Characterization of Mn-Sb-O thin films for water splitting catalysts in acid

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Introduction

Splitting water into hydrogen and oxygen by electrolysis is a promising technique to produce sustainable and green fuels for transport applications or large-scale energy storage. Using acidic solutions offers many advantages for developing powerful and efficient electrolyzers. However, catalysts which present non-corrosive properties in acid are made up of precious metals, which limits its large-scale application. Therefore, developing an efficient water splitting catalyst composed of earth-abundant elements would represent an immense advance in the field. Recently, the $MnSb_2O_6$ rutile phase in Mn-Sb-O systems has shown impressive catalytic performance in acid.[1,2]

Objective

Characterizing Mn-Sb-O catalysts is crucial to optimize the catalytic properties of this system. In this study, an emphasis is focused on:

- Understanding rutile phase formation mechanism, which is still unclear
- Analyzing phase transitions in Mn-Sb-O systems and identifying secondary phases formation, which worsen the catalytic performance.

Methodology

Mn-Sb-O catalysts are characterized from two different precursor thin films, both deposited by co-sputtering on a Si substrate:

- A $Mn_xSb_{1-x}O_z$ ($0.19 \leq x \leq 0.9$) oxide precursor thin film, co-sputtered in an Ar/O_2 (4:1) background atmosphere.
- A Mn_xSb_{1-x} ($0.18 \leq x \leq 0.92$) metal precursor thin film, co-sputtered in pure Ar background atmosphere.

With a background atmosphere pressure of 6 mTorr, the average grain size at the surface of both films is 40 nm.

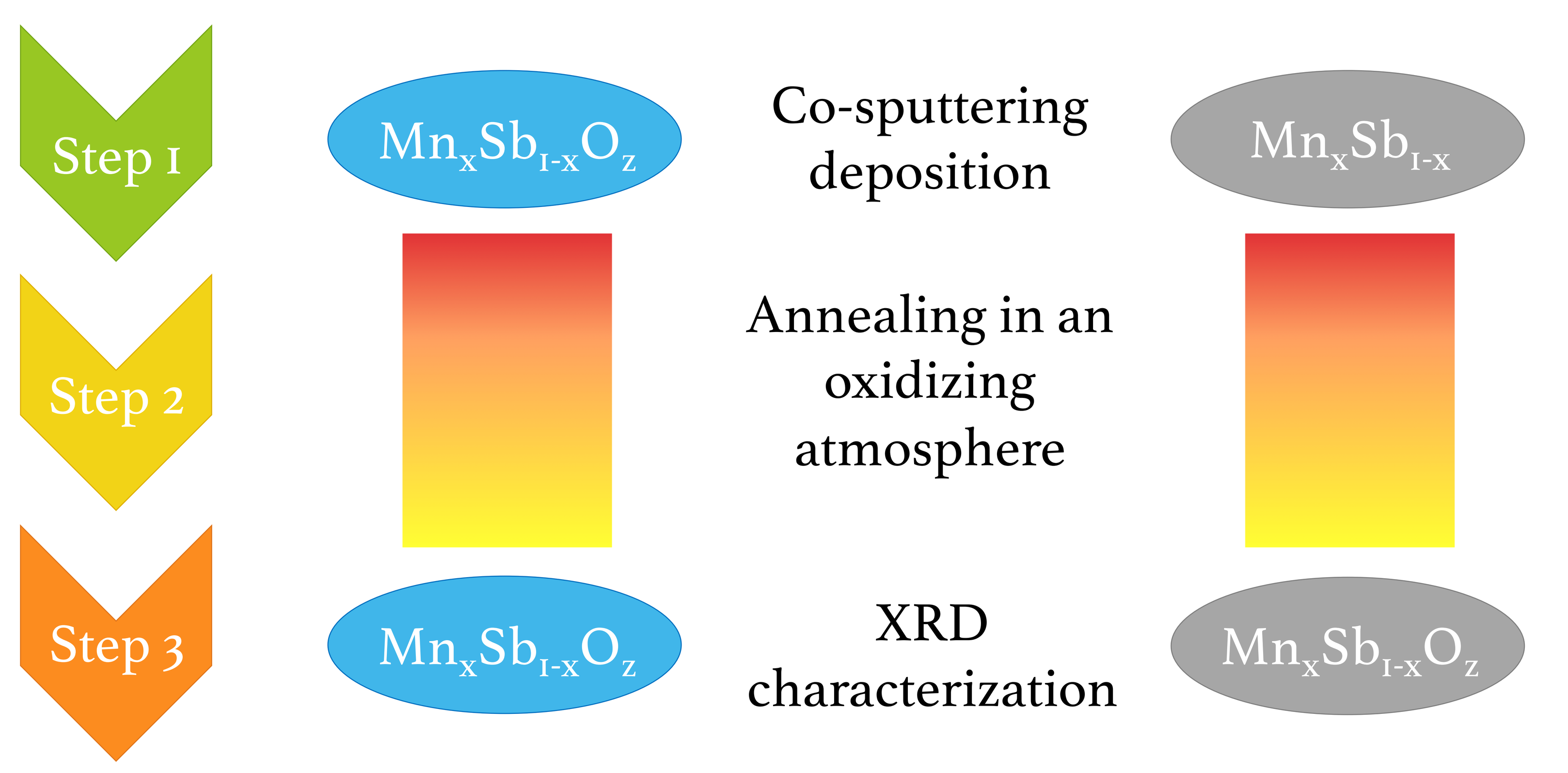

Figure 1: Methodology used to analyze phase transitions in Mn-Sb-O catalysts.

Bibliography

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[3] J. Grins et al, *Rutile-Type $Mn_{1-x}Sb_{1+x}O_4$ phases, $0 \leq x \leq 1/3$, Synthesized by the Sol-Gel Technique*. In: *Acta Chen. Sc.*, 47 (1993), pp 1053-1056.

Results

Phase transitions in the $Mn_xSb_{1-x}O_z$ precursor thin film:

- $MnSb_2O_6$ rutile is the first phase to crystallize from the amorphous film for a wide composition range ($0.11 \leq x \leq 0.82$).
- The crystallization temperature onset decreases with increasing Mn content.
- A $MnSb_2O_6$ rutile – hexagonal phase transition occurs at 900°C.

Phase transitions in the Mn_xSb_{1-x} precursor thin film:

- No $MnSb_2O_6$ rutile phase formation at any temperature.
- $MnSb_2O_6$ hexagonal formed from 800°C.
- Various Mn- and Sb- oxides formed.

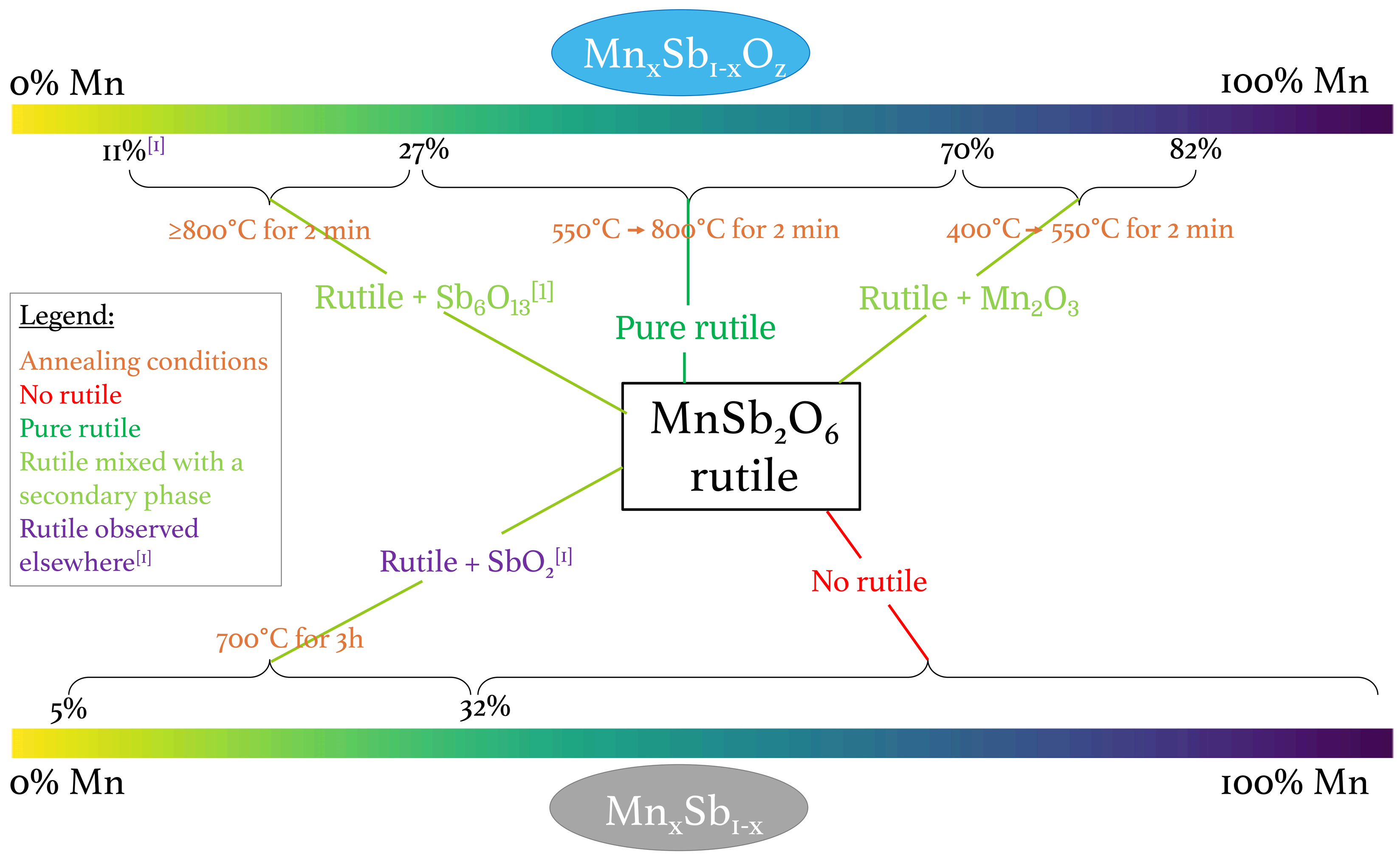

Figure 2: Conditions to synthesize $MnSb_2O_6$ rutile phase from sputtered $Mn_xSb_{1-x}O_z$ and Mn_xSb_{1-x} precursor thin films.

Discussion

Rutile phase formation in $Mn_xSb_{1-x}O_z$ precursor films:

- $MnSb_2O_6$ rutile is metastable and has a lower surface energy than its hexagonal polymorph. With grains as small as 40 nm at the surface, the surface energy overweighs the bulk energy. Therefore, the rutile phase is first crystallized.
- $MnSb_2O_6$ hexagonal is the most stable $MnSb_2O_6$ polymorph and is formed at high temperature (above 900°C).

No rutile observed from Mn_xSb_{1-x} precursor films in this study:

- The deposition parameters have an influence on the rutile phase formation.

Conclusion

Pure $MnSb_2O_6$ rutile phase is formed from $Mn_xSb_{1-x}O_z$ ($0.27 \leq x \leq 0.7$) precursor thin film deposited by co-sputtering when annealed under specific conditions. However, the rutile phase formation depends highly on the deposition parameters and the deposition technique.[3] Therefore, characterizing Mn-Sb-O catalysts under other deposition methods than sputtering is required to enable a large-scale water splitting usage.

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