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Optical Second Harmonic Generation as a tool for in-situ, real-time monitor of thin film epitaxial growth

Andrea Rubano[1,a], Tim Günter[2], Martin Lilienblum[2], Domenico Paparo[1], Lorenzo Marrucci[1], Fabio Miletto Granozio[1], Umberto Scotti di Uccio[1] and Manfred Fiebig[2]

[1] CNR-SPIN and Università Federico II, Monte S. Angelo, via Cintia, 80126 Napoli, Italy.

[2] HISKP, Universität Bonn, Nussallee 14-16, 53115 Bonn, Germany.

[a]rubano@fisica.unina.it

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Abstract. Oxide-based hetero-structures are promising candidates for building the next generation of functional devices. In order to achieve this goal, it is required to have solid and reliable sensors for monitoring the growth of thin films with single-atomic-layer sensitivity. So far, the most popular in-situ diagnostic tool is Reflection High Energy Electron Diffraction, which provides information on the structural properties of the growing films, and not a direct access to the desired interfacial physical properties of interest. Furthermore, it needs a strong human-machine interaction, preventing its use into industrial mass production. Standard optics applied on buried interfaces suffers the disadvantage to have a probing depth which is orders of magnitude larger than the interface layer. Here we propose to overcome this problem by resorting to optical Second Harmonic Generation and we present some example to show the potential of this technique as a real-time monitor system for thin-film crystal growth.

Introduction

Thin-film and multilayer-based technologies have experienced exponential growth in the past 15 years, they are used today in many systems for tailoring electronic, magnetic, optical, chemical and thermal properties. In thin films and multilayers, indeed, one length scale (the thickness of the film and of the individual layers, respectively) is under control, but impurities, vacancies, dislocations and grain boundaries have a crucial role in determining the physical properties of the material. Recent advances in deposition techniques, made the structural quality of oxide hetero-structures competitive with that of the best conventional semiconductors, opening new perspectives in the study of interface effects in such hetero-structures [1]. Nowadays in-situ real-time control of the deposition process is achieved by Reflection High Energy Electron Diffraction (RHEED). The RHEED is probably the most widely employed real-time diagnostic tool since it probes a surface layer with thickness on the atomic scale [5, 6]. However the physical information it can provide is limited to the structural and morphological aspects and its application to industrial manufacturing environment presents several limitations. To tackle this limit, we propose to use optical Second Harmonic Generation (SHG). It is a non-standard optical technique with inherently high surface/interface sensitivity [2-4]. SHG is based on a second-order phenomenon in which the frequency of some of the incident photons is doubled during their interaction with the material [7]. The surface/interface sensitivity of SHG arises because the second-order nonlinear susceptibility which characterize the SHG response of the material vanishes in the bulk of centrosymmetric media, e.g. in most of the substrate single crystals, semiconductors or metals. In contrast, where the inversion symmetry is broken (e.g. at a surface and/or interface) a relatively strong response is obtained. Beside the interface-only sensitivity, which is clearly the most relevant feature for epitaxial growth monitoring, SHG can be implemented in several layouts, to access different

physical features, according to the most relevant one for obtaining the desired physical property. The range goes from simple monitoring of the SHG yield during growth to SHG spectral recording, and from SHG spatial resolved Imaging to phase-resolved SHG. The present work will focus on the latter case, presenting a test-case on $SrTiO_3/NdGaO_3$ (STO/NGO) hetero-structures, which is an interesting material class because $SrTiO_3$ films grown epitaxially on $NdGaO_3$ presents a stable SrO-plane terminated surface [8]. Details about SHG Imaging experiment can be found in Ref.s [2-4], and all details about samples growth can be found in Ref. [8].

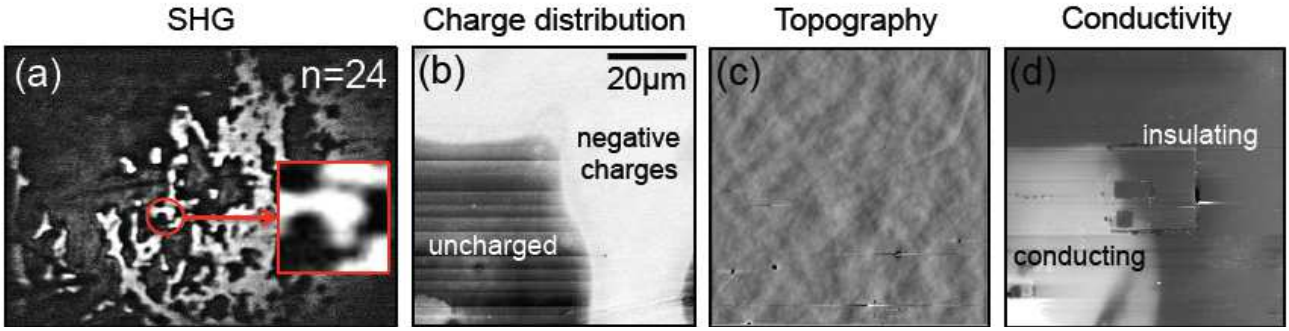

Fig.1: *(a) Spatially resolved SHG image of $NdGaO_3$ with n=24 epitaxially grown monolayers of $SrTiO_3$. (b) Charge distribution as revealed by PFM. (c) Surface topography as obtained by AFM. (d) Conductivity distribution as measured by EFM. See text for details.*

Second Harmonic Imaging

We investigated 6 samples of $SrTiO_3/NdGaO_3$ with different thickness. Most samples nicely reproduce the Gaussian intensity profile of the incident laser beam, and hence can be considered "good" samples, showing an homogeneous surface. A totally different picture is obtained in the case of the n=24 sample in Fig.1a, which shows various "cow-patterned" dark and bright areas with a lateral extension up to several millimeters. The SHG image indicates that two phases are stabilized in a single sample with a lateral extension of millimeters, i.e. exceeding the optical resolution of the experiment. In order to address this issue, the experimental setup was modified to enable phase-sensitive SHG imaging. The results indicate a phase shift of 1.05±0.08 π between dark and bright areas, while the dark areas are in-phase with the SHG signal recorded from a pure STO substrate surface. This finding suggests that bright regions display different physical properties with respect to dark regions. In order to explain the origin of the 180° phase shift in the SHG signal the fundamental symmetry aspects of SHG must be recalled. In general, a 180° phase shift occurs when one mirror-symmetry is broken. In the case of $SrTiO_3/NdGaO_3$ heterostructures two possible mechanisms yielding a breaking of mirror-symmetry can be considered. First, strain-induced ferroelectricity in the $SrTiO_3$ film as reported by several experimental and theoretical works [9-11]. Second, a change of the surface or interface termination which yields areas with a breaking of inversion symmetry between SrO and TiO_2 planes. Since SHG cannot distinguish between these two, scanning force microscopy was consulted to infer the origin of the phase shift.

Piezoresponse and Electrostatic force microscopy

Piezoresponse force microscopy (PFM) gives a detailed map of the charge distribution with nm resolution [12, 13]. Electrostatic force microscopy (EFM) is a non-contact AFM mode similar to PFM that allows for imaging of localized and free charges [14]. Fig.1a illustrates the SHG image of the n=24 sample with an additional zoom into an area that shows a roughly equal distribution of the distinguished areas. In Fig.1b the corresponding charge distribution in this area is revealed by PFM.

The EFM picture (Fig.1d) shows the same pattern of the PFM, but in this case the dark area corresponds to a conductive area. On the one hand, the bright areas in the electron density correspond to negatively charged but insulating areas at the sample surface. On the other hand, the bright areas in the conductivity profile correspond to conducting areas at the sample surface. Consequently, it appears that the bright contrast in the PFM image is caused by charged areas, whereas conducting areas appears dark in PFM, EFM and SHG images. It is clear that both the charge distribution seen by PFM and the conductivity seen by EFM are reproducing the inhomogeneous structure formerly revealed by SHG, thus unambiguously relating it to the electronic structure of the surface. On the other hand, the AFM scan depicted in Fig.1c reveals a perfectly flat surface topography. The presence of an inhomogeneous charge distribution on a structural homogeneous surface limits the amount of mechanisms leading to the pronounced SHG contrast. A pure crystallographic origin, such as a change of the substrate termination, can be safely excluded, since it would not affect the electronic structure as indicated by PFM and EFM. Further tests on the charged areas revealed that no permanent switching can be obtained, as one would expect for a ferroelectric material. This finding implies the following conclusions: (i) due to the presence of conductivity and the absence of a switching behavior a ferroelectric state in the $SrTiO_3$ film causing the SHG contrast can be safely excluded, (ii) a surface termination effects can be excluded, since the large scale inhomogeneities do neither coincide with crystallographic steps nor are capable to cause conducting areas.

Summary

In summary, the most likely scenario that accounts for the observed localized surface charges and conductive islands relies on the well-known influence of oxygen vacancies and ionic excess within the $SrTiO_3$ film that leads to the inhomogeneous charge distribution at the surface. What it is important to point out here, is that, regardless of the physical origin of the investigated imperfections, the results presented in this work demonstrate the potential of SHG as a surface sensitive probe. We demonstrated that SHG is capable to resolve in-plane inhomogeneities in the charge distribution with a resolution given by the diffraction limit (in the order of hundreds of nanometers, using optical wavelengths), probably caused by growth-induced defects or non-reproducible growth conditions leading to surface impurities. Especially for the in-situ quality detection and analysis of thin films, i.e. during the growth process, epitaxial growth would be hampered by contextual local probes such as scanning force microscopy, whereas SHG is a suitable technique as both the light source and the detector can be placed far from the sample. More technical advantages over well-established surface-sensitive techniques root in a short acquisition time (some seconds/minutes, depending on the amount of detectable signal) and the large extension of the resulting images (microns to millimeters). Thus, in combination with standard characterization techniques, such as reflection high energy electron diffraction (RHEED), which probe the vertical homogeneity, SHG reveals valuable information on the complementary in-plane homogeneity of the material. The additional phase resolution of SHG might help to clarify the origin of an inhomogeneous SHG response and could for example act as a probe for strain-induced ferroic states in ultrathin oxide heterostructures. Future work in this direction will focus on the direct implementation of an SHG setup in real growth-conditions, and on the possible influence of the laser irradiation on the sample during the growth. These findings open new possibilities for the characterization and technical implementation of oxide hetero-structures in modern electronics.

References

[1] E. Dagotto, Science **318** (2007), p. 1076

[2] A. Rubano, D. Paparo, A. Marino, D. Maccariello, F. Miletto Granozio, U. Scotti di Uccio, C. Richter, S. Paetel, J. Mannhart, L. Marrucci and M. Fiebig, Phys. Rev. B **83** (2011), p. 155405

[3] T. Günter, A. Rubano, D. Paparo, M. Lilienblum, L. Marrucci, F. Miletto Granozio, U. Scotti di Uccio, R. Jany, C. Richter, J. Mannhart and M. Fiebig, Phys. Rev. B **86** (2012), p. 235418

[4] A. Rubano, T. Günter, T. Fink, D. Paparo, L. Marrucci, C. Cancellieri, S. Gariglio, J.-M. Triscone, and M. Fiebig, Phys. Rev. B **88** (2013), p. 035405

[5] J.H. Haeni et al., Journal of Electroceramics **4** (2000), p. 385

[6] J. Choi et al., Appl. Phys. Lett. **79** (2001), p. 1447

[7] Y.R. Shen, Surf. Sci. 299/300 (1994), p. 551

[8] M. Radovic, N. Lampis, F. Miletto Granozio, P. Perna, Z. Ristic, M. Salluzzo, C. M. Schlepütz, and U. Scotti di Uccio, Appl. Phys. Lett. **94** (2009), p. 022901

[9] M.D. Biegalski, Y. Jia, D.G. Schlom, S. Trolier-McKinstry, S.K. Streiffer, V. Sherman, R. Uecker and P. Reiche, Appl. Phys. Lett. **88** (2006), p. 192907

[10] T. Hashimoto, T. Nishimatsu, H. Mizuseki, Y. Kawazoe, A. Sasaki and Y. Ikeda, Jpn. J. Appl. Phys. **44** (2005), p. 7134

[11] R. Woerdenweber, E. Hollmann, R. Ott, T. Huertgen and T.K. Lee, J. Electroceram. **22** (2009), p. 363

[12] M. Alexe and A. Gruverman, *Nanoscale Characterisation of Ferroelectric Materials* (Berlin: Springer, Germany 2004)

[13] T. Jungk, A. Hoffmann and E. Soergel, Appl. Phys. Lett. **89** (2006), p. 163507

[14] T. Jungk, A. Hoffmann and E. Soergel, New J. Phys. **11** (2009), p. 033029