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Optical second harmonic imaging as a diagnostic tool for monitoring epitaxial oxide thin-film growth

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ABSTRACT

Optical second harmonic generation is proposed as a tool for non-invasive, non-destructive, real-time, in-situ imaging of oxide epitaxial film growth. The films can be monitored by surface imaging with a lateral resolution of $\leq$1 μm on an area of size up to 1 cm^2. We demonstrate the potential of the proposed technique by an ex-situ analysis of thin epitaxial $SrTiO_3$ films grown on (1 1 0) $NdGaO_3$ single crystals. Our data show that second harmonic generation provides complementary information to established in-situ monitoring techniques such as reflection high-energy electron diffraction. We demonstrate that this technique can reveal otherwise elusive in-plane inhomogeneities of electrostatic, chemical or structural nature. The presence of such inhomogeneities is independently confirmed by scanning probe microscopy.

1. Introduction

Monitoring the quality of evolving surfaces and interfaces is recognized today as a major challenge in materials science and technology, including surface catalysis, etching/corrosion, fracture formation, growth of nanostructures and of epitaxial thin films. The latter ones, in particular, are crucial for fabrication processes of countless cutting-edge applications, in fields such as nanoelectronics, sensing, microactuation, microelectronics, and so on [1]. For over 30 years, the reflection high energy electron diffraction (RHEED) technique has a leading role for real time monitoring of epitaxial film growth [2,3]. RHEED allows one to monitor the surface crystallinity of the growing sample. As discovered in 1981 by Harris and coworkers [4], the intensity of RHEED specular and/or diffracted spots can oscillate as a function of deposition-time, during a highly ordered layer-by-layer deposition process, with a period that corresponds to the coverage by a single growth unit.

Notwithstanding the tremendous contribution of RHEED to the improvement of epitaxial growth processes, scientists are in search of complementary methods, possibly offering spectroscopic and/or imaging capabilities [5] that standard RHEED systems do not provide.

Optical techniques are certainly good candidates for this purpose: visible photons can be manipulated easily compared to electrons, ions, neutrons, X-rays or sound waves and they travel almost unaffected through most gas environments and through glass windows, thus allowing one to employ tabletop sources and detectors placed outside the growth chamber. Today available laser sources and detectors provide high fluence and single-photon sensitivity. Unfortunately, applications to surface/interface science and in particular to film growth monitoring has been hampered so

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far by the probing depth of optical photons, typically too large to provide the required surface sensitivity.

In this article, the potential application of second harmonic generation (SHG) for monitoring the in-plane quality of transition metal oxide systems is discussed. Oxide materials and their interfaces [6] are emerging as next-generation functional systems in fields spanning from electronics to spintronics, sensing, microactuation and energy conversion. SHG is proposed here as a promising tool for real-time in-situ imaging of the growth process into, e.g., a pulsed laser deposition setup. While the capability to obtain spectrally resolved information is well established [7,8], we will focus on some other aspects such as surface sensitivity, acquisition time and imaging capability, that have not been addressed jointly, so far, in this context.

2. Second harmonic generation and oxide interfaces

Let us begin by giving a brief introduction to SHG. The second order contribution to the electric polarization generated in a material is proportional to the square of the electric field of the incident light wave. This gives rise to a nonlinear, i.e., frequency-doubled response [9]. The relationship between the incident optical field $\vec{E}(\omega)$ and the induced non-linear polarization $\vec{P}^{NL}(2\omega)$ is described by the equation:

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

The component $\chi_{ijk}^{(2)}$ 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. By exploiting the lateral degree of freedom of spatial resolution inherent to optical experiments we can visualize the in-plane spatial distribution of the interface-related SHG signal by imaging. This procedure is described in detail in Ref. [10]; in the following we will restrict ourselves to discussing the most relevant aspects for monitoring the growth process. Major parameters characterizing the growth quality test by SHG are its high lateral resolution of $\lessapprox 1\ \mu m$, its high sensitivity to chemical inhomogeneities, and its large acquisition area of up to 1 cm^2. As mentioned before, SHG shows an advantage with respect to other optical techniques for probing thin film growth: its interface-only sensitivity. In the leading order, $\hat{\chi}^{(2)}$ vanishes in centrosymmetric systems [9]. Since interfaces and ultrathin films inherently break the inversion symmetry, they generate a SHG signal that can be virtually free of any background contributions if the adjacent constituents are centrosymmetric, such as most metals, semiconductors, and oxides [7,8,11–13]. This consideration also implies that an *a priori* determination of the probing depth of SHG along the perpendicular direction is not possible: the signal is produced always within the interfacial layer, defined as the material volume in which the presence of an interface significantly alter the bulk material structure and properties [7]. The probing depth of SHG along the normal direction to the interfacial plane has been for instance demonstrated to be as thin as half a unit cell (few angstroms) by comparison between SrO and TiO_2 terminations in LAO/STO heterostructures [12]. In order to study the case of non-centrosymmetric materials, it is important to remark that different tensor components of $\chi_{ijk}^{(2)}$ can be measured by an appropriate choice of the input and output light polarizations: as the presence of the interface will, in general, change the symmetry, it could be possible to single out one (or more) specific tensor components, which could be still considered free from bulk background contributions. Anyway, this will not be discussed in the present work.

The few in-situ SHG experimental studies reported so far were limited to semiconductors [14] and ferromagnets [15], and lacking the lateral degree of freedom. Moreover, the SHG yield from semiconductors and simple covalent systems, or systems in which there is little or no residual dipole present in the unit cell, is pretty small. Therefore, considering the power limitations of the previously available laser sources, the imaging of large sample areas was not possible. Unlike semiconductors, oxides generally display pronounced polar asymmetries at interfaces, thus being an ideal material class for the application of SHG as an in-situ diagnostic tool. $SrTiO_3$ is often considered as the prototypical transition metal oxide. It is a very-high-K cubic perovskite exhibiting a number of quite remarkable properties, such as strain-induced ferroelectricity [16], blue luminescence [17–20], superconductivity [21], magnetism [22] and the formation of a highly mobile 2D electron gas [23]. In particular, for our case, $SrTiO_3$ is suitable for SHG characterization, as evidenced by recent investigations of the electronic reconstruction at the $LaAlO_3/SrTiO_3$ interface [7,8,11–13]. Our test system for analyzing STO growth is a batch of (0 0 1) oriented, Sr-terminated $SrTiO_3$ (STO) films epitaxially grown on Nd-terminated (1 1 0) $NdGaO_3$ (NGO) substrates (see Ref. [24] for details). The results reported in the following refer to two samples, one of which is shown to pass, and the other one to fail, the "homogeneity test" implemented by our SHG setup.

3. Experiment

The concept of the proposed experimental setup for SHG growth quality testing is depicted in Fig. 1. The setup we employed in this work is designed to be compatible with real in-situ growth geometric constraints in a real PLD chamber. In particular, as large illumination areas require long focal length lenses (500 mm in our case), all optics can be mounted outside of the chamber. The incident probing light is provided by an amplified laser system, with pulses of ~100 fs at ~1 mJ maximum energy with a repetition rate of 1 kHz. The typical pulse energy we employed for the measurements presented here is 30 μJ. The pulses are not focused onto a tight spot on the deposited film in our experiment, but instead they illuminated the entire growth area, ideally with a "top hat" intensity distribution. As a consequence, the typical laser fluence is about 0.1 mJ/cm^2. A separate power and spectral analysis of the output light confirmed the presence of a clear SHG spectral contribution, with no detectable contributions by luminescence or other sources of artifacts. After suppressing the fundamental light with optical filters, SHG is projected onto a liquid-nitrogen-cooled digital

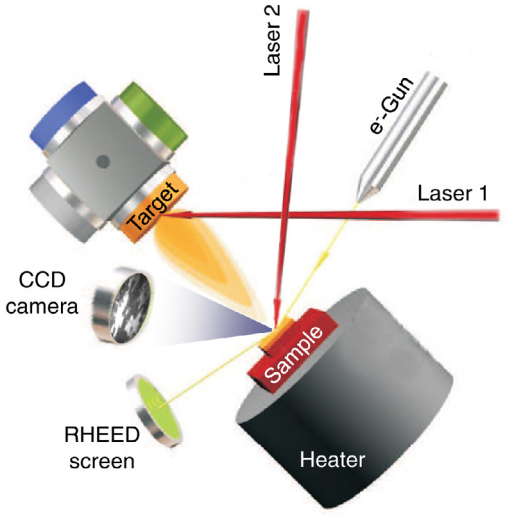

Fig. 1. Schematic layout showing a possible device concept for in-situ monitoring of epitaxial film growth by SHG. The usual geometry of the PLD chamber is not affected by the presence of an additional laser beam as both source and detector could be placed outside of the growth chamber.