Azimuthal SHG with epsilon-near-zero enhancement from ultrathin TiN epitaxial films

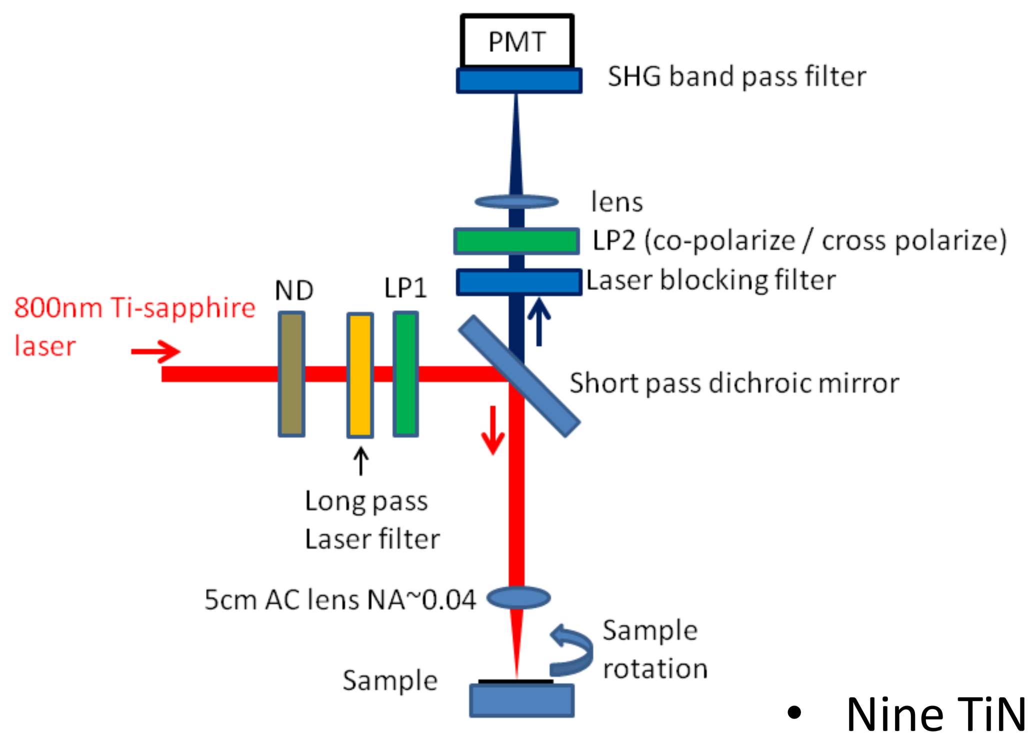
Wei-Liang Chen[1]*, Man-Hong Lai[1], Ching-Wen Chang[2,3], Shao-Yu Chen[1], Shangjr Gwo[3], Yu-Ming Chang[1]

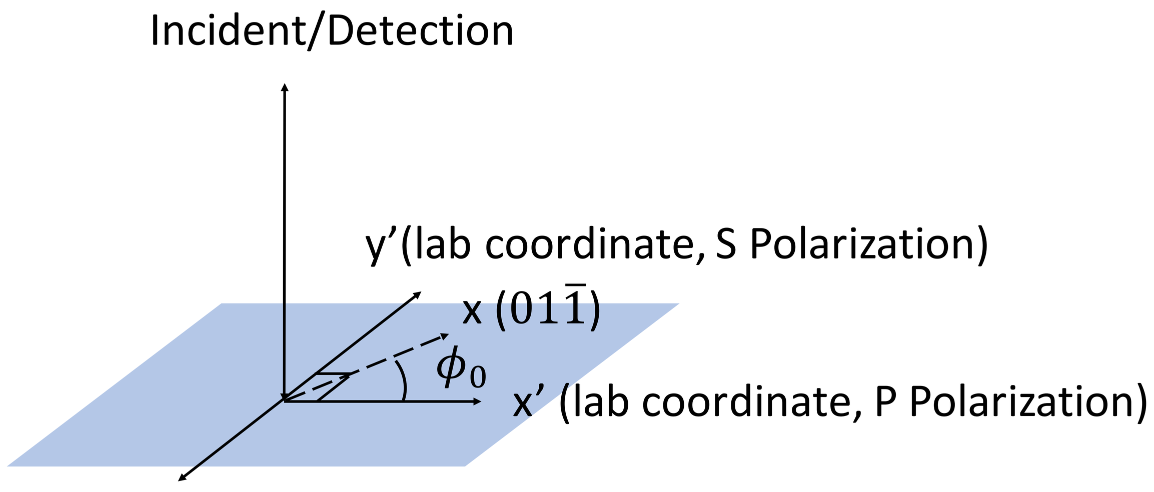
[1]*Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan*
[2]*Research Center for Applied Sciences, National Sun Yat-Sen University, Kaohsiung, Taiwan*
[3]*Department of Physics, National Tsing Hua University, Hsinchu, Taiwan*

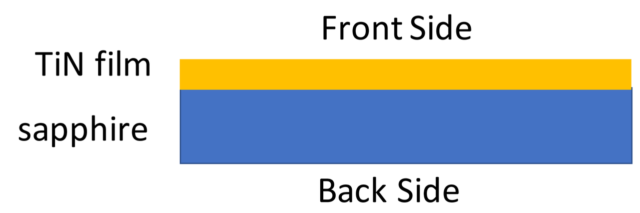
Abstract

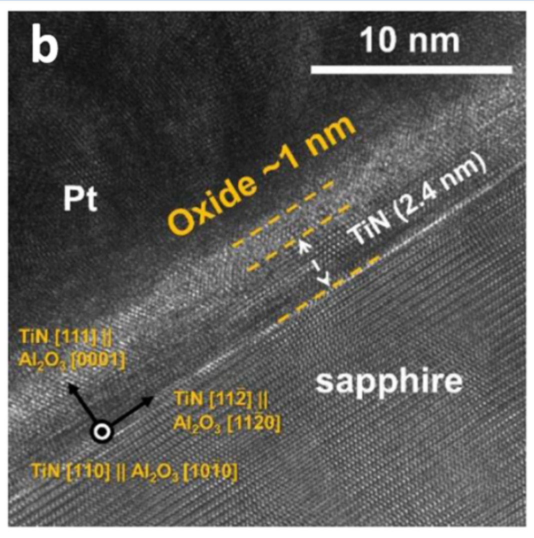
In this work we investigated the second harmonic generation (SHG) from TiN epitaxial films grown on c-plane sapphire. The ultrathin TiN films with thickness from 2-46 nm were grown by molecular-beam epitaxy (MBE) to produce high-quality stoichiometric TiN films. By rotating the samples along the propagation axis of the 800nm laser excitation, we measured the reflected SHG polarized parallel (co-polarized) and perpendicular (cross-polarized) to the laser polarization. We observed nearly two orders of magnitude increase in the SHG as the film thickness decreases from 46nm to 2nm. We associate the rapid increase in the SHG intensity below the 10nm TiN thickness with the onset of redshift in the ENZ (epsilon-near-zero) wavelength below 10nm reported previously[1].

AZSHG Experimental Setup and Measurement









SEM showing 2.4nm TiN grown on c-plane Sapphire substrate [1]

- Nine TiN thin film samples with varied film thickness from 2nm to 46nm, were measured in this study.

Theory

For cubic centrosymmetric materials such as TiN, the SHG polarization due to surface and bulk contribution can be expressed as

$$P_{i\,(2\omega)} = \chi^{(2)}_{ijk} E_j\, E_k + \Gamma_{ijkl}\, E_j\, \nabla_k\, E_l$$

The first term is the electric-dipole term and can only come from the surface while the second term corresponding to electric-quadrupole/magnetic-dipole effects, give rise to the bulk contributed SHG. Both surface and bulk have anisotropic contributions. The combined SHG E-field from TiN(111) thin film has the phenomenological form of[1]

$$\mathrm{E}(2\omega) = \alpha - \beta\cos 3\phi$$

Isotropic term, contributed by the surface, bulk and interface for non perpendicular incident beams.

Anisotropic term, depends on $\chi^{(2)}_{xxy}$ of the TiN(111) surface structure (*3m* crystal class) and bulk contribution.

Furthermore, we find that an additional isotropic term γ was necessary in the fitting formula to quantify the isotropic AZSHG curves observed in the plotted AZSHG curves shown in the right column.

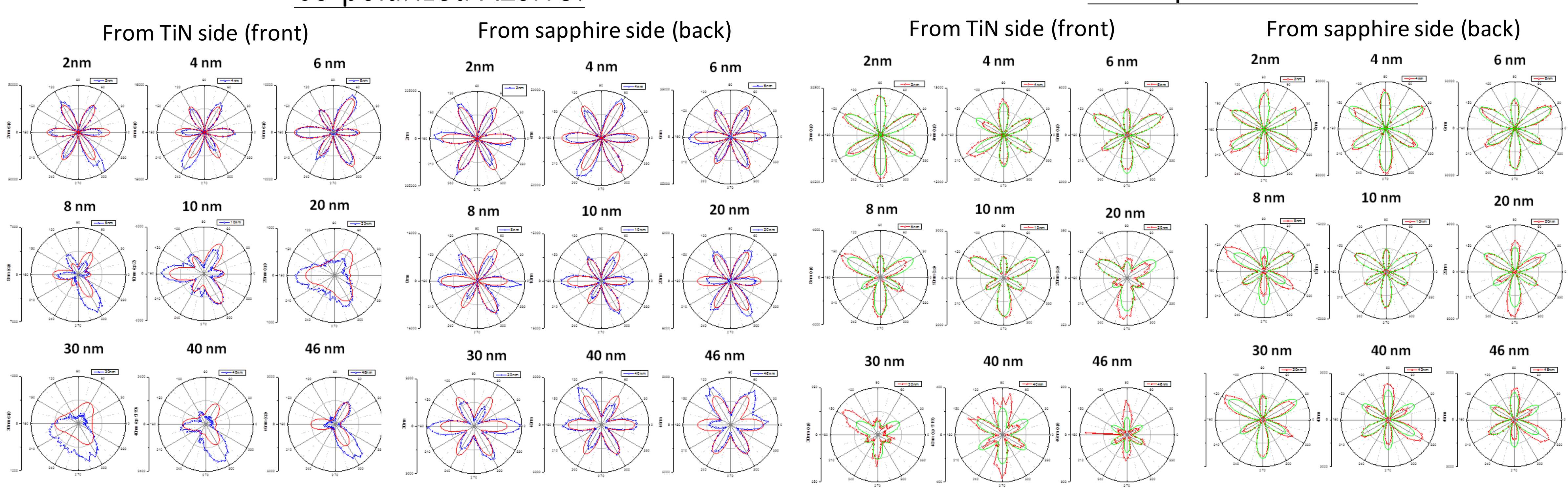
Co-polarized: $\mathrm{I}(2\omega) = |\boldsymbol{\alpha} - \boldsymbol{\beta}\cos(3(\phi - \phi_0))|^2 + \boldsymbol{\gamma}^2$

Cross-polarized: $\mathrm{I}(2\omega) = |\boldsymbol{\alpha} + \boldsymbol{\beta}\sin(3(\phi - \phi_0))|^2 + \boldsymbol{\gamma}^2$

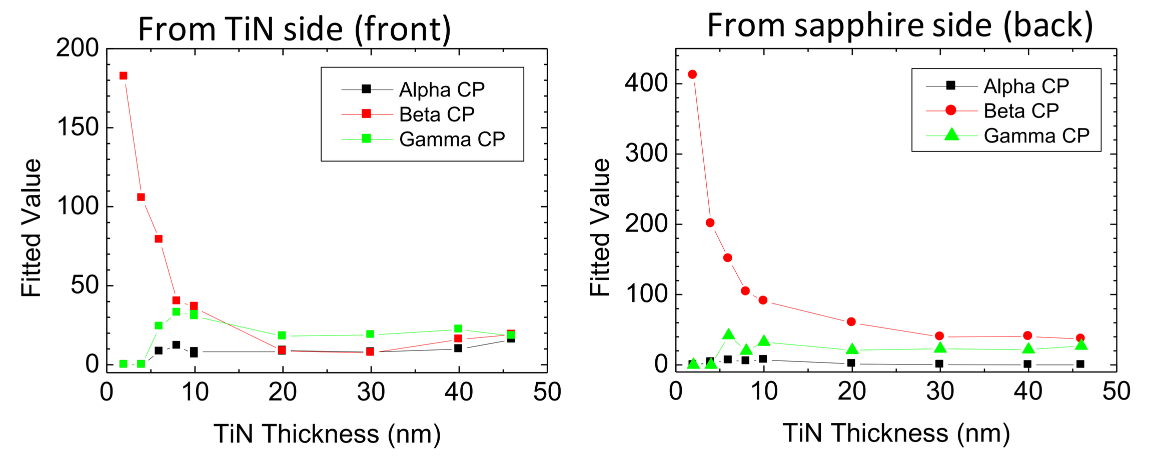
ϕ_0 : defines the initial angle between the incident E field and crystal x $(01\bar{1})$ axis

Results

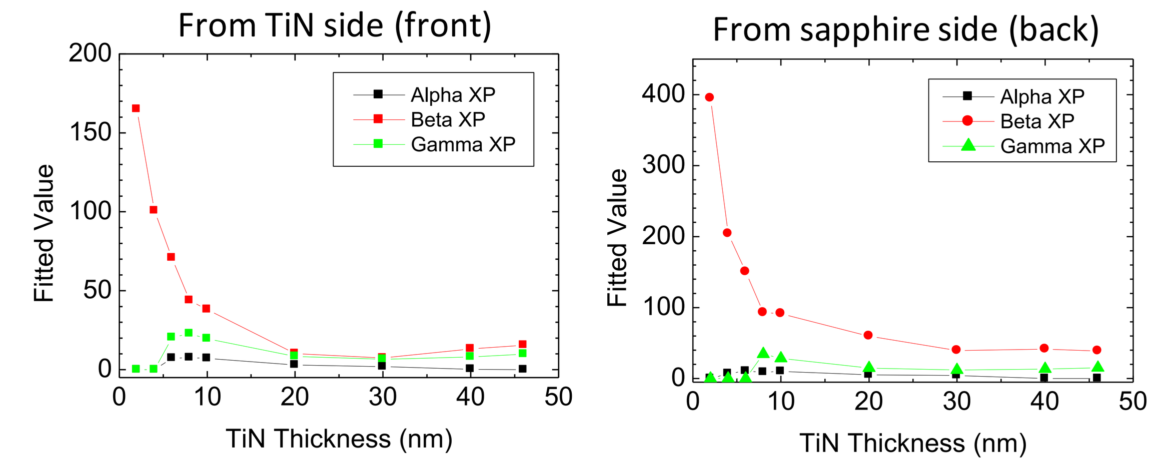
Co-polarized AZSHG: / Cross-polarized AZSHG:



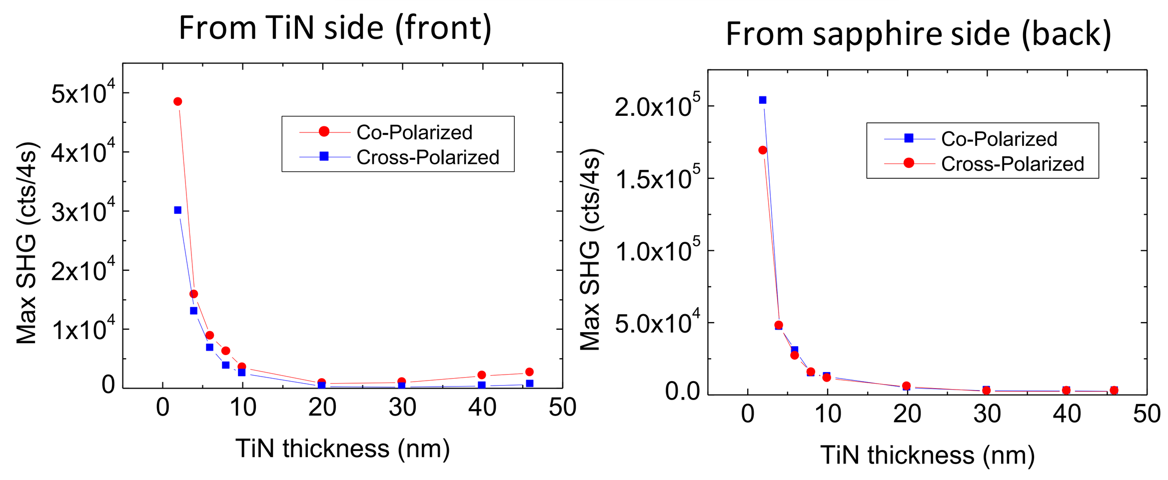
Co-polarized fitting parameters:



Cross-polarized fitting parameters:



Max SHG vs TiN thickness:



- A rapid increase in SHG occurs below 10nm TiN thickness, which we associate with Epsilon-Near-Zero (ENZ) enhancement.

- For excitation incident perpendicular to the TiN (111) surface, both surface and bulk TiN can only contribute to the anisotropic β term.
- Fitting of the Co-polarized and Cross-polarized AZSHG from both front and back of the sample show that the anisotropic term β dominates the AZSHG signal.
- For thickness above 20nm, we observe more asymmetry in the AZSHG pattern from the front side, which we associate with possible surface degradation due to exposure to air or less ideal TiN crystal structure .

Discussion & Conclusion

- The additional isotropic term γ diminished as the TiN film thickness increases. We can attribute this term to the SHG contributed from the lattice mismatch between the TiN/sapphire heterointerface.
- In ultrathin TiN sample, the combination of surface and heterointerface SHG gives the feature of three-fold symmetry AZSHG in both polarization configuration.
- The bulk contributed AZSHG, due to electric quadrupole effect, dominates the total AZSHG in thick TiN samples (note: increasing α/β ratio). This effect is only observable in co-polarization configuration (note: increasing α term in co-polarization).
- Surface contributed AZSHG diminished when the film thickness is increasing (note: decreasing β in both polarization configuration).
- In both polarization configuration, the isotropic term γ do not diminished completely in thicker sample. The origin of this isotropic AZSHG signal need to be further investigated in the future.

NSTC 國家科學及技術委員會 National Science and Technology Council

Ultrafast Laser Spectroscopy Laboratory 超快雷射光譜實驗室

Reference:
1. Appl. Phys. A 59, 545-552 (1994)
2. 2. ACS Appl. Mater. Interfaces 2022, 14, 16839-16845

Acknowledgement:
The work done at National Taiwan University is supported by the Ministry of Science and Technology under the following funding grants: MOST 111-2112-M-002 -035 -MY3, NSTC 111-2119-M-002-013 -MBK, and NSTC 112-2811-M-002-078.