄ epitaxially grew on the YSZ, forming the matrix, where part of small irregular WO₃ grains were embedded in. Other large-sized sub-stoichiometric WO₃-δ (0<δ<3) grains with stacking faults lay on the film surface, which may contribute to the compressed strain of BiVO₄ matrix vertically. Compared to the typical vertical heteroepitaxial nanocomposite of WO₃-BiVO₄ film grown at 600 °C by pulsed laser deposition, in the annealed composite film, the vertical lattice mismatched strain at WO₃/BiVO₄ interface decreased and lead to the disappearance of metastable hexagonal WO₃.

1. Introduction
Vertical heteroepitaxial nanocomposite (VHN) thin films have recently stimulated significant research interest for creating promising oxide thin films with optimized and tunable properties [1, 2]. In VHN films, the net strain state has been mainly dominated by the vertical strain rather than the lateral one induced by the substrate, especially in thick films [3,4]. The key of achieving tunable vertical strain and multifunctionalities, is comprehensive understanding of growth mechanisms to realize controlled growth of VHN structure [3]. Up to now, people are still trying various ways to understand the growth of VHN, including synchrotron radiation and transmission electron microscope (TEM), to achieve the desired nanostructures and functionalities [2, 5, 6].

The WO₃-BiVO₄ (WO-BVO) VHN film grown shows enhanced photoactivity than that of each component phase [7]. In our previous research [8], the amorphous film has been found in the sample
grown at 400 °C resulted by the low driving forces for nucleation and diffusion. When the substrate temperature is higher than 500 °C, the composite film was crystallized and a typical VHN with WO nanopillars embedded in the BVO matrix formed. In continues to our previous works on the microstructure evolution of WO-BVO VHN film, we aim to study the impact of thermal annealing on the structural properties of WO-BVO amorphous composite film. In this work, by annealing the WO-BVO amorphous film at 600 °C in air, the crystallization and phase separation were studied systematically by a combining of X-ray diffraction (XRD) pattern, TEM and X-ray energy dispersive spectrometer (EDS).

2. Experiments

2.1. Annealing of the amorphous WO$_3$-BiVO$_4$ film

The growth process of WO-BVO films with different substrate temperatures by pulsed laser deposition (PLD) was reported before [8]. The amorphous WO-BVO film grown at 400 °C was annealed using a muffle programmable furnace (LHT02/16, Nabertherm, Germany) in air. The sample was heated at 5 °C/min to the annealing temperature of 600 °C, holding for 1 h, then cooled to room temperature at 10 °C/min in the furnace. The film grown at 400 °C, 600 °C, and the annealed film were abbreviated as 400WB, 600WB, and annealed WB, respectively.

2.2. Microstructure characterizations

XRD (D8 Discover, Bruker, Germany) was performed on the films, to examine the crystal structure and phase composition. mechanical grinding, polishing, precision dimpling, and ion milling ect., which is the standard procedure of TEM specimens, was performed to prepare cross-section TEM specimens. Transmission electron microscope (JEM-2100F, JEOL, Co., Japan), and energy-dispersive X-ray (MAX-80T, Oxford Instruments, Inc, the United Kingdom) were applied to analyze the microstructure and chemical composition.

3. Results and discussion

In Figure 1(a), the XRD results of WO-BVO composite films prepared at 400 °C and 600 °C were displayed for comparison [8]. It can be clearly seen that after annealed at 600 °C in air, the amorphous WO-BVO film crystallized into monoclinic BVO and orthorhombic WO (o-WO). BVO epitaxially grew along the (001) YSZ substrate, while the o-WO shows polycrystalline growth. Compared to the XRD pattern of WO-BVO film grown at 600 °C, there is no diffraction peak of hexagonal WO (h-WO) in the annealed WB film. To achieving more information, the 2θ form 22° to 32° was enlarged in Figure 1(b). The BVO (004) peak of annealed WB sample is at the right of 600WB sample, and the plane distances were 2.915 Å and 2.925 Å (the bulk value is 2.926 Å), respectively. It shows that the BVO in the annealed sample was subjected to a compressed strain along the vertical direction, whereas the BVO in the 600WB sample was in a relaxed state.

Figure 1(c) shows the low magnification TEM image of the annealed WB sample. After annealed at 600 °C in air, the internal structure of WO-BVO composite film is not very continuous and there are some voids without film compositions, highlighted by green dotted lines. Moreover, the distribution of the two phases is completely different from that of 600WB sample [8]. Part of irregularly-shaped WO nanocrystals were wrapped in the BVO matrix, and other large-sized WO grains directly grew on the film surface. The selected area electron diffraction (SAED) pattern in Figure 2(d) shows that BVO grows epitaxially along the substrate with (001) BVO// (001) YSZ and [100] BVO// [100] YSZ; while WO grains exhibit polycrystalline features.
Figure 1. (a) θ-2θ XRD results of 400WB, 600WB and annealed WB samples. (b) XRD spectra of BVO (004) and YSZ (002) peaks from 22° to 32°. (c) The cross-section TEM morphology of annealed WO-BVO sample. (d) The corresponding SAED pattern of the composite film in Figure 1(c).

As shown in Figure 2(a), inside the film, the WO grains randomly grown in the BVO matrix with an average size of 25.6 nm. Figure 2(b) illustrates the interface structure between BVO matrix and YSZ substrate. There is still an amorphous layer with thickness of ~2.9 nm at the film interface. Figure 2(c) shows the stacking faults inside the large-sized WO grains grown on the film surface, which are also revealed by the yellow arrow marked streaking in the SAED pattern, implying that the large-sized WO grains composition is sub-stoichiometric WO$_{3-\delta}$ (0<\delta<3)[9]. Figure 2(d) depicts the HRTEM image of the red box marked area in Figure 2(c). Above the stacking faults, there is normal WO structure along the [011] zone axis with the inset Fast Fourier transformed (FFT) pattern calibrated. In the lower FFT pattern of abnormal WO structure, some extinction lattice planes reappeared due to the misalignment of lattice planes, as the yellow circle marked diffraction spots shown.
Figure 2. (a) The HRTEM image of the composite film showing WO grains distributed in the BVO matrix. (b) The HRTEM result of the BVO/YSZ interface. (c) The medium magnification TEM image of the WO on the film surface, the inset image is the corresponding SAED pattern. (d) The HRTEM image of the red box marked area in (c), the inset images are the FFT patterns of the areas above and below the stacking faults, respectively.

In Figure 3(a), as the distributions of Bi/V/W elements shown, the composite film grown at 600 °C is a typical VHN nanostructure, in which WO nanopillars inserted in BVO. Nevertheless in the annealed WB sample (Figure 3b), the film is not compact with some voids, the distribution of Bi/V/W elements indicated that some WO grains filled in the BVO matrix and other large-sized WO grains lay on the film surface.

When the WO-BVO amorphous film is annealed at 600 °C in air, the lattice mismatch between BVO and the YSZ substrate is smaller than WO/YSZ [8], BVO preferentially crystallized and grew along the surface of the substrate. Some WO crystal grains were embedded in the BVO matrix and restricted by the surrounding BVO, making it difficult to grow into large size. Other WO grains on the film surface, which were in direct contact with air and less restricted, can grow rapidly under the drive of thermal energy. Distinguished from the WO-BVO film grown at 600 °C by PLD with sufficient oxygen pressure, the composite film annealed in air without enough oxygen can easily form defects, such as the stacking faults in WO, which has been reported elsewhere [10]. In comparison with the WO-BVO film grown at 600°C, there is no h-WO phase in the annealed WB sample. As discussed in our previous papers [8], the driving force of the semi-stable hexagonal WO phase was tensile strain derived from the thermal expansion coefficient mismatch and the crystal lattice mismatch along the WO/BVO epitaxy vertical interface. The growth mode of WO-BVO film annealed at 600°C in air was changed drastically, the irregular WO grains in the BVO matrix decreased the vertical lattice-mismatched strain, thus the
metastable h-WO may not be stabilized, similar to the 700WB sample [8]. The density of o-WO (7.149 g/cm³) is higher than that of BVO (6.25 g/cm³), hence in the annealed WB film, the large WO grains with the lateral size of ~500nm on the film surface may contribute to the compressed strain state of BVO matrix vertically.

**Figure 3.** (a) The EDS mapping of (a) 600WB sample; (b) annealed WB sample.

### 4. Conclusions
The microstructure evolution of amorphous WO-BVO film by annealing at 600°C in air was investigated by XRD, SEM, HRTEM and EDS. Distinguished from the typical VHN composite film grown at 600°C by PLD, after annealed, BVO grew epitaxially along the surface of YSZ substrate, WO formed both irregular polycrystal grains wrapped in BVO matrix and large-sized grains lying on the film surface. The metastable h-WO did not form mainly due to the decreased lattice mismatched strain effect at WO/BVO interface. The large-sized WO grains on the film surface may result in the out of plane compressed state of BVO matrix. In the future, in-situ heating TEM technology will be applied to explore the process of crystallization and phase separation deeply and clearly.

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