MEASUREMENT

Application note

New insights into the electronic structure of the c-Si interface by optical second-harmonic generation spectroscopy at temperatures ranging from 4 K to 300 K

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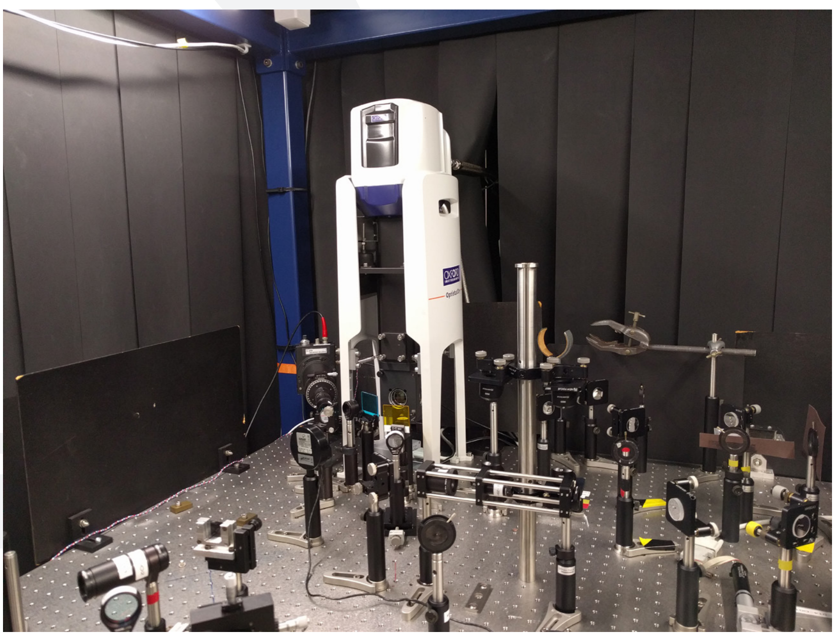
Introduction

This application note describes the characterisation of the c-Si/Al_2O_3 interface with the nonlinear optical technique of second-harmonic generation (SHG) spectroscopy at temperatures ranging from 4 K up to 300 K using the Oxford Instruments' **Optistat**™Dry **Cryofree**® cryostat. The buried silicon/dielectric interface plays a key role in the performance of most semiconductor devices and therefore its characterisation is essential. Valuable information on the structure, electronic properties, and built-in charge near this interface has been obtained by performing SHG spectroscopy over a wide temperature range.



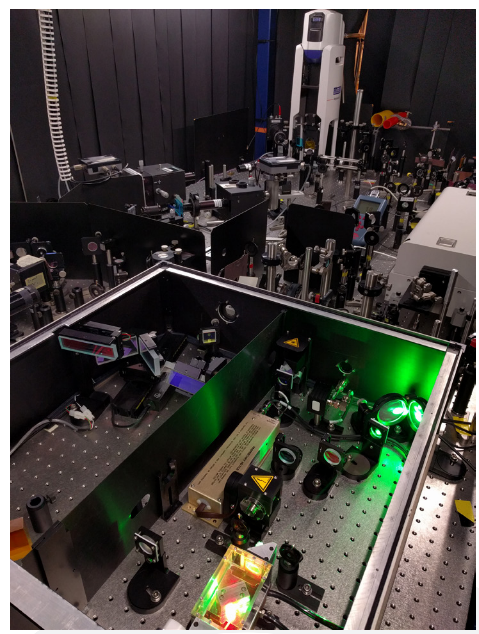


Figure 1: The SHG spectroscopy setup in which the Oxford Instruments' OptistatDry Cryofree cryostat was integrated.

Equipment used

Oxford Instruments' **Optistat**Dry **Cryofree** cryostat
Oxford Instruments' **FlexAL** atomic layer deposition (ALD) system
Oxford Instruments' **Mercury**iTC intelligent temperature controller

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Background: SHG of c-Si

In SHG, two photons from an ultrashort laser pulse mix to form a new photon at twice the photon energy, see also Fig. 2 (a). It can be shown that SHG is inherently interface selective in centrosymmetric materials such as c-Si, amorphous SiO_2, and amorphous Al_2O_3 due to its nonlinear nature. This property makes the SHG process excellently suited to study interface properties and phenomena. Typically, the SHG signal of an interface is very weak - it is an second-order phenomenon with a low cross section and it only takes place at an interface - but the SHG signal is resonantly enhanced by electronic transitions of interface states. Therefore, the electronic structure of the interface is reflected in the spectral shape of a SHG spectra. Moreover, it has been demonstrated that SHG is very sensitive to built-in charge near the interface due to the electric-field induced SHG (EFISH) effect in c-Si.

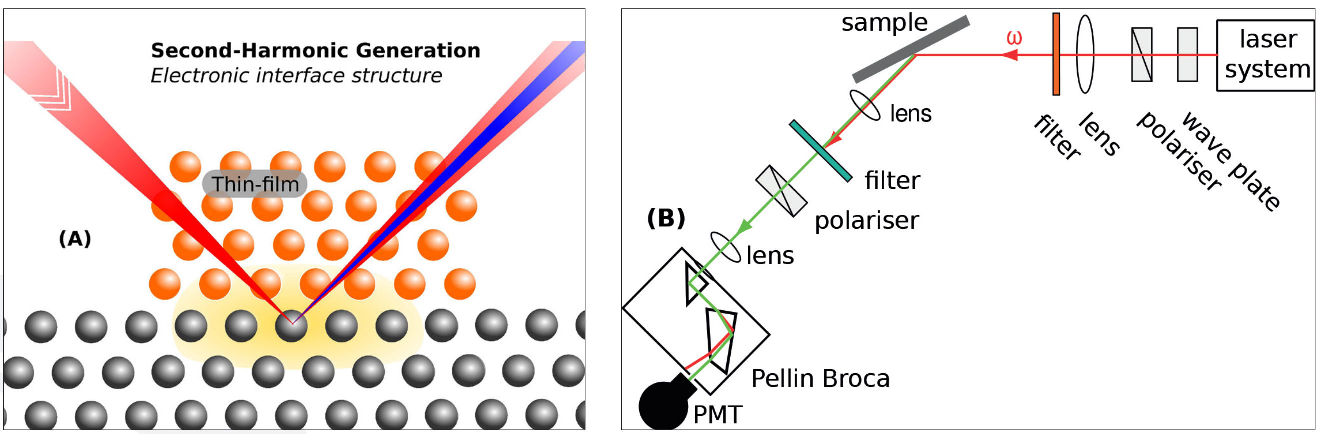

Figure 2: (a) Schematic representation of the SHG process in the geometry used in the experiments. A laser beam impinges on a sample consisting, in this case, of a substrate (c-Si) with a thin-film on top (SiO_2 or Al_2O_3). At the interface between the two materials a SHG signal is generated due to lower local symmetry; in the bulk of both materials no SHG signals are generated. This SHG signal propagates in the same direction as the reflected laser beam. (b) A schematic of the SHG setup into which the Oxford Instruments' **Optistat**Dry **Cryofree** cryostat was integrated at the location of the sample.

The capability of SHG to probe built-in charge without contacting the sample using the EFISH effect is of practical interest and it has been utilized to study the passivation properties of dielectrics such as Al_2O_3 for photovoltaic (PV) applications. To employ SHG as a metrology technique, however, a better fundamental understanding of the SHG response of silicon is required. The SHG response of the c-Si interface at room temperature is fairly well understood and typically shows an electronic transition at 3.3 eV. This transition is related to a surface state and it is similar in position to the bulk E1 transition although shifted by 0.1 eV to lower energies. Moreover, the aforementioned EFISH contribution is situated at 3.4 eV with its amplitude proportional to the built-in charge density. For virtually charge free samples such as Si(100) with a dry thermally grown SiO_2 film on top, the EFISH contribution is small. On the other hand, annealed Al_2O_3 films are known for their large amount of built-in charges resulting in an EFISH contribution dominating the SHG response. How the spectral SHG response of c-Si varies with temperature has not been studied extensively and might reveal if the E1-like resonance is composed of multiple contributions like its bulk counterpart. Therefore, the spectral SHG response of the prototypical c-Si/Al_2O_3 interface was studied using the **Optistat**Dry **Cryofree** cryostat at temperatures ranging between 4 K and 300 K.

Spectral SHG response of Si/Al²O³ between 4 K and 300 K

The Si/Al_2O_3 sample was prepared by growing a 30 nm Al_2O_3 film on a Si(100) substrate by plasma-assisted atomic-layer deposition (ALD) using an Oxford Instruments' **FlexAL**® system. To perform temperature dependent SHG studies, the Oxford Instruments' **Optistat**Dry **Cryofree** cryostat was integrated into our SHG setup. In Figure 2(b), the cryostat takes the place of the sample where the alignment of the sample is now done using the adjustable mount of the cryostat. For each measurement, the sample was mounted in the cryostat and the sample chamber was evacuated to a pressure $< 1 \cdot 10^{-6}$ mbar. The temperature of the sample was controlled between 4 K and 300 K using the He compressor and the Oxford Instruments' **Mercury**iTC temperature controller. The SHG measurements were performed using a 90 fs tunable laser system by stepping through the desired wavelength range while detecting the SHG signal using a single photon detector.

The temperature of the sample was stepped from 4 K up to 300 K and at each temperature a SHG spectrum was recorded. Figure 3 shows the SHG spectra acquired using this procedure. The spectrum recorded at 300 K is in-line with results obtained in a separate experiment without cryostat. The overall signal strength increased with decreasing temperature and a new feature appears at ~3.75 eV. At 4 K, the 3.75 eV contribution is dominant but an inflection point can be seen at 3.4 eV. This is similar to what is observed for the linear optical response of bulk c-Si and indicates that the E1 peak is actually a superposition of two contributions.

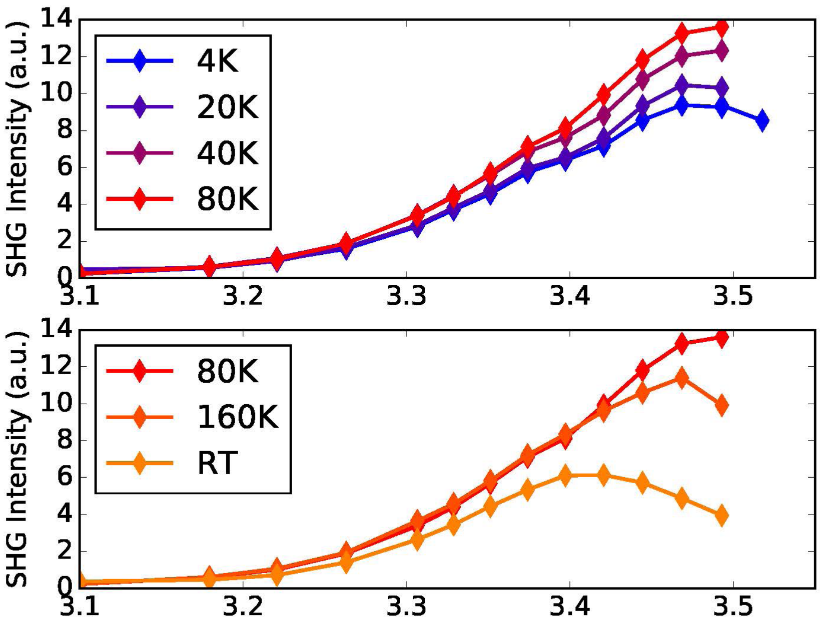

Figure 3: The SHG spectra acquired at selected temperatures between 4 K and 300 K of the c-Al_2O_3 sample using the Oxford Instruments' **Optistat**Dry **Cryofree** cryostat.

Conclusions and outlook

The temperature dependence of the spectral SHG response of the c-Si/Al_2O_3 interface was studied using the **Optistat**Dry **Cryofree** cryostat at temperatures ranging between 4 K and 300 K. The layout and design of the cryostat are such that it allows for easy (optical) access and alignment of the cryostat. As a result, it was easily integrated into the already existing SHG setup. The **Optistat**Dry **Cryofree** cryostat has extended our capabilities significantly and has led to new insights into the origin of the EFISH contribution. Since the sample can also be contacted electronically, unique opto-electronic experiments are possible in the future.

We also expect that the **Optistat**Dry **Cryofree** cryostat integrates well with our broadband sum-frequency generation (BB-SFG) setup. This nonlinear optical techniques probes the vibrational fingerprint of surface species such as -CH_3 and -OH groups using 90 fs laser pulses. Performing BB-SFG spectroscopy at low temperatures should allow the determination of fundamental parameters such the coupling between vibrational modes and vibrational dephasing times.

OptistatDry **Cryofree** cryostat

FlexAL atomic layer deposition (ALD) system

About the **Optistat**Dry **Cryofree** cryostat

The **Optistat**Dry provides a temperature controlled sample in vacuum measurement environment within a **Cryofree** cryostat. The **Optistat**Dry comprises a range of compact cryostats with optical access cooled by a closed cycle refrigerator. The system is capable of cooling samples to helium temperatures without the need for liquid cryogens. This provides significant benefits in terms of ease of use and running costs. The system enables optical and electrical measurements to be carried out on your samples, as shown in this application note.

About the **FlexAL** ALD system

Oxford Instruments' **FlexAL** systems provide a new range of flexibility and capability in the engineering of nanoscale structures and devices by offering remote plasma atomic layer deposition (ALD) processes and thermal ALD within a single ALD system. The Si/Al_2O_3 sample was prepared by growing a 30 nm Al_2O_3 film on a Si(100) substrate by plasma-assisted atomic-layer deposition (ALD) using **FlexAL** system, as mentioned in this application note.

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