Optics and Lasers in Engineering 104 (2018) 300–303

Contents lists available at ScienceDirect

Optics and Lasers in Engineering

journal homepage: www.elsevier.com/locate/optlaseng

Monitoring the interfacial electric field in pure and doped $SrTiO_3$ surfaces by means of phase-resolved optical second harmonic generation

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ARTICLE INFO

Keywords:
Second harmonic generation
RHEED
PLD
Epitaxial growth
Nonlinear optics

ABSTRACT

Oxides and new functional materials such as oxide-based hetero-structures are very good candidates to achieve the goal of the next generation electronics. One of the main features that rules the electronic behavior of these compounds is the interfacial electric field which confines the charge carriers to a quasi-two-dimensional space region. The sign of the confined charge clearly depends on the electric field direction, which is however a very elusive quantity, as most techniques can only detect its absolute value. Even more valuable would be to access the sign of the interfacial electric field directly during the sample growth, being thus able to optimize the growth conditions directly looking at the feature of interest. For this aim, solid and reliable sensors are needed for monitoring the thin films while grown. Recently optical second harmonic generation has been proposed by us as a tool for non-invasive, non-destructive, real-time, in-situ imaging of oxide epitaxial film growth. The spatial resolution of this technique has been exploited to obtain real-time images of the sample under investigation. Here we propose to exploit another very important physical property of the second harmonic wave: its phase, which is directly coupled with the electric field direction, as shown by our measurements.

1. Introduction

Film- and heterostructure-based device technology has grown exponentially in the past 15 years: today electronic, magnetic, optical, chemical and thermal properties can be controlled with unprecedented precision and easiness. In thin-films and multilayers, indeed, the thickness of the whole film and of the single layers can be controlled, yet many other important properties such as impurities, vacancies, dislocations and grain boundaries are not in full control, although they play an important role in determining the physical properties and the final device performance. Recent improvements in the deposition techniques developed several protocols for the best structural quality of oxide heterostructures, competitive with that of the best conventional semiconductors, thus opening new perspectives in the study of interfacial effects in such structures [1]. In-situ and real-time control of the deposition process is typically achieved by the Reflection High Energy Electron Diffraction (RHEED) technique. This technique is nowadays probably the most widely employed real-time diagnostic tool as it probes the superficial layer on the atomic scale [2,3]. Yet, it can give insight only on the structural and morphological aspects of the growth process. Moreover, its use in the industrial manufacturing environment can be very challenging. To overcome this limit, we recently proposed to use optical Second Harmonic Generation (SHG), which is a non-standard optical technique with inherently high surface/interface sensitivity [4–13]. So far, the spatial degree of freedom of SHG has been exploited in order to visualize a map of the in-plane polarization domains, showing the potential of SHG as a possible future in-situ monitor during the sample growth. This technique has been demonstrated in particular on one specific oxide material and its related heterostructures: the strontium titanate $SrTiO_3$ (STO). Anyway, it was not possible to distinguish the actual source of the imaging contrast hitherto, because a difference in the overall SHG yield in a given region of the sample can be ascribed both to a difference in the wave amplitude (related with the surface / interface polarizability) or to a wave interference (related to the presence of interfacial fields with opposite direction). In this manuscript we will stay focused on the same class of materials, but we will take advantage of one additional feature of the SHG light wave, which is its optical phase, as it is closely related with the sign of the interfacial electric field responsible of the charge carrier confinement in this class of materials. We investigate the amplitude and phase of the interfacial electric field on pure and Nb-doped STO which do have an opposite interfacial electric field direction, in order to demonstrate the potential of the phase-resolved SHG technique. Indeed, the generation of light with double frequency, in any material, requires a breaking of the inversion symmetry, which is intrinsically present at hetero-interfaces (STO-air in our case). As the single components are bulk-inversion-symmetric, the resulting total SHG yield will be generated exclusively in the interfa-

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http://dx.doi.org/10.1016/j.optlaseng.2017.06.025
Received 12 April 2017; Received in revised form 28 June 2017; Accepted 29 June 2017
Available online 6 July 2017
0143-8166/

cial region, providing thus a perfect background-free signal. The structural, chemical and electrical properties of $SrTiO_3$ have been studied more or less continuously since now about 50 years, so that we could consider this prototype perovskite an "evergreen" material. The reason for this peculiarity lies in a remarkably large coexistence of different properties which are of interest for very different research fields. Recently, a large amount of attention has been paid in particular to the electric properties of its surface and interfaces with other perovskites. Among many, we can cite (i) ferroelectricity: STO by itself it is not a ferroelectric, but rather an "incipient" or "quantum prevented" ferroelectric because at very low temperatures the ferroelectric state is prevented by quantum fluctuations, though it can be induced by strain [14]; (ii) phase transitions: when the STO surface is covered by a polar material it can experience an insulator-to-metal phase transition [15,16] showing an high-mobility 2D electron gas, which can even become superconductive at low temperatures [17]; (iii) surface electronic reconstruction: a similar effect does also take place in a vacuum-cleaved STO surface [18,19], and indeed the bare STO surface is still today extensively investigated as its properties are far from being understood [20]; (iv) device fabrication: by interfacing different oxide materials their physical properties such as charge, orbital and spin reconstructions, magneto-electric coupling can be easily tuned, and the possibility of patterning to design circuits of any kind has been demonstrated too [21].

Regarding the insulator-to-metal transition, one of the most popular models which have been proposed to explain the observations was the so-called "polar catastrophe" [22]: the stacking of charge-neutral atomic layers in (001) STO, and alternately charged atomic layers in the epitaxial oxide film (usually $LaAlO_3$, LAO) produces an electrostatic potential which diverges with the film thickness and quickly becomes the dominant energy in the system, so that some reconstruction must occur. This reconstruction can be structural, as happens for interfaces between polar and non-polar semiconductors, where the interface reconstructs atomically by changing stoichiometry and roughening, or it can be purely electronic, thanks to the peculiarity of transition metal ions to acquire a mixed-valence ionic character, whose charge balances the polar discontinuity. In the specific case of STO, the titanium ions shift from Ti^{4+} to Ti^{3+}. As this simple model is intriguing and certainly captures most physics of the observed phenomenon [23–25], it still cannot explain several observations. One of them is, for instance, the discovery of a similar 2D electron gas in the case of interfaces between STO and amorphous LAO: as the amorphous film does not obviously have any polar ordering, the electron of the 2D-gas were ascribed most likely to growth-induced oxygen vacancies [26]. Moreover, it was demonstrated [27] that charge injection takes place (in crystalline interfaces) for different surface orientations, such as (110), where no dipole discontinuity is present across the interface. The build-up of an interfacial electric field due to the presence of a polar overlayer seems to be elusive [28]. All these and others reports pose the quest for a more refined model.

2. Theoretical framework and experimental layout

Let us give a brief introduction to SHG theory and experiment. In the SHG process, two photons with frequency ω are mixed to create a single photon having double frequency 2ω. The detected SHG signal, that is the number of emitted 2ω-photons, is proportional to the absolute square of the second-order susceptibility tensor $\tilde{\chi}^{(2)}$ characterizing the interface. In the interfacial region between STO and air, where the inversion symmetry is broken, some specific $\chi^{(2)}_{ijk}$ components are nonzero. This nonlinear term in the wave-equation gives rise to a nonlinear, i.e., frequency-doubled, response [29]. Under dipole approximation the relationship between the incident optical field $\vec{E}(\omega)$ and the induced nonlinear polarization $\vec{P}^{NL}(2\omega)$ is described by the following constitutive equation:

$$P_i^{NL}(2\omega) = \varepsilon_0 \chi^{(2)}_{ijk} E_j(\omega) E_k(\omega) \quad (1)$$

The component $\chi^{(2)}_{ijk}$ of the nonlinear susceptibility tensor $\hat{\chi}^{(2)}$ couples j- and k-polarized contributions of the incident light field to an i-polarized contribution of the SHG light field. It is easy to show that the presence of an inversion symmetry in the system, i.e. a symmetry operation of the type $\vec{r} \rightarrow -\vec{r}$, implies that the tensor $\tilde{\chi}^{(2)}$ vanishes identically. We therefore safely assume here, and in the following, that $\tilde{\chi}^{(2)} \neq 0$ only within a thin interfacial (polar) region in which the inversion symmetry is removed, while both the substrate (the STO) and the air are centro-symmetric and hence have a vanishing $\tilde{\chi}^{(2)}$. For a given symmetry of the system (4mm in the STO case), it is possible to measure each single component of the $\chi^{(2)}_{ijk}$ tensor by an appropriate choice of the incoming and outcoming light polarizations, and to correlate the resonances of the SHG signal, measured as a function of the photon frequency, with the relevant electronic transitions of the system [8]. Anyway this will not be the aim of the present work. We measure the SHG yield far from any resonance of the system ($\hbar\omega = 1.5$ eV, $2\hbar\omega = 3$ eV), to ensure that we are collecting only the non-resonant contribution to the SHG, given by the interfacial polar asymmetry, regardless from any change in the electronic density of states and/or population of the two electronic states involved in a specific resonant transition. The two different sets of samples we investigated are: (i) label "STO", commercial pure STO (001) samples and (ii) label "StoNb", commercial STO:Nb samples with 0.2%wt nominal Nb doping. STO is a wide band-gap insulator that may become conductive by doping with Nb. The two sets of samples have been chemically etched in a similar fashion to achieve a chemically clean surface. The experimental layout is given in Fig. 1: the light source is an amplified pulsed laser (pulse duration - 35 fs, repetition rate - 1 KHz, pulse energy - <4 mJ, central wavelength - ~800 nm), the pulses are adjusted in energy (typical fluence of 10^{-2} J/cm^2) and in polarization by appropriate optical components, the SHG signal is spectrally separated from the reflected fundamental by colored filters and a monochromator, and finally revealed by a photon multiplier. The input-output linear polarization chosen for the here presented results was p-in p-out where p is the direction parallel to the incident plane. In order to measure the phase of the emitted SHG signal, a reference crystal, GaN(0001) - 100 μm thick, was placed on a motorized stage (remotely controlled) in order to generate a reference SHG signal by conversion of a fraction of the fundamental beam reflected by the sample. As the index of refraction n of the air is different for 800 nm and 400 nm light, the relative optical path d between the SHG light emitted by the sample surface and that emitted by the reference is given by: $d = x\Delta n$ where $\Delta n = n_{800nm} - n_{400nm} = 7.185 \times 10^{-6}$ is the index of refraction difference and x is the distance between the sample and the reference. By moving

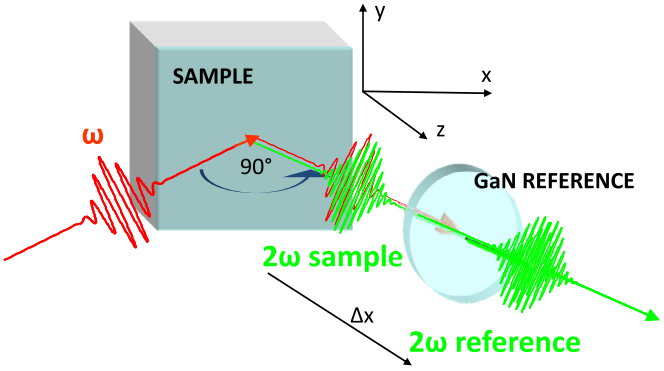

Fig. 1. Schematic picture of the experimental setup: the incident light at frequency ω generates light with double frequency 2ω at an angle of $\pi/2$. The reflected fundamental also generate a reference SHG by means of a GaN crystal after traveling in air and acquiring thus a phase shift of $n\Delta x$. The SHG signal is finally filtered and recorded as a function of the sample-reference distance Δx.