Structure and ferroelectricity of GeTe thin films for thermoelectrics

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General framework:

Thermoelectric modules are solid-state energy converters that allow direct and reversible conversion of heat into electricity and are considered as a promising **clean-energy technology** [1]. The past decade has witnessed a sustained boom in new thermoelectric materials, among which **GeTe has shown one of the highest performances** [2-7]. So far, thermoelectrics have been optimized *via* (i) the increase of electric conductivity, creating degenerate or resonant energy states close to the Fermi level, and (ii) a decrease of thermal conductivity through defects or meso-scale structures to increase phonon scattering. We propose a new strategy to enhance and drive the thermoelectric properties of GeTe ***via* the control of the ferroelectricity in single crystalline thin films**. Indeed ferroelectric materials such as rhombohedral GeTe bring an additional degree of freedom in the structure design, namely the electric polarization. GeTe thin films contain different polarization states known as ferroelectric domains that are separated by narrow interfaces, called domain walls, where large structural distortions occur. These lattice distortions may couple to phonons and considerably reduce the thermal conductivity. In addition, polarization discontinuities especially at charged domain walls can trap free charge carriers and tremendously enhance the electrical conductivity [8-13]. **Therefore we propose a new paradigm where domain engineering at the nanoscale can drive the thermoelectric performances**.

In the perspective of both **fundamental research and future technological applications**, the manipulation of ferroelectric domains in thin films must fulfil two requirements: (i) be based on **materials with a high technological potential** and (ii) be studied on a **model system** to control and elucidate the basic mechanisms responsible for the targeted thermoelectric performances. Therefore, we propose to base our project on **GeTe**, that is already well-established in microelectronics (*e.g.* Phase Change Memories [14]). Moreover the epitaxial growth of GeTe on silicon and silicon-on-insulator (SOI) substrates ensures the compatibility of the system with the silicon technology.

Research project and approaches:

In order to tackle the ferroelectric properties of GeTe thin films: (i) domain structure, polarization dependence on (ii) temperature and (iii) thickness at the nanometer scale, we plane to use Mirror Electron Microscopy (MEM), Low Energy Electron Microscopy (LEEM) in the temperature RT to 1500 K [9] as well as transmission electron microscopy (TEM) and *in situ* X-ray diffraction at radiation synchrotron facilities (ESRF and SOLEIL).

Before studying the ferroelectric properties, the project will be first devoted to the **growth and characterization of two dimensional layers of GeTe** obtained by Molecular

Beam Epitaxy (MBE) grown **on miscut Si substrates and Silicon-On-Insulator(111) single crystal**. The growth parameters will be adjusted to improve the layer quality measuring *in situ* the diffraction pattern by RHEED (Reflection High Energy Electron Diffraction). In addition the layer structure and ferroelectric domains will be analyzed through *ex situ* **HRTEM** measurements and **X-ray diffraction**.

As GeTe(111) thin films are obtained, **the ferroelectric domain dynamics will be studied by Low Energy Electron Microscopy**. The domain polarization switching as function of temperature and thickness will be studied until the Curie temperature. We propose also to "write" on the GeTe film using a highly focused electron beam to favour the polarisation orientation in the field direction.

Depending on the advance in the research project, the experimental protocol developed in the case of GeTe thin films will be extended to other ferroelectrics and to multiferroics (e.g. $Ge_{1-x}Mn_xTe$ alloys).

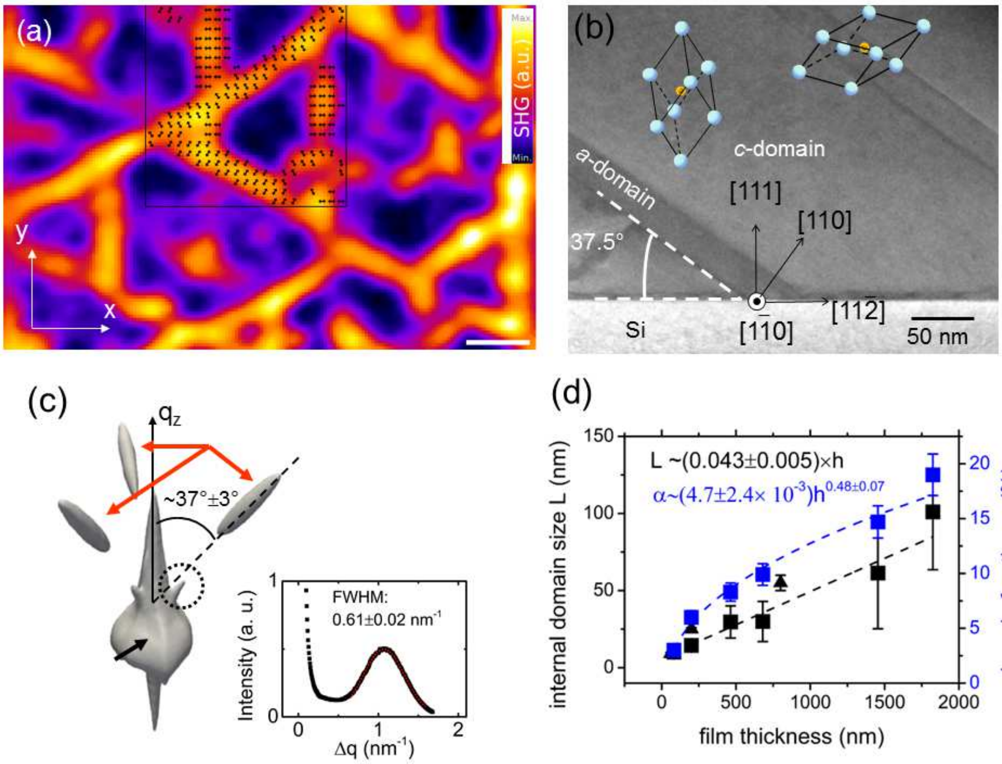

Figure: (a) Isotropic secondary harmonic generation (SHG) image revealing the domain structure of a 1825 nm-thick GeTe film. The black arrows indicate the local in-plane polarization orientation in the nanodomains. The a-domains contributions (yellow-orange) with in-plane polarization are superimposed to the background (dark-purple) signal exhibiting out-of-plane polarization (c-domains). Scale bar 5 μm. (b) Cross-section TEM showing inclined a-domains inside the GeTe layer on Si(111). (c) 3D-reciprocal space map obtained by X-ray diffraction showing 4 Bragg peaks from c-domains (black arrow) and a-domains (red arrows). (d) a-domains size and volume fraction as function of GeTe film thickness. From B. Croes *et al.* Phys. Rev. Mat. 5, 124415 (2021) [15].

Environment:

The project is part of an **ANR national project FETh** in close collaboration with Institut Néel (Grenoble) and IPCMS (Strasbourg).

The « Surface and structure team » at the CINaM lab has already a strong expertise on GeTe thin films [15-17]. The experimental setup combines a MBE growth chamber coupled under UHV to LEEM and STM apparatus. The CINaM lab is equipped with HRTEM for structural characterization.

Profile and skills required:

Highly motivated candidates in experimental physics with a PhD degree in condensed matter physics or materials science. A prior experience in physical deposition growth would be appreciated. **A strong involvement on the MBE chamber will be expected and/or characterization via HRTEM or STM**. Qualities such as pragmatism, professionalism, taste for teamwork, but also autonomy are expected. A good English level will be appreciated. Gross salary about 2500-3000€/month.

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