Chapter 1

Introduction

1.1 Historical overview

A new branch of physics, nonlinear optics, was born in 1961 when Franken *et al*. [1] first demonstrated second-harmonic generation in a quartz crystal. Numerous nonlinear optical phenomena have been discovered since then. As laser technology progressed, nonlinear optics has become increasingly more mature and several comprehensive text books have been written on this subject [2-5]. Within the vast area of nonlinear optics, second-harmonic generation (SHG), or the frequency doubling of light, plays an essential role.

In 1962, theoretical investigations dealing with the behavior of light waves by solving the Maxwell's equations in a nonlinear dielectric and at the boundary of nonlinear media were perform by Armstrong *et al.* [6] and Bloembergen *et al*. [7], respectively. The classical laws of optical reflection and refraction were generalized to treat the nonlinear optical response. The predicted laws of nonlinear reflection were verified by Ducuing *et al*. [8] and both the real and imaginary parts of the complex nonlinear susceptibility were measured by Chang *et al*. [9].

SHG in a medium with a center of inversion symmetry was first observed by Terhune *et al.* in calcite [10]. They introduced a nonlinear term of quadrupolar origin in the form of a second-harmonic (SH) polarization proportional to the product of the fundamental field and its gradient. The most careful observation of the quadrupole effect in a phase matched propagation geometry in calcite was carried out by

Bjorkholm and Siegman [11]. In cubic and isotropic media with inversion symmetry, the quadrupole term does not give rise to transmitted harmonic radiation as the polarization source of the quadrupolar origin has only a longitudinal component.

Initial experiments on cubic centrosymmetric materials, particularly Si and Ge, were carried out by Bloembergen *et al.* [12]. The resulting SH signal was believed to originate solely from the nonlinear quadrupolar source term and independent of surface conditions. Moreover, the SH signal was found to be independent of the orientation of the surface cut with respect to the crystallographic axes. Wang first proposed that SHG from isotropic media originated from a surface dipole layer by inferring from studies on liquid-air interfaces [13]. The exist of a dipole layer at the interface responsible for the observed signal implies the surface sensitivity of this technique. The surface sensitivity of SHG was demonstrated by Brown and Matsuoka in 1969 [14] and by Chen *et al.* in 1973 [15] through observation of dramatic change in SHG upon surface modification.

The development of nonlinear optics during the decade of the sixties was followed by a decade with relatively little activity. Since 1980, the subject has experienced a period of continuous growth. As described by Bloembergen in a historical overview paper [16], for this topic one may designate the decade of the sixties as the period of “classical antiquity”, the seventies as the Middle Ages, with the renaissance starting in 1980. Downer described that today’s nonlinear optics is probably in “a new low” and a new era is about to begin [17].

The potential of SHG as a surface-specific tool was not fully exploited until the decade of the eighties. Shen [18, 19] and Richmond *et al.* [20] have reviewed the progress on SHG at interfaces of media with inversion symmetry made during the eighties. SHG as a surface probe has received much attention because of it simplicity, surface specificity, and versatility. In 1983, the potential of SHG was demonstrated for its surface-specific spectroscopy [21], and the ability to measure molecular adsorbate orientation [22]. The discovery of the dependence of SHG on crystal orientation by Guidotti *et al.* [23], however, showed that SHG has a bulk contribution. The anisotropic SH signal from both Si and Ge was observed by measuring the SH signal reflected from these surfaces while azimuthally rotating the substrates. The SH anisotropy was attributed to the bulk electric-dipole mechanism being permitted through inversion-symmetry breaking by high-density photo-induced carriers. The rotational-anisotropy SHG (RA-SHG) from Si surfaces was also demonstrated by Tom *et al.* [24], but the anisotropy of SHG was claimed to originate from the bulk quadrupole effect. The explanation of Litwin *et al*. [25] agreed with the bulk quadrupole model and it was generally accepted later.

If one intends to use the SHG technique as a probe for surface-specific properties, one must be able to distinguish surface and bulk contributions. Guyot-Sionnest *et al*. [26] discussed various conditions under which the surface contribution is expected to be large relative to the bulk contribution. Sipe *et al.* [27] developed a phenomenological theory of SHG for cubic centrosymmetric crystals and discussed the possibility of bulk and surface discrimination. It has been shown that separation of bulk and surface SH contributions is a problem of fundamental difficulty in the use of SHG as a strictly surface probe [28]. However, in most cases strict separation is not needed because the surface SHG usually dominates over the bulk SHG.

In recent years, SHG has matured into a versatile and powerful technique for probing the electronic and structural properties of surface or interfaces, as described in several excellent review papers [29-31]. With the advent of the mode-locked Ti:sapphire laser [32] and the tunable short pulse optical parametric amplifier/oscillator systems, spectroscopic SHG studies could be carried out over a wide wavelength range on important semiconductor interfaces. The demonstration of resonant enhancement of SHG at the Si-SiO_2 interface provided insight into electronic structures at the interface [33]. Microscopic theories have been developed to predict and explain the SH spectra [34, 35]. Among the later significant developments in Si surfaces, the studies demonstrating the dc field enhancement of SHG [36, 37] and the time-dependence of SHG [38] are related to this work.

1.2 This work

SHG has been recognized and used for more than two decades in basic research on the physical and chemical properties of surfaces or interfaces. Using the SHG technique as a surface-specific probe is based on the principle that SHG is electric-dipole forbidden in the bulk of media with inversion symmetry, such as Si and Ge, but allowed at the surface where the inversion symmetry is broken. Existence of the bulk SHG in the total SH signal is against the basic principle of surface selectivity of SHG, and it is generally believed to be a fundamental problem for using the surface SHG technique. Most previous surface SHG studies neglected or inadequately addressed the bulk SH contribution. However, we take advantage of the natural co-existence of bulk and surface SH contributions and use the interference between them to monitor the phase of the surface SH field. We also investigate the relative size of bulk and surface SH contributions by varying with photon energy.

We use the SHG technique to study the buried SiO_2-Si interface. Since the SHG technique is an optical probe, it can access buried interfaces if the top medium is transparent. The significant advantages of the SHG probe include capabilities of non-contact, non-invasive, and in situ sampling. Spatial and/or temporal resolution of the laser beam is also potentially attractive. The SiO_2-Si interface is of enormous technological importance to integrated circuit manufacturers. It occurs in the channel region of metal-oxide-semiconductor field-effect-transistors, which are the basic building blocks of modern integrated circuits.

Crystalline Si is one of the most intensively studied media, thus the medium properties can be easily related to the measured SH signal. Physical properties (density: 2.33 g/cm^3, melting point: 1415 ^{o}C, band gap: 1.12 eV, electron mobility: 1350 cm /Vs, hole mobility: 480 cm /Vs, resistivity: 2.5 x 10^5 Ω-cm, etc.) [39] and lattice structures and symmetry (structure: diamond structure with a=5.42 Å, space group: $Fd\bar{3}m$, crystal class: $\overline{m}3m$ (international notation) or O_h^7 (Schonfliess notation), symmetry formula: $3L_4 4L_3 6L_2 9PC$) [40] are well known for single crystal Si. Our Si samples were provided by Virginia Semiconductor, Inc.

We study the SHG mainly from Si surfaces with (001) orientation. The SHG response from this surface can be characterized by a relatively small number of susceptibility tensor elements, which is an advantage in separating the bulk and surface SH contributions. Practically speaking, microelectronic circuits are built exclusively on wafers with the (001) orientation. The structural quality of SiO_2-

Si(001) interfaces is superior over SiO_2-Si(111) interfaces. The SH response of the Si(001) interface is usually much weaker than that from the more intensity studied Si(111) surface. SHG studies of the Si(001) surface have been comparatively few in number, incomplete, or controversial in significant ways. It is timely and important to perform a comprehensive spectroscopic SHG study on the technologically important Si(001) surface.

A good SiO_2-Si interface should be nearly atomically smooth, have as few electrically active defects as possible, and have a minimal concentration of carrier traps that can be charged, either permanently or temporarily. Charge trapping can modify the electronic state at the interface, which can be monitored by time-dependent SHG (TD-SHG). For oxidized Si surfaces, especially those with thin oxide layers, phenomenological susceptibility tensors are not constant values, because laser interaction with the interfacial medium may cause quasi-static time-dependent effects. For example, charge transfer by photo-injection across the SiO_2-Si interface may build up an effective dc electric field, which causes time-dependence of SHG.

This thesis is mainly a spectroscopic study of SHG from principal (flatcut) Si(001) surfaces. Some results of SHG on vicinal (miscut by a small angle from principal face) Si(001) surfaces are presented in an appendix. In addition to the SH intensity, we observe the variation of the phase of SH field with photon energy. By comparing SH signals from different surfaces, we investigate the relationship between the observed SH signal and the interfacial properties. Some of these results are also presented elsewhere in publications [41, 42].

We first discuss, in the next section, the general experimental setup used during the SHG experiments. In Chapter 2, we use a phenomenological theory of SHG to predict the symmetry property of SHG and extend to calculation of bulk and surface electric-field-induced SHG (EFISH) effects from either principal or vicinal Si(001) surfaces. In addition, we discuss the possibility of separating bulk and surface SH contributions and present methods for uniquely determining susceptibility tensor elements. In Chapter 3, we study bulk and surface contributions to resonant SHG from Si(001) surfaces and show that interference between bulk and surface contributions can modify the apparent spectrum obtained for a fixed azimuthal angle. In Chapter 4, we present the observation of the phase inversion in rotational-anisotropy SHG at Si(001) interfaces, which can be induced by either varying the photon energy or by surface modification. In Chapter 5, we compare RA-SHG spectroscopy and time-dependent SHG results from Cr-SiO_2-Si(001) structures with an ultrathin Cr coating film and SiO_2-Si(001) surfaces with coating. The difference in the SHG signal between Cr coated and uncoated samples was attributed to additional SH sources caused by the ultrathin Cr film. In Chapter 6, we study the effect of thermal oxidation of Si(001) samples on SHG. We show that RA-SHG, TD-SHG, and SHG spectroscopy depend strongly on the interface width caused by thermal oxidation. For the same sample, the resonant behaviors of SHG are polarization dependent. In Chapter 7, we summarize the results of SHG on Si(001) surfaces and their implications, and present our view of the weakness and strongpoint of the surface SHG technique. In the appendix, we present the results of SHG on vicinal Si(001) surfaces.

1.3 Experimental setup

SHG from Si surfaces is a very weak effect because the main SHG contribution comes from only a few monolayers of atoms with broken inversion symmetry. This requires the use of short pulsed lasers to generate high peak powers and photon-counting to detect the weak signals. SHG signals are collected as a function of the azimuthal angle of the sample and as a function of time with the same basic apparatus.

The apparatus for measuring SHG is shown in Fig. 1.1. This apparatus can measure both rotational-anisotropy SHG (RA-SHG) and time-dependent SHG (TD-SHG). Both of these are discussed in more detail in the following chapters. RA-SHG provides information about the symmetry of the interface and the interference of different SHG contributions. TD-SHG is sensitive to the carrier dynamics at the interface, which affects the SHG signal.

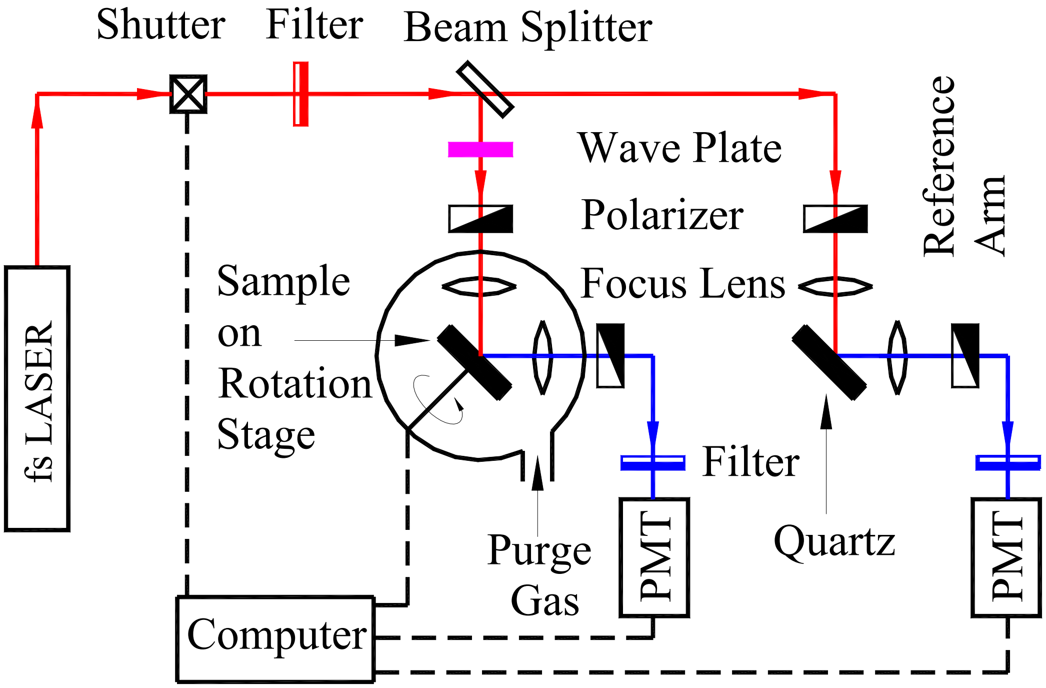

Fig. 1.1. Experimental setup for surface SHG. Components are described in text.

The laser pulses are generated by a Kerr-lens-modelocked Ti:sapphire laser (Coherent Mira 900). The Ti:sapphire laser is pumped by either an argon-ion laser (Coherent Innova 300) or a diode-pumped solid-state laser (Coherent Verdi V10). The pulse width is typically about 150 fs, but increases at edges of the spectral range to about 200 fs (more strongly at the blue edge). The pulse repetition rate is about 76 MHz. Output of the Ti:sapphire laser can be tuned from 700 to 900 nm (photon energies of 1.38-1.77 eV). An optical parametric oscillator (OPO) (Coherent APE OPO Basic) synchronously pumped by the Ti:sapphire laser is used to realize additional spectroscopic tuning. It is based on a collinear, noncritical phasematched process in KTP crystals and made for a frequency transformation from the Ti:sapphire range to 1050~1600 nm. To further extend the spectroscopic tuning range, a BBO crystal is used to double the frequency of the output pulses from the OPO to obtain pulses around 550 nm. A prism pair is used to compensate for the group-velocity-dispersion and simultaneously to eliminate unwanted spectral bands. If such a prism pair is not used, an important consideration in experimental design is to minimize the amount of material that the pulses traverse. Material group-velocity-dispersion stretches the pulses, thereby reducing the peak intensity and hence the nonlinear signal.

The laser pulses pass through a filter to remove any residual scattered background pump light. They are then split between signal and reference arms by a dielectric beam splitter that is designed to be 50% reflective at 750 nm. The beam in the signal arm passes through a half-wave plate and a polarizer before being focused on the sample. The focusing lens is a gradient index lens with a 10 mm focal length.

This lens is chosen to give the tightest possible focus while passing through the smallest possible amount of glass. It can produce close to a diffraction-limited spot of 4 μm. The beam is incident on the sample at an angle of 45^o from the surface normal. The reflected beam, which now includes SH light, is collimated by a UV-fused-silica lens. The reflected beam passes through a polarizer and then a filter that transmits the SH light while absorbing the fundamental light. The SH signal is detected using a photomultiplier tube (PMT) that has a photocathode with a large work function so that it is insensitive to the fundamental light (nevertheless multi-photon processes at the photocathode can result in a signal from the fundamental if it is too strong). The optical path of the reference arm, which is used for normalization, is essentially the same as the signal arm, with the exception that the half-wave plate is omitted. Neutral density filters are included in the signal arm before the sample to control the incident power onto the silicon samples. A neutral density filter is included in the reference arm after the sample to avoid overloading the detection electronics; there is no risk of damaging the quartz sample in the reference arm with the available power levels. SHG from the optical elements is unmeasurable, even if they had an SHG efficiency as high as silicon, the fact that they are only exposed to an unfocused beam means that their response would be several orders of magnitude less than that from the sample.

The average power on the sample is between 40 and 80 mW (varies with wavelength). At this power level, heating of the Si samples is negligible. Because of the tight focus and short pulses, these modest average power levels correspond to a peak intensity of 3 GW/cm^2.

The signals from both PMTs are recorded by a computer interfaced with photon-counting electronics. The computer controls a rotation stage on which the sample in the signal arm is mounted. The rotation axis is in the surface normal direction. This allows data to be collected as a function of the sample azimuthal angle for the RA-SHG measurements. The computer also controls a shutter in the incident laser beam. This is used for the TD-SHG measurements. It is also used to allow the sample to discharge in the dark before and between RA-SHG scans.

The polarization optical elements are used to select orientation of the excitation beams and to analyze the SHG beams. The polarizers in the incident beams are either borosilicate glass with aligned silver particles or Glan Thompson prisms. The half-wave plate is zero order to obtain the greatest possible bandwidth and is made from a birefringent polymer stack on BK7 glass to obtain as thin an element as possible. The polarizers in the reflected beams are Glan Taylor prisms.

The test sample is enclosed in a chamber that can be purged. This is required because different gases in the ambient may have different influences on the oxide charging phenomena and on the properties at the medium-ambient interface, which in turn affect the SHG signal. The laser beams enter and exit the purge chamber via 1.5 mm thick UV-fused silica windows. The stream of the purging gas is directed towards the sample in order to improve the purity.

A reference arm is introduced for spectroscopic calibration, as shown in Fig. 1.1. Variation of the pulse width and intensity with tuning of wavelength is normalized out by measuring the ratio of the SHG from the sample and the SHG from a z-cut quartz plate in the reference arm. Quartz is chosen here to generate the SHG for calibration because it is a wide bandgap (8.9 eV) medium [43, 44], thus dispersion of the linear and SHG susceptibility is small in the tuning range. In the reference arm, the polarization configuration is fixed to be p-in/p-out and the orientation of the quartz crystal is fixed at where the SHG signal is maximized as the crystal is rotated about its surface normal. The quartz plate is 1.5 mm thick. For one incident beam, there are two spatially separated linear or SH beams reflected from the plate: one from the front surface and the other from the back surface. The SHG signal reflected from the back surface is used for the spectroscopic calibration, because our measured SHG signal from the back surface is about 500 times stronger than that from the front surface. However, SHG spectroscopic behaviors are about the same for both beams.