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Ellipsometric investigations of Bi₂Te₃ thin films grown by electrodeposition

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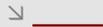
Introduction & Objectives

Bismuth telluride (Bi_2Te_3) based compounds have attracted considerable interest for thermoelectric conversion at room temperature.

This material can be used as an interlayer at the back contact to improve the long term stability of the CdTe thin film solar.

A route of synthesis of Bi_2Te_3 is done by electrochemistry: polycrystalline thin films have been grown on gold substrates by electrodeposition.

The determination of the transport properties is not obvious for thermoelectric thin films. Ellipsometry may be an alternative and powerful method to characterize thin films through their optical, morphological and electronic properties.

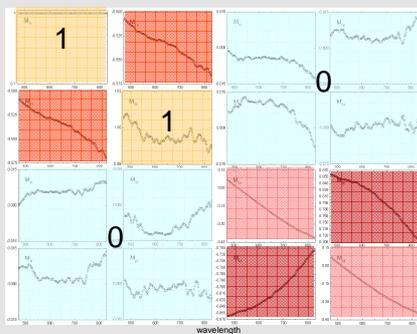


This work presents the analysis of electroplated Bi_2Te_3 layers by different ellipsometric techniques both in situ and ex situ modes.

- the optical behaviour of potentially anisotropic films of uniaxially bismuth telluride
- the electronic parameters through the analysis of the dielectric function
- the film growth during electroplating

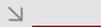
Results

Experimental Mueller Matrix Data



Mueller-matrix of a 4 μm -thick $\text{Bi}_{2.0}\text{Te}_{3.0}$ sample.

The spectra were realized at different angles of incidence ($\phi=65, 70$ and 75°) and for multiple azimuth angles ($\psi, \psi+45^\circ$).



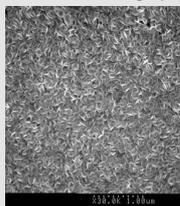
Comments:

Eight off-diagonal blocks elements $M_{ij} = 0$ polycrystalline films appear optically isotropic
Moreover no depolarization effect exists.

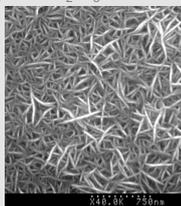
In situ study

Confirmation of optical isotropy from the first steps of the growth until several micrometers thick films.

SEM micrographs of electroplated Bi_2Te_3 films



15s growth time



3600s growth time

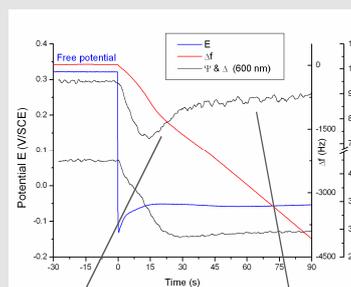
Discussion :

the random azimuthal orientation of anisotropic crystallized is optically equivalent to an isotropic material

In situ real time spectroscopic ellipsometric study combined with Electrochemical Quartz Cristal Microbalance

Simultaneous and synchronised records of :

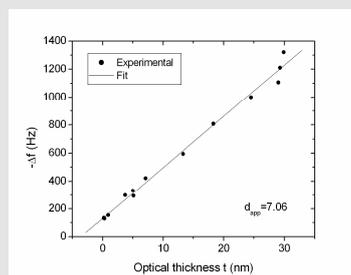
1. Real time visible ellipsometric spectra (RTSRCE)
2. Gravimetric data (EQCM)
3. Coulometric data (Potentiostat)



Comments:

The ECD process of Bi_2Te_3 includes a progressive covering stage in the first 30 seconds.

The following stage corresponds to a regular growth in which the optical constants vary slightly and are linked to the growth of needles

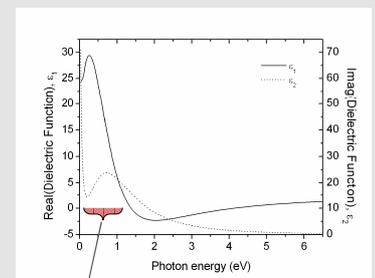


Growth rate : 1 $\text{nm}\cdot\text{s}^{-1}$

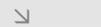
Porosity:

The optical thickness and mass are consistent with an apparent density of 7.06.
By comparison with the bulk density, a porosity P of 10 % may be calculated through the relation:
 $P=1-d_{\text{app}}/d_{\text{theo}}$

Analysis of the Dielectric Function (DF) of the electroplated films



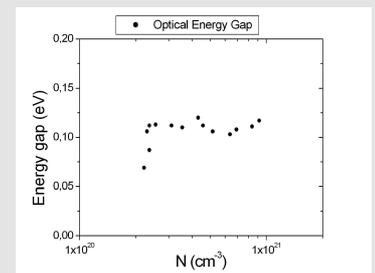
Modeled pseudo-dielectric function of a 4 μm -thick film of Bi_2Te_3



Comments:

In the InfraRed range, the DF of the samples is expressed as : $\epsilon(E)=\epsilon_{\text{DRD}}(E)+\epsilon_{\text{TL}}(E)$

with a **Drude contribution (DRD)** to the DF and a **Tauc-Lorentz contribution (TL)**.
In particular, the electrical resistivity and the band gap (E_g) can be extracted.
The carrier concentration (N) and mobility (μ) are deduced through the value of the effective mass.



Discussion:

The analysis was successfully extended to different compositions from $\text{Bi}_{1.8}\text{Te}_{3.2}$ up to $\text{Bi}_{2.2}\text{Te}_{2.8}$, leading to different carrier concentrations.

The N values show that the compounds are **heavily doped semiconductors**.

No significant variation of E_g with N is observed. Some compensation seems to occur with both tailoring phenomena:

- **Band-gap widening** by the Burstein-Moss effect ($\propto N^{2/3}$)
- **Band-gap shrinkage** due to many-body effects (electrons-electrons effects and electron-ion scattering)

Conclusion

■ This work has shown that Spectroscopic Ellipsometry can be a **powerful technique** to study electroplating.

■ **In situ data** allowed to monitor the growth of Bi_2Te_3 films, providing their growth rate, their porosity, growth mechanisms and their optical behavior.

■ **Dielectric Functions** were established, leading to the determination of the electronic parameters (E_g , resistivity, mobility) of thin films without any electrical contacts.

Acknowledgments

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