

Electrochemical and structural characterization of BITAVOX.20 thin films.

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Introduction

The BIMEVOX.100x are a family of solid electrolytes of general formula $\text{Bi}_2\text{Me}_x\text{V}_{1-x}\text{O}_{5.5-\delta}$ the ionic conductivity of which is the highest known among the O^{2-} solid state conductors at intermediate temperatures (400 – 600°C) [1]. They derive from the $\text{Bi}_4\text{V}_2\text{O}_{11}$ parent compound [2], which high temperature polymorph γ has been stabilized by partially substituting vanadium by either aliovalent ions (Cu^{II} , $\text{CO}^{\text{II}}\dots$) or isovalent ions (Ta^{V} , Nb^{V} , etc...) [3, 4]. The first ones permit to reach the highest conductivity levels, with about $10^{-1} \text{ S.cm}^{-1}$ at 600°C However, they are likely to transform into a less conductive α -related phase after several hundred hours long thermal treatment at 450°C. [5] The second ones exhibit slightly lower conduction performances, but are more thermally stable. [4] Moreover, all these materials are quite reducible and must therefore be used for oxygen-rich atmosphere applications only. [6]

Experimental details

BITAVOX coatings were deposited using an Alcatel SCM 450 reactor, consisting in a 40 liters chamber pumped down with a turbomolecular pump system allowing a base vacuum of less than 10^{-4} Pa before refilling with argon and oxygen at the desired pressure around 0.5 Pa. The metallic targets ($\varnothing = 145$ mm, thickness = 3 mm) are powered by a Pinnacle+ generator produced by Advanced Energy for the vanadium and tantalum targets and by a MDX500 generator produced by Advanced Energy for the bismuth target. The argon and oxygen flow rates are controlled with Brooks flowmeters and the total pressure is measured using a MKS Baratron gauge. The coatings are sputter deposited on dense alumina pellets (Keral99, thickness = 0.63 mm, $\varnothing = 16$ mm) produced by Keramol Gmbh and on glass slides.

Coating thickness was determined by the step method with an Altysurf profilometer produced by Altimet society equipped with tungsten micro force probe inductive allowing an accuracy of about 20 nm. Before each measurement, the calibration of the experimental device was realised with a reference sample number 787569 accredited by CETIM organisation. The structural features of the coatings were performed in Bragg Brentano configuration X-ray diffraction using a BRUKER D8 focus diffractometer ($\text{CoK}_{\alpha 1+\alpha 2}$ radiations) equipped with the LynxEye linear detector. Diffractograms were collected under

air flow during 10 min in the [20°-80°] scattering angle range by steps of 0.019°. Thermodiffractograms were recorded on a $\theta/2\theta$ Bragg-Brentano D8 Bruker AXS diffractometer (CuK α_{1+2} radiations) equipped with the vante detector and a HTK 1200 Anton Paar chamber. Diffractograms were collected under air flow (5L/h) during 16 min in the [10°-80°] scattering angle range, with a 0.0148° step from 25°C to 750°C (heating rate 0.1°C/s). The morphology of the coatings was observed on brittle fracture cross sections and on their top surface via a Jeol JSM 5800LV scanning electron microscope (SEM). The chemical compositions were achieved by energy dispersive X-ray spectroscopy (EDS) from coatings deposited on glass slides under 15 kV high voltage.

Results

The sputtering parameters for the deposition of the Bi₄V₂O₁₁ parent compound have first been searched. The argon and oxygen flow rates used were 40 sccm and 10 sccm, respectively, so that the targets are sputtered in the compound mode. In order to avoid melting and evaporation, the intensity dissipated on the bismuth target was fixed at 0.1 A and that of vanadium target (I_V) was varied. Bi₄V₂O₁₁ was obtained for $I_V = 1.1$ A. BITAVOX.20 was then deposited by decreasing I_V and sputtering simultaneously tantalum. A convenient Bi/Ta atomic ratio of 10.6 was obtained for $I_{Ta} = 0.2$ A, and the vanadium content of the films was investigated in the $0.75 \text{ A} \leq I_V \leq 0.9 \text{ A}$ domain. Chemical composition analysis shows a linear variation of the elemental rates with I_V . (Fig.1) The expected composition is not exactly reached in the investigated domain. Yet, an approximate value of 0.7 A can be deduced from linear regression to get the right composition. After a two hours annealing at 600°C, these results are also confirmed by X-ray diffraction: the intensity of the parasitic BiVO₄ phase reflections decrease with decreasing I_V and are clearly visible for 0.8 A and 0.75 A. Moreover, the as-annealed coatings are dense according to cross section observations.

Crystallization of the film deposited under $I_V = 0.8$ A has also been assessed by X-ray diffraction in temperature. As-deposited films are amorphous and their crystallizations begins at 400°C. The corresponding phase can be seen as a fluorine structure with a tetragonal distortion and cationic disorder. At 425°C, these ions start ordering, and BITAVOX reflections are observed.

However, the deposition rate in these sputtering conditions is limited to about 300 nm.h⁻¹. Thus, the sputtering chamber was equipped with a quartz microbalance in order to check bismuth deposition rate. By paying attention to its cooling, I_{Bi} could be increased up to 0.3 A while avoiding evaporation (Fig. 2). After adjusting the sputtering parameters of vanadium and tantalum, the deposition rate reached about 1.25 $\mu\text{m.h}^{-1}$.

Since conductivity of BIMEVOX compound is affected by the substitution rate for vanadium by another metal, different compositions were deposited in the BITAVOX.05 – BITAVOX.30 domain. Only X-ray diffraction has been performed at this time, showing that only BITAVOX and a small amount of parasitic BiVO₄ phase are present in the films for all

these composition but BITAVOX.05. In this case, another parasitic phase, Bi₂VO₅, also appears.

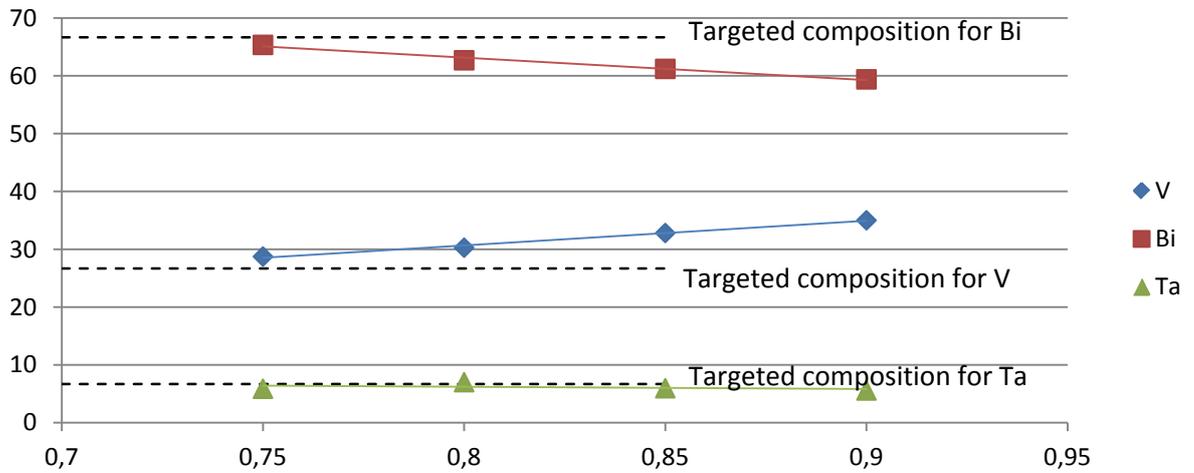


Figure 1: Evolution of the elemental ratios with I_v .

Finally, the influence of pressure was also investigated. The sputtering parameters used for these experiments are summarized in table 1. As-deposited films sputtered between 0.44 Pa and 2.0 Pa both have the same dense aspect. However, this is no longer true after a two hours annealing at 700°C. Indeed, the coating deposited at 0.44 Pa is porous whereas this deposited under 2.0 Pa seems to remain dense and exhibits grains of several hundred nanometers in diameter. The apparition of porosity is not clearly explained at the moment. The grains observed in the second film are due to a large amount of BiVO₄ in it. This might be due to the erosion of the bismuth target.

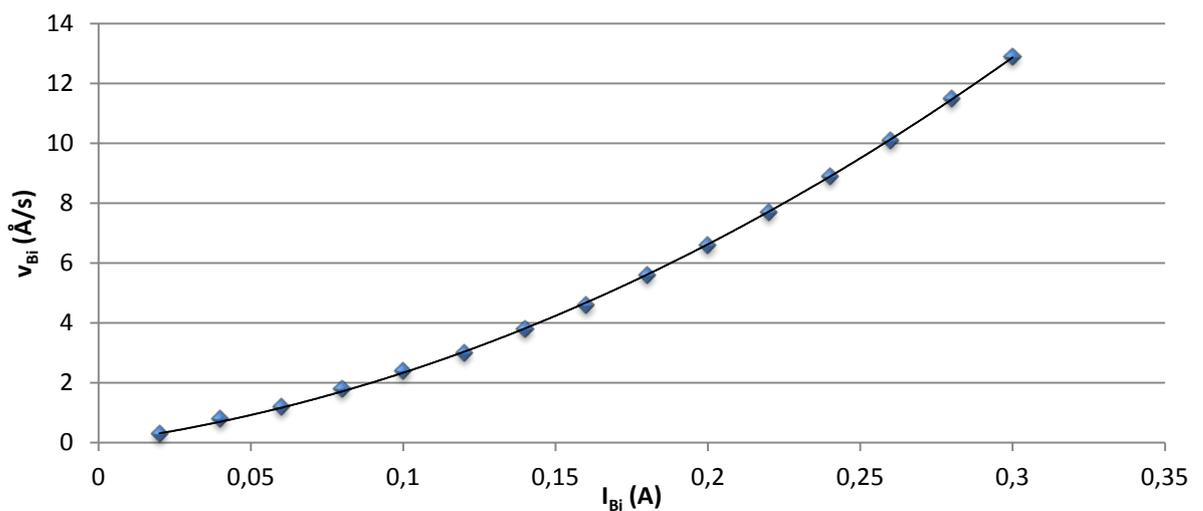


Figure 2: Bismuth deposition rate measured by the quartz microbalance as a function of the intensity dissipated on the bismuth target.

Table 1: sputtering parameters of BITAVOX films deposited under different pressures.

I_{Bi} (A)	I_{Ta} (A)	I_{V} (A)	D_{O_2} (sccm)	D_{Ar} (sccm)	P_{tot} (Pa)
0.3	0.57	2.15	40	15	0.44
			90	35	1.17
			120	50	2.0

Conclusion

BITAVOX.20 coatings have been synthesized by reactive magnetron co-sputtering. As-deposited films are amorphous and crystallize in the BIMEVOX structure via an intermediate disordered and tetragonally-distorted structure. Melting and evaporation of the bismuth target could be avoided by optimizing its cooling and controlling the deposition rate thanks to a quartz microbalance, which permitted to increase the deposition rate from 0.3 to 1.2 $\mu\text{m/h}$. Annealing films at 600°C leads to dense coatings whereas they were porous after a 700°C annealing. The consequences of varying the Ta/V ratio still have to be investigated from an electrochemical point of view, despite it has already been shown that a too small amount of tantalum leads to the apparition of a Bi_2VO_5 parasitic phase. Finally, the effect of pressure on the microstructure of as-deposited films seems to be negligible. Its consequences after annealing would require further investigation, especially to avoid the effect of target erosion.

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