

Thermoelectric properties of tellurium thick films prepared by electrodeposition

¹B. Abad*, ¹M. Rull, ²Y. R. Koh, ³S. Hodson, ³X. Xu, ²A. Shakouri, ²T. Sands, ¹M.S. Martín-González

¹IMM-Instituto de Microelectrónica de Madrid (CNM-CSIC), Isaac Newton 8, PTM, E-28760 Tres Cantos, Madrid, Spain

²Electrical Engineering Department, Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana 47907, USA

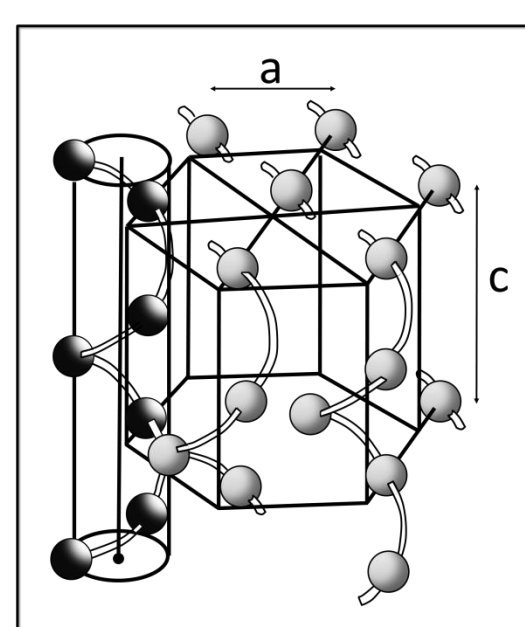
³Mechanical Engineering Department, Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana 47907 USA

*email of corresponding author: b.abad@imm.cnm.csic.es

Tellurium

Tellurium is a p-type semiconductor with a narrow bandgap (0.34 eV) and highly anisotropic crystal structure. It consists of helical chains which are bounded by covalent unions between the atoms and bound with other chains by Van der Waals interactions. These chains turn into a hexagonal lattice whose c axis is perpendicular to the hexagonal base or parallel to the helical chains [1].

Tellurium thin films have been studied for applications such as gas sensors, piezoelectric, photoconductor, photonic crystal, wave detector, thermoelectric devices, etc.

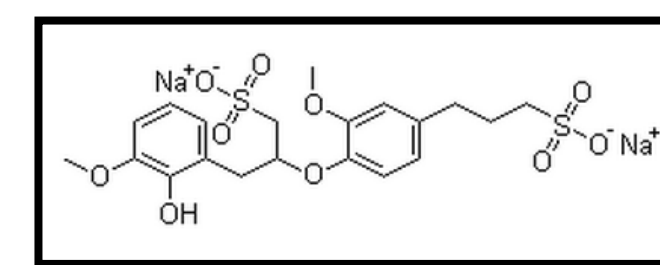


INTRODUCTION

$$zT = \frac{S^2}{\rho \kappa} T$$

Bulk Tellurium [2,3,4]:
 $S \approx 500 \mu\text{V/K}$ (p-type)
 $\rho \approx (100-5000) \mu\Omega\cdot\text{m}$
 $\kappa \approx 3 \text{ W/m}\cdot\text{K}$

Sodium lignosulfonate (SLS)



SLS is a surfactant which is added to the solutions to improve the quality of the films grown by electrodeposition [5].

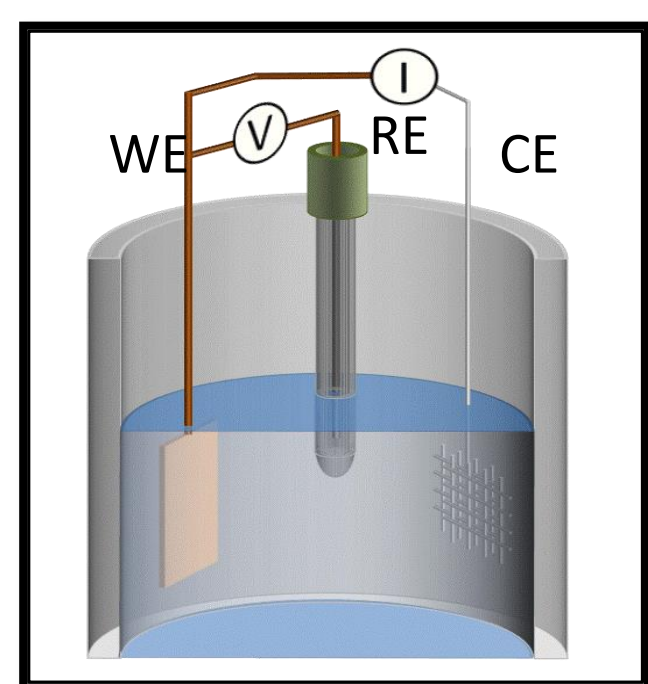
The formation of tellurium inclusion during electrodeposition of many tellurides families such as Bi-Te, Cd-Te, Zn-Te, Pb-Te, etc., is well documented.[6] Recently, the addition of SLS to the electrochemical bath as a possible way to reduce the amount of those inclusions has been claimed. [5] But, the real effect of SLS on Te growth has not been studied yet.

What is the effect of SLS addition in Te growth and its thermoelectric properties?

ELECTRODEPOSITION

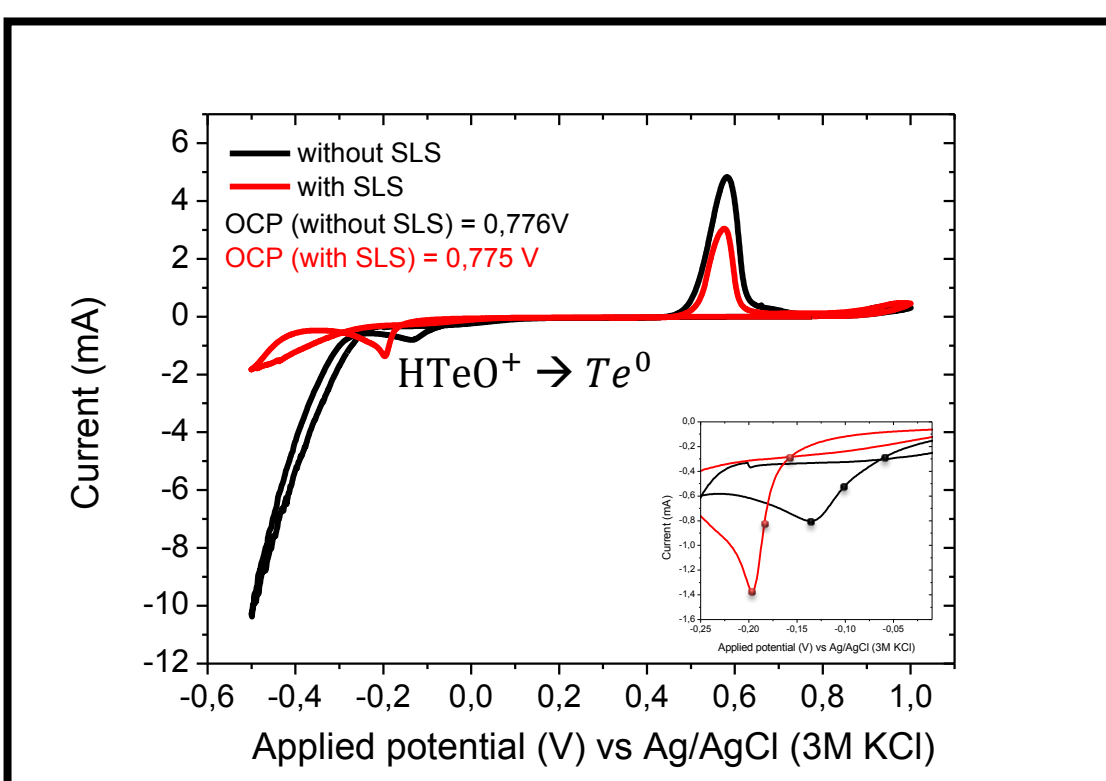
Three-electrodes conventional cell:

CE: Pt mesh
 RE: Ag/AgCl
 WE: 150 nm Pt/Cr/Si



Solutions

0.01 M HTeO_2^+ + 1 M HNO_3
 1) Without SLS
 2) With 0.06 g/L SLS

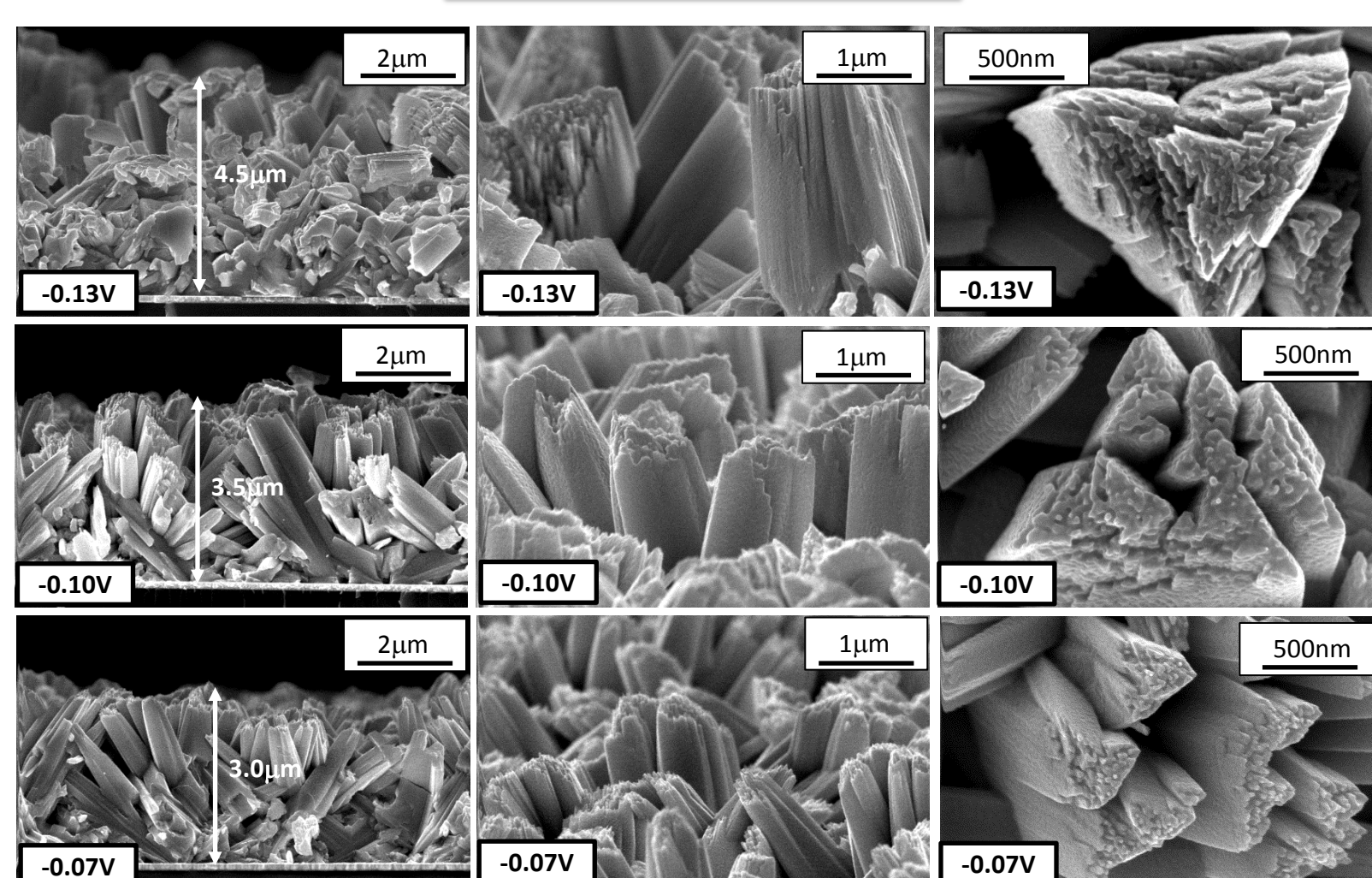


Reduction peak positions:
 1) Without SLS: $V = -0.13\text{V}$
 2) With SLS: $V = -0.20\text{V}$

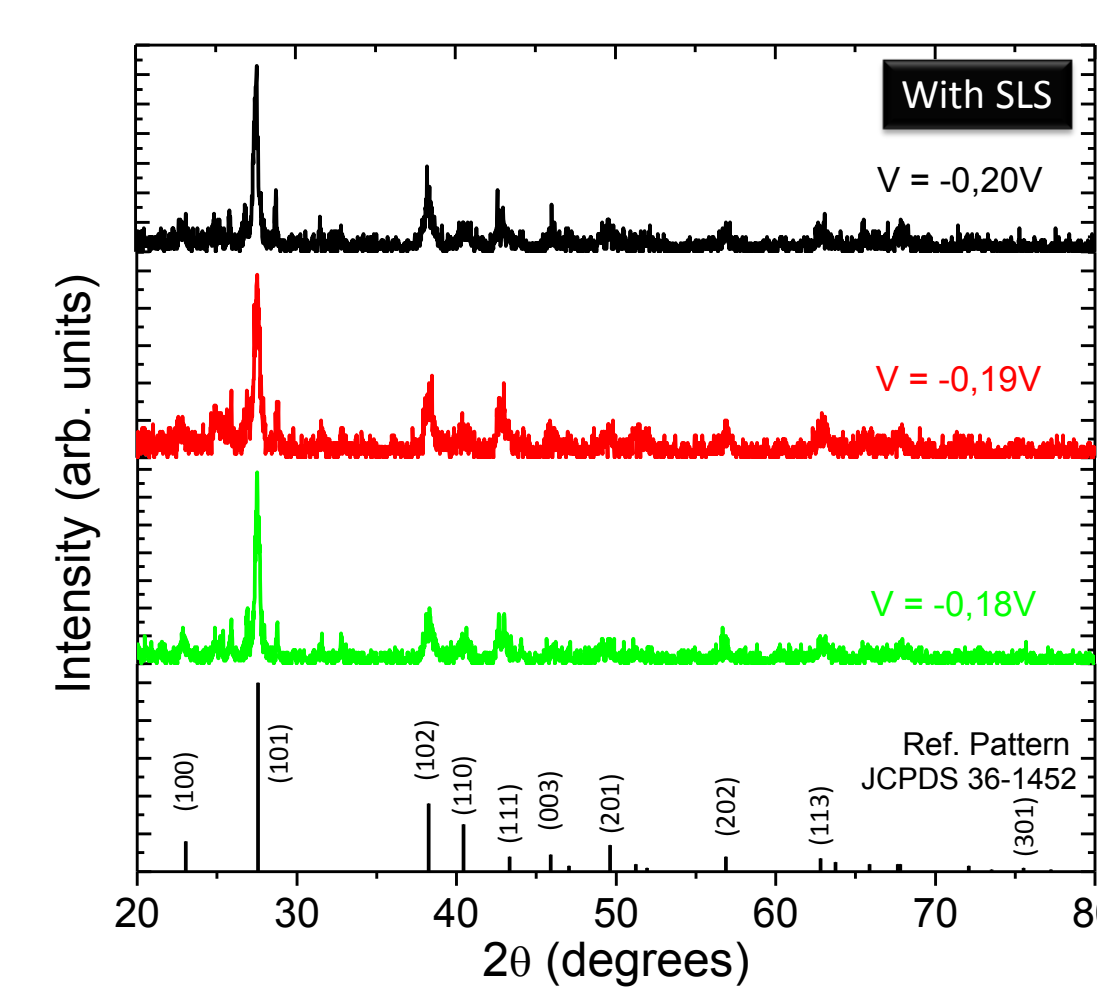
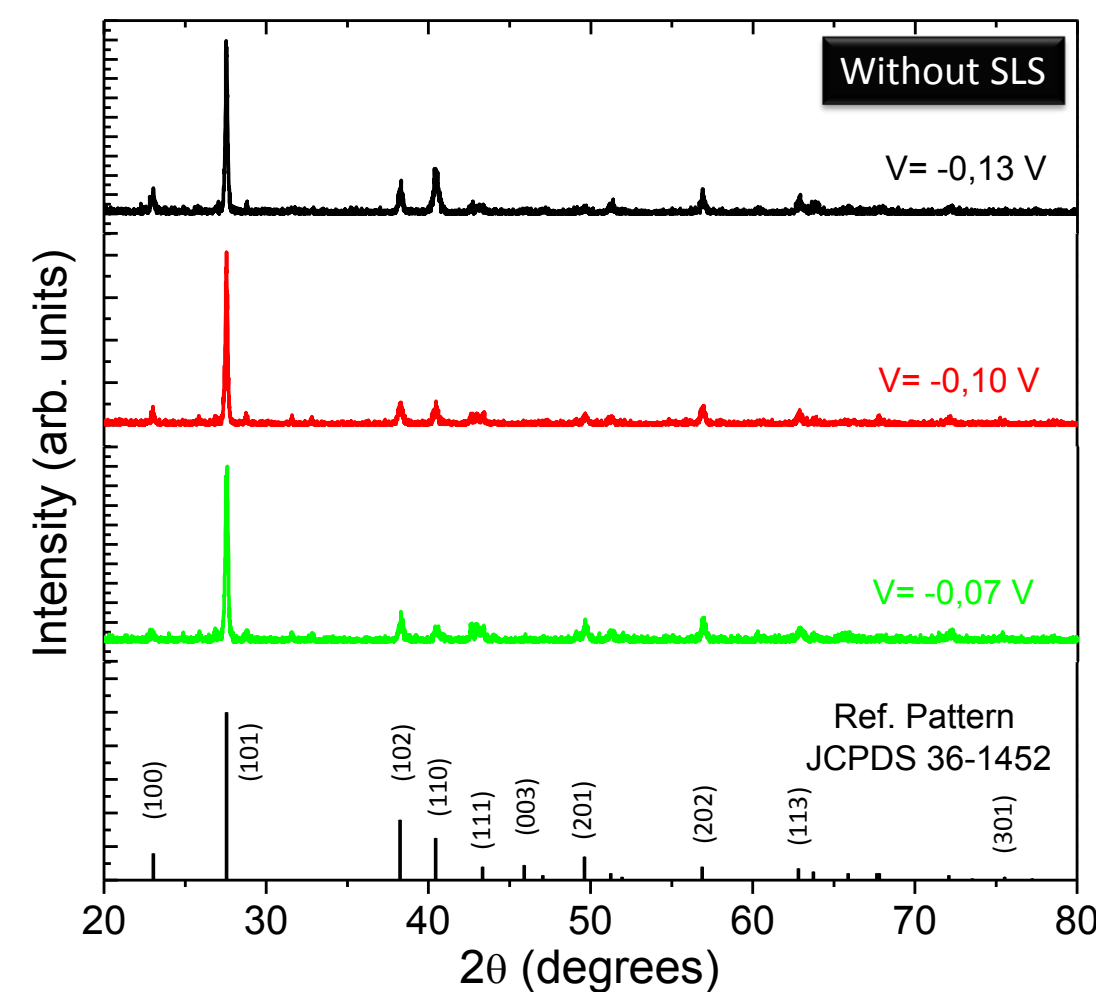
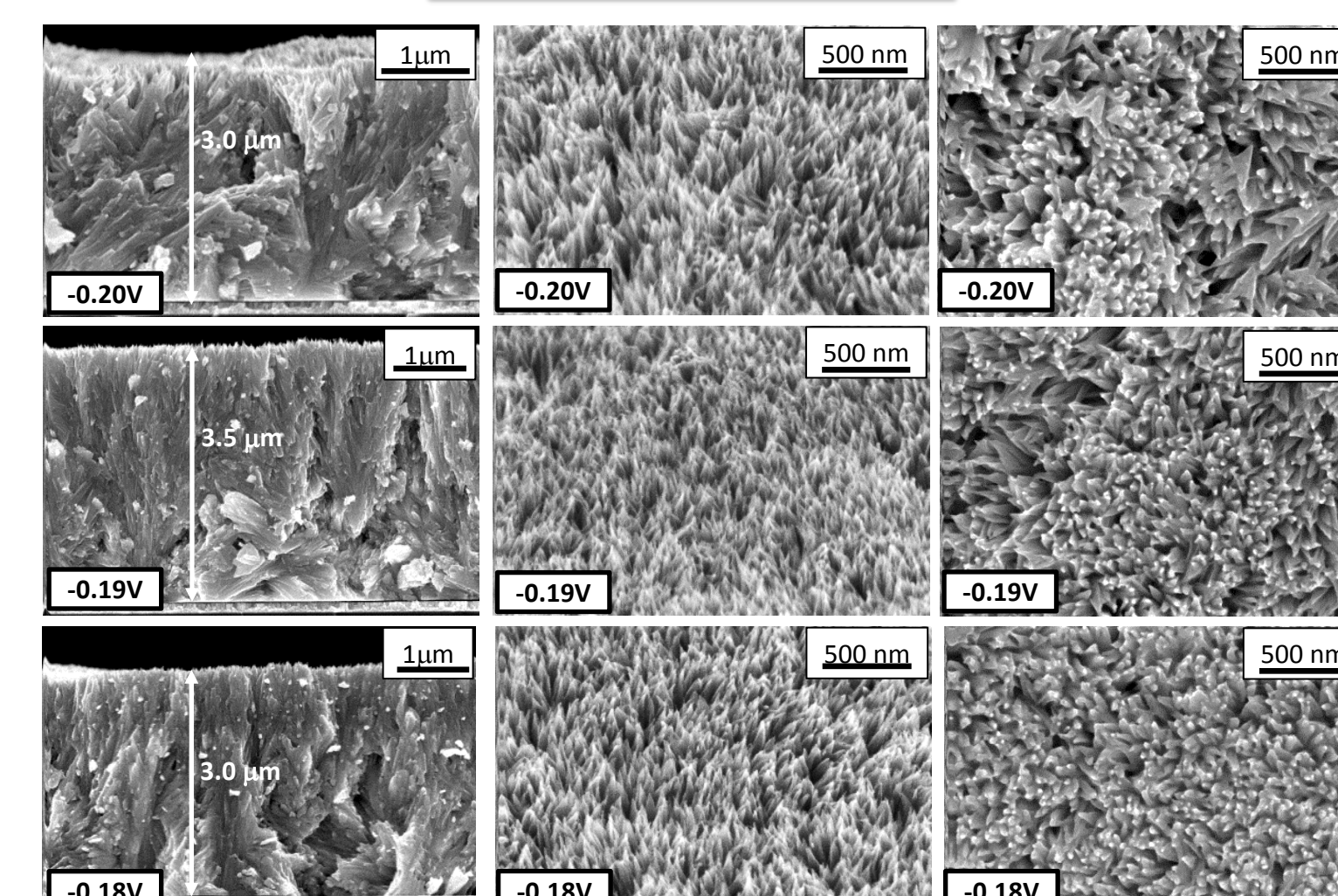
The displacement between the reduction peaks can be explained if the SLS is inhibiting the tellurium reduction.

STRUCTURAL AND MORPHOLOGICAL CHARACTERIZATION (SEM AND XRD)

WITHOUT SLS



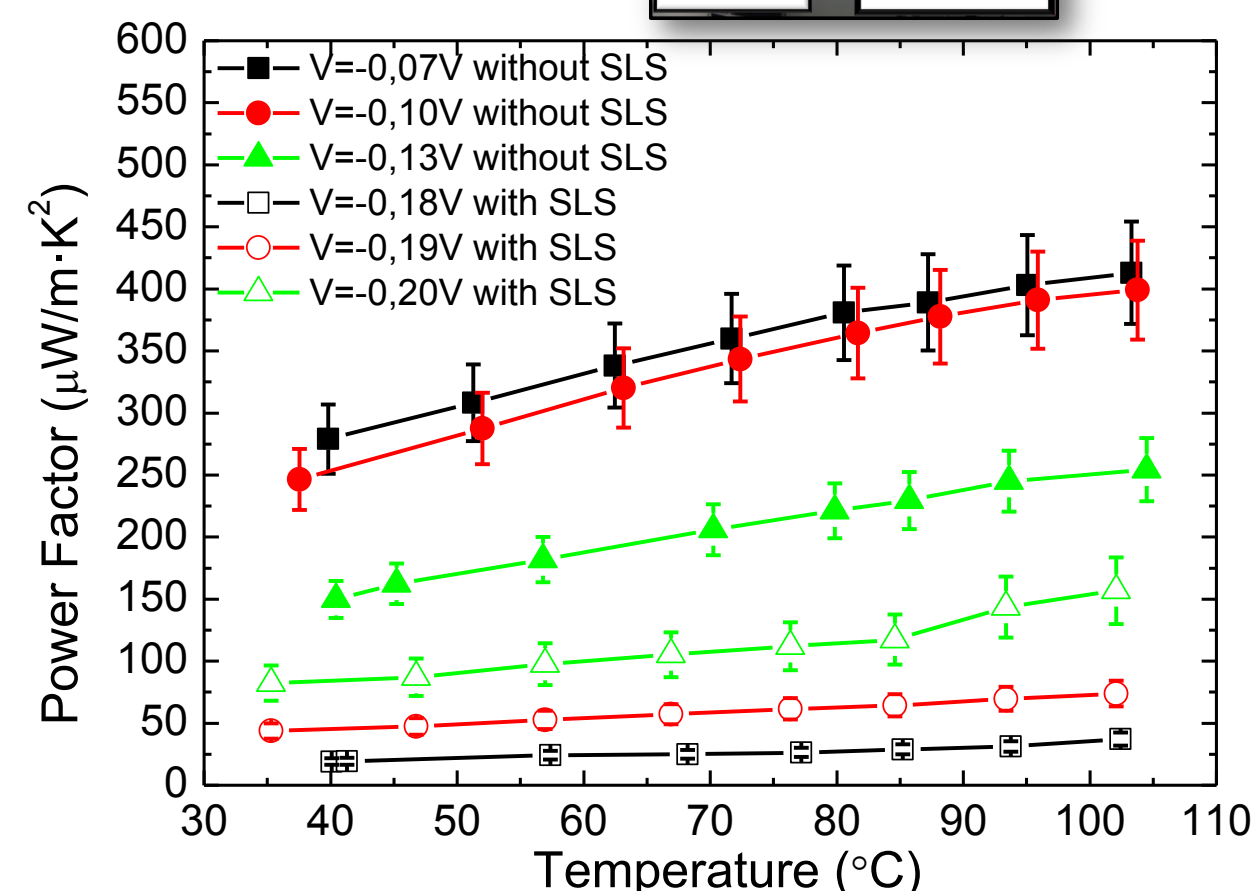
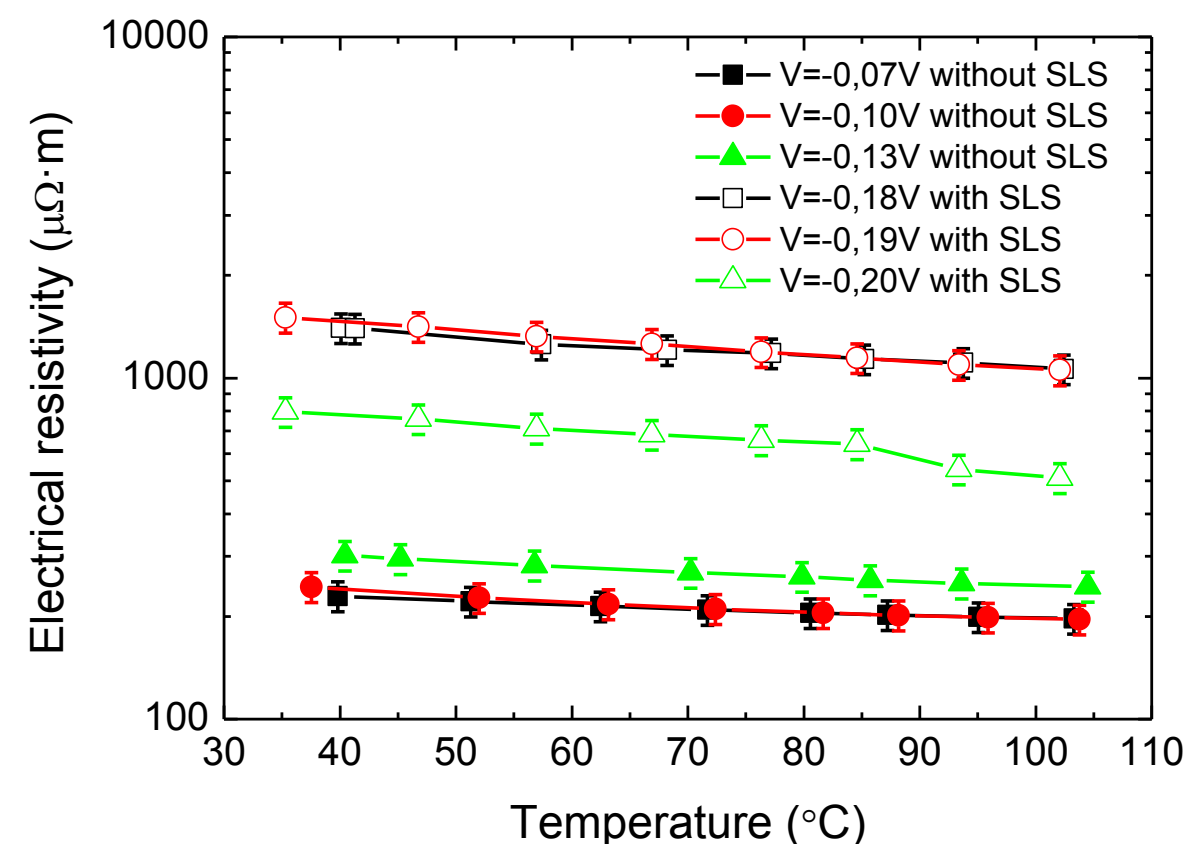
WITH SLS



The typical Te growth mechanism is modified by the addition of SLS which acts as an "anti-coagulation agent" that inhibits Te particle growth.

- The films are polycrystalline without preferential orientation.
- SLS seems to promote the dispersal of Te particles so smaller crystallite sizes are detected by the full width at half maximum (FWHM). The FWHM is higher in the case of the films from the SLS solution (smaller grain size).

POWER FACTOR ($S^2\sigma$) CHARACTERIZATION



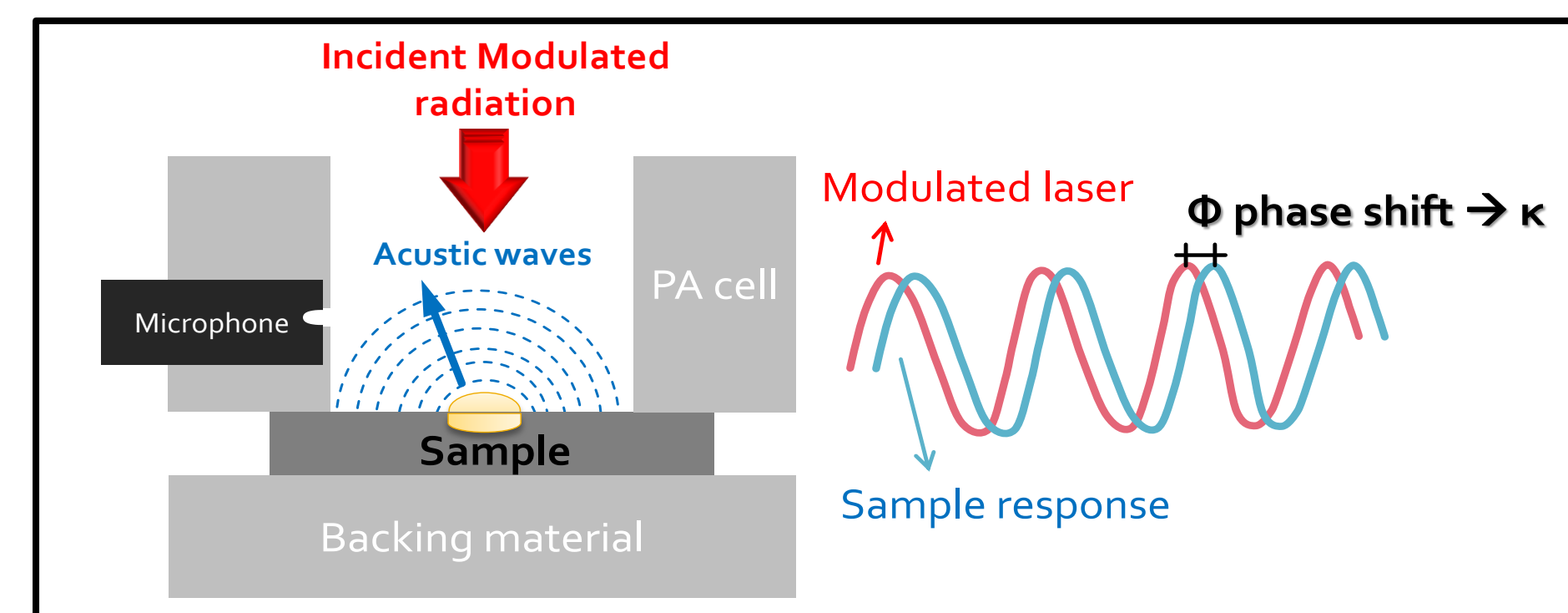
| Maximun values | Applied voltage (V) | PF @ RT ($\mu\text{W/m}\cdot\text{K}^2$) | PF @ 105 °C ($\mu\text{W/m}\cdot\text{K}^2$) |
|----------------|---------------------|--|--|
| Without SLS | -0.07 | 280±48 | 413±70 |
| With SLS | -0.20 | 82±14 | 157±27 |

Same order of magnitude as the Bi_2Te_3 PF films grown by electrodeposition in previous works [5,7]

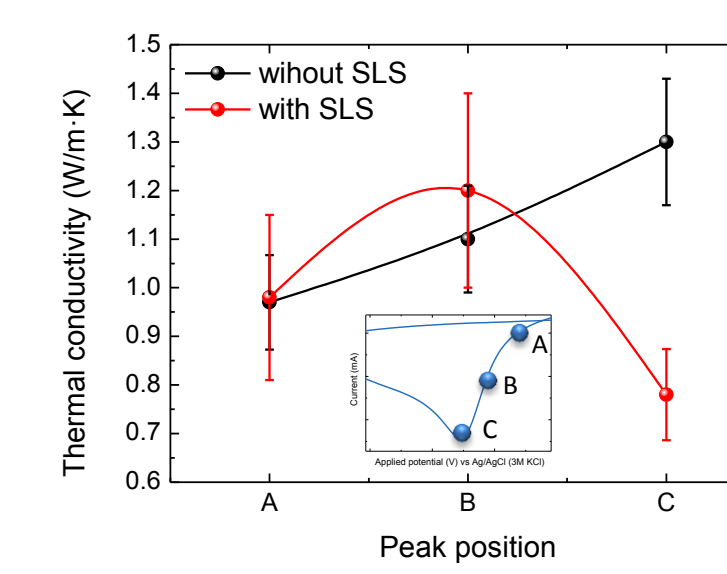
The ρ increases when SLS is added to the solution due to the reduction of the grain size.

THERMAL CONDUCTIVITY (κ) CHARACTERIZATION

Photoacoustic technique (PA) (IMM-CSIC)



| Surfactant | Applied voltage (V) | κ (W/m·K) PA technique | PF ($\mu\text{W/m}\cdot\text{K}^2$) |
|------------|---------------------|-------------------------------|---------------------------------------|
| - | -0.07 | 1.0±0.1 | 280 |
| - | -0.10 | 1.1±0.1 | 246 |
| - | -0.13 | 1.3±0.1 | 152 |
| SLS | -0.18 | 1.0±0.1 | 19 |
| SLS | -0.19 | 1.2±0.1 | 44 |
| SLS | -0.20 | 0.78±0.08 | 82 |



- The κ values of the Te electrodeposited films are in both cases around a third of the bulk value [4].
- The κ reduction could be explained in terms of nanostructuring of the films. The grain boundaries could be interrupting the phonon transport along the structure so that the phonon scattering is favoured.

CONCLUSIONS

- The Te growth mechanism changes completely by adding SLS. It can be concluded that SLS acts as an inhibitor of the Te growth promoting smaller grain size.
- The Power Factor values obtained near RT, 280 $\mu\text{W/m}\cdot\text{K}^2$ (without SLS) and 82 $\mu\text{W/m}\cdot\text{K}^2$ (with SLS) are in the same order of magnitude of the Power Factor of Bi_2Te_3 grown by electrodeposition in similar conditions [5,7].
- The κ of electrodeposited tellurium films is $\approx 1\text{W/m}\cdot\text{K}$, lower than the bulk value ($\approx 3\text{W/m}\cdot\text{K}$).

REFERENCES

[1] A.S. Epstein, H. Fritzsche, K. Lark-Horowitz, Physical Review, 107 (1957) 412-419.
 [2] V.E. Bottom, Science, 115 (1952) 570-571.
 [3] A. Goswami, S.M. Ojha, Thin Solid Films, 16 (1973) 187-197.
 [4] C.Y. Ho, R.W. Powel, P.E. Liley, Journal of Physical and Chemical reference data, Vol. 3, (1974)
 [5] O. Caballero-Calero, P. Díaz-Chao, B. Abad, C.V. Manzano, M.D. Ynsa, J.J. Romero, M.M. Rojo, M.S. Martín-González, Electrochimica Acta, 123 (2014) 117-126.
 [6] X.W. Zhou, D.K. Ward, B.M. Wong, F.P. Doty, J.A. Zimmerman, G.N. Nielson, J.L. Cruz-Campa, V.P. Gupta, J.E. Granata, J.J. Chavez, D. Zubia, Physical Review B, 85 (2012) 245302
 [7] C.V. Manzano, A.A. Rojas, M. Decepeda, B. Abad, Y. Feliz, O. Caballero-Calero, D.A. Borca-Tasciuc, M. Martin-Gonzalez, Journal of Solid State Electrochemistry, (2013) 1-8.

ACKNOWLEDGEMENTS



PHOTOACOUSTIC MEASUREMENTS OF NANOSTRUCTURES FOR THERMOELECTRIC APPLICATIONS (PHOMENTA)