In-Situ TEM assessment of phase transformation in VO2-based thin films with Ho addition

Ellen Suhr[1], Dr. Aleksander Kostka[2], Prof. Dr.-Ing. Alfred Ludwig[1]

[1]Institute for Materials, Ruhr University Bochum (RUB), , Bochum, Germany, [2]ZGH, Ruhr University Bochum (RUB), , Bochum, Germany

Background incl. aims
We present the fabrication and characterization of VO2-based thin films with Ho addition. The thin films were prepared as so-called materials libraries by reactive co-sputtering from two targets (V, Ho) to achieve a composition gradient. The effect of Ho on the phase transformation and its functional properties, like the thermochromic effect, has not been studied yet, and the materials libraries enable a screening of a large composition spread in relatively short time. The materials libraries were characterized in a high-throughput approach regarding their chemical composition, crystallinity, and electrical resistance at different temperatures to study the phase transformation. TEM investigations were carried out on two types of samples, both selected from specific composition region of the materials library: (i) focused ion beam (FIB) prepared TEM lamella, for analysis of the present Ho-rich precipitates, and (ii) sputtered on SiN Wildfire (DENSsolution) chips for in-situ TEM heating experiments to assess the phase transformation – to avoid Ga-ion contamination and its effects on the phase transformation.[1]

Methods
The thin films were prepared by reactive co-sputtering on 4-inch Si wafer and the Wildfire chips from two targets: V and Ho2O3. The positioning of the targets results in two gradients across the thin film library (see Figure 1) the composition gradient along the diagonal from lower right to upper left with decreasing Ho-content, and a thickness gradient along the other diagonal. The substrates were heated to 500 °C and the oxygen flow was controlled using plasma emission monitoring.[2] The thin film thickness was controlled by the deposition time: 30 min (approx. 150 to 350 nm) for the materials library on Si (SEM, EDS, XRD, resistance measurements) and 5 min for the depositions on the Wildfire chips (approx. 40 nm).

Results
The materials library was first characterized regarding its chemical composition (EDS), crystallinity (XRD, Figure 2) and electrical resistance (in the range of 20 to 120 °C, Figure 4) getting the first overview of the thin films properties using high-throughput automated measurements.[3]

The preliminary investigations of the library suggested a single-phase solid solution with a monoclinic VO2 phase. The temperature-dependent resistance measurements reveal a slight shift of the transformation temperature towards lower temperatures with increasing Ho content (Figure 4).

TEM analysis of the selected composition region revealed the presence of small Ho-rich precipitates and larger VO2 crystals. The in-situ heating experiments showed that the phase transformation starts at 54 °C and it is completed at about 60 °C. The transformation is well visible in the electron diffraction but does not result in microstructural changes; grain size and morphology remain unchanged.

Future work shall focus on the investigation of the thin films functional properties and their possible applications in nanoactuators or in thermochromic coatings for windows.

Graphic:

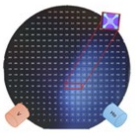

Figure 1: Deposition set-up showing the target positions during fabrication of the materials library. The tiny numbers are showing the measurement areas for the high throughput measurements (EDS, XRD, electrical resistance measurements). Marked in red are the areas, where the Wildfire chips were placed for deposition.

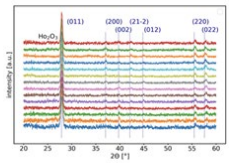

Figure 2: XRD results along the diagonal from the Ho-rich side to the other side of the library. All peaks could be indicated using only a VO_2 powder pattern as reference.

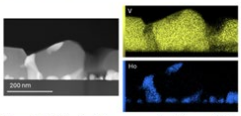

Figure 3: TEM analysis from a more Ho-rich area. ADF STEM image above and V- and Ho-maps below. TEM images resolved that Ho-rich precipitates are formed. The latter is pure monoclinic VO_2.

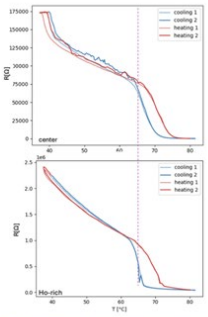

Figure 4: Temperature dependent electrical resistance measurements on different locations of the library. It is evident that VO_2 transforms, and the transformation temperature decreases with increasing Ho-content.

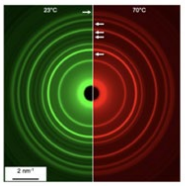

Figure 5: Results of In-situ heating TEM experiments. The TEM image on the left shows no change morphology, only a slight shift in contrast, which is related to thermal drift and focus change. On the right side the electron diffraction as rotational averaged pattern. Changes are marked with arrows.

Keywords:

In-situ TEM, vanadium-dioxide, high-throughput characterisation

Reference:

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