

**ELECTROCHEMICAL QUARTZ CRYSTAL
MICROGRAVIMETRY ANALYSIS OF THE
ELECTRODEPOSITION AND STRIPPING OF
Bi₂Te₃ FILMS**

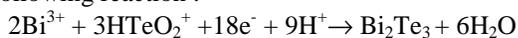
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Due to their high figure of merit at room temperature, bismuth telluride semiconductors are commonly used as thermoelectric materials, in particular for thermoelectric refrigeration. At present, industrial purposes are to reduce the size of the cooling generators. In this context of miniaturization, the alternative solution to produce thin films by electrodeposition appears to be competitive in comparison with classical growth techniques as molten, hot-press, press-sintering, evaporation and sputtering. Indeed, an electrochemical deposition process may provide a large area, high thickness at lower cost and with higher growth rates.

The electrodeposition growth has been successfully applied to produce bismuth telluride binaries [1-4]. Our laboratory actually works on the global process of micro-Peltier devices using electrochemical technique [5]. We have already showed the feasibility to realise homogeneous thermoelectric films at a wafer level [6]. This step is necessary to ensure a direct industrialization of micro-Peltier devices. The overall aim of this work is to study by Electrochemical Quartz Crystal Microbalance (EQCM) the performance of the electrochemical growth process of Bi₂Te₃ films.

At first, electrodeposition and stripping of bismuth telluride have been studied by means of simultaneous voltammetric and electrogravimetric experiments. The experiments were performed in 1M HNO₃ solution containing Bi^{III} and Te^{IV} cations. The voltammetric curve exhibits one cathodic peak and one anodic peak, which correspond to one deposition/stripping process [fig. 1]. So those investigations suggest that a deposition is able to induce a single phase binary alloy electroformation according to the following reaction :



Growth experiments at potentiostatic mode have been monitored by EQCM. They exhibit constant and high linear growth rates (about 10µm/h) with good faradic efficiencies.

As a Peltier device is constituted of successive *n-p* junctions, we have investigated several experimental growth conditions, leading to different stoichiometry of Bi₂Te₃ [7]. Indeed a default or an excess of bismuth corresponds theoretically respectively to *n* or *p*-type semiconductor for this material. We have analysed the film composition by combining coulometric and electrogravimetric data. This original procedure was verified by *ex situ* measurement using an Electron Probe Microanalysis. The results confirm that the stoichiometry of Bi₂Te₃ can be finely modulated according to the growth potential applied to the working electrode.

Moreover a study of the anodic dissolution of Bi₂Te₃ film was realised. Stripping experiments monitored by EQCM were carried out in the same growth electrolytes. The dissolution efficiencies in galvanostatic and potentiostatic mode are superior to 95%. So this electrochemical etching technique seems to be as efficient as classical chemical wet etching. The electrodeposition and the electrochemical stripping of Bi₂Te₃ films appear to be adapted to a global technology for thermoelectric devices with processes commonly used for microelectronics.

Figures :

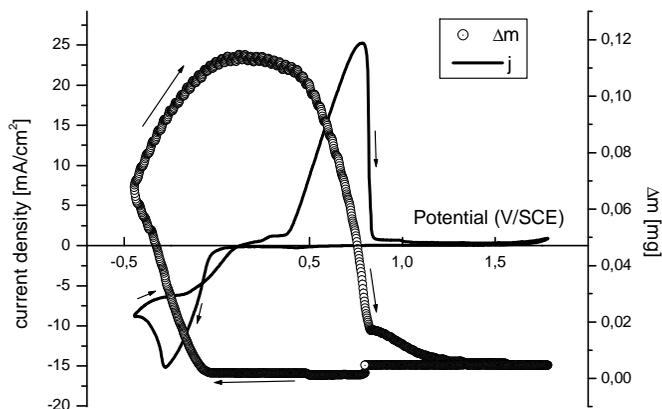


figure 1 : voltammetric curve and mass changes on polished platinum working electrode without stirring. Scan rate : 40mV/s. Electrolyte : 2.10⁻²M HTeO₂⁺ + 2.10⁻²M (BiNO₃)₂ + HNO₃ 1M.

References :

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- [7] to be published, Michel S., Diliberto S., Boulanger C., Lecuire J.M.