

Chapter 6

SHG from thermally oxidized Si(001) surfaces

6.1 Introduction

Silicon plays an essential role in today's semiconductor industry. It is the inexpensive silicon CMOS technology that initiated and maintains the information revolution. However, the particular role played by silicon is not solely due to its superior properties as a semiconductor. The superior properties of silicon dioxide (SiO_2) and the quality of SiO_2 -Si interface greatly contribute to this role as well. The SiO_2 layer is a natural electrical insulator and a natural chemical protector, which is not only easy to produce but also stable and chemically very inert. The quality of the SiO_2 -Si interface depends strongly on processing conditions. The characteristics of the interface are critical in determining integrated circuit performance. However, the interface is buried below the oxide and thus not accessible to direct microscopic measurement. Based on the symmetry breaking at the interface, the nonlinear optical technique of surface SHG has been developed as a sensitive and versatile probe for buried interfaces. A number of experiments on SHG at the SiO_2 -Si interface have been performed showing the influence of interfacial stain [86, 87], charge and electric field [66, 76], preparation and interface roughness [57, 58], steps on vicinal surfaces [52, 88, 89], the possible presence of a crystalline oxide interface layer [55], and the oxide thickness [90-92]. These various observation and interpretations suggest that SHG at the SiO_2 -Si interface is a complex process of nonlinear polarization that is influence by multiple factors.

The observed SHG dependence on a particular interfacial property may not be attributed to that property alone but to incidental or alternative effects. For example, the sensitivity of SHG to interface roughness [57, 58] is possibly explained in terms of charge traps and electric-field-induced SHG. This happens because the SHG measurement is an indirect method for interface roughness. In order to use the SHG technique, one has to relate the measured SHG signal to the roughness being detected. It is convenient that interface roughness at the SiO₂-Si interface can be measured by x-ray scattering [93]. By combining SHG and x-ray scattering measurements, it has been shown that there is a monotonic correlation between SHG signal and interface roughness [57]. The observed trend is that the ratio of the isotropic to anisotropic SH coefficients increases as interface roughness decreases, which is consistent with earlier SHG measurements, where roughness was characterized by atomic force microscopy (AFM) [58]. However, this trend is opposite to our recent results of SHG on a series of thermally oxidized Si(001) samples. The samples are the same samples as before [57], but the laser used here is at shorter wavelengths. As has been shown, the SiO₂-Si interface becomes smoother with increasing oxidation time due to kinetic smoothing of the buried interface [93]. At first glance, interface roughness is well related to the SHG signal by performing SHG studies on the set of thermally oxidized samples. However, it is still not persuasive to say that interface roughness is the main factor of influence to SHG, because side effects, such as changes in charge traps and thermal oxides could cause variation of SHG as well.

In order to use SHG as a probe of the buried SiO₂-Si interface, it is important to understand how the oxide layer influences the total SH signal. Since the oxide

layer has a refractive index between air and Si, and is transparent throughout a large part of the spectrum, multiple reflection for both the fundamental and the SH beams should play a role. As has been shown, the observed periodic variation with oxide thickness of the (p, s) polarized SH signal from Si(111) surfaces [91] is explained by multiple reflection in the oxide film. It is important to note that in order to study only the multiple reflection effect, the structure of the SiO₂-Si(111) interface should be unchanged by varying oxide thickness because the (p, s) SHG from a Si(111) surface has both bulk and surface contributions [27]. Such a condition could be realized by etching the very thick oxide covering the Si sample down to the thickness needed.

In this chapter, we present a systematic study of the effect of thermal oxidation of the Si(001) surface on the SH response from the SiO₂-Si interface. The thermal oxidation time is controlled, so that the transition width from Si to SiO₂ (interface width) and the thickness of the thermal oxide are systematically controlled at the same time. Therefore, both the multiple reflection and interface modification effects may contribute to the dependence of SHG on thermal oxidation. To separate out only the multiple reflection effect, we use a combination of polarization selection and rotational-anisotropy SHG (RA-SHG). The (p, s) polarized RA-SHG from the Si(001) surface is generated only from the bulk, and interface modification is an irrelevant factor, thus multiple reflection is readily known from oxide thickness dependence of SHG. We use the (p, p) RA-SHG signal to study the influence of interface conditions on SHG and find that larger interface width corresponds to stronger SHG signal. By comparing time-dependent SHG (TD-SHG) signals from samples with different thicknesses of thermal oxide, we show that samples with

thinner oxide have stronger charging effect [38, 66], which is explained in terms of interface width and related charge traps. By performing spectroscopic studies, we find that a peak of the RA-SHG signal can be turned into a valley by varying photon energy. The RA-SHG signal shows eightfold symmetry at a certain critical photon energy. This critical photon energy varies monotonically with thickness of thermal oxide thus providing a means of interface identification. To study the effect of thermal oxidation on the spectra of SHG, we measure the SH spectra on a very thick thermal oxide Si(001) surface under different polarization configurations. By comparison to thinner oxide Si samples, we show that both thermal oxidation and polarization configuration affect the SH spectra.

6.2 Sample preparation and experimental conditions

To study the effect of thermal oxidation on SHG from the SiO₂-Si interface, we prepared a series of Si samples with various thermally grown oxides. The Si(001) wafers, boron doped to 1-2 $\Omega \cdot cm$, were first cleaned in an H₂SO₄/H₂O₂ solution, followed by a 100:1 H₂O/HF dip. The oxides were grown by rapid thermal oxidation in a pure O₂ environment at a temperature of 1000 °C. The thickness of the oxide was controlled by oxidation time; longer oxidation time corresponds to thicker oxide. The thickness of the oxide was determined by ellipsometry. Interface width was measured using x-ray scattering [94]. The crystal orientation of the Si wafers was known from the sample supplier prior to the experiment.

The experimental setup was the same as in Chapter 1. RA-SHG curves were obtained by recording the SH signal as the sample was rotated about its surface normal. TD-SHG signals were obtained by sampling the SH signal as a function of

the time of laser illumination on the sample. The laser illumination started from time zero. The test sample was held in a chamber purged by N₂ to reduce O₂ induced charging effect.

6.3 Effect of thermal oxidation on SHG

Surface SHG experiments have shown that the thermal history plays a determinant role in the structures of the interfacial transition region between the crystalline Si substrate and the amorphous SiO₂ layer [95-100]. These SHG studies were performed on the Si(111) surface. For this interface, bulk and surface SH contributions can not be separated by selecting polarization; therefore, interpretation of the results was difficult. Such a difficulty is partially circumvented by using the Si(001) surface.

6.3.1 Isotropic and anisotropic SH contributions

SHG from bulk crystalline Si includes both anisotropic and isotropic components, but SHG from the Si(001) surface or interface is only isotropic. With the polarizations (*g* or *h*) limited to *s* and *p* states, the *h*-polarized SH fields $E_{g,h}^{(2\omega)}$ from a Si(001) crystal face for the *g*-polarized incident fundamental fields E_g can be written as (see Chapter 2)

$$E_{g,p}^{(2\omega)} = [a_{0,(g,p)} + a_{4,(g,p)} \cos(4\phi)] e^{i\delta_{g,p}} E_g^2, \quad (6.1)$$

$$E_{g,s}^{(2\omega)} = a_{4,(g,s)} \sin(4\phi) e^{i\delta_{g,s}} E_g^2. \quad (6.2)$$

Here ϕ is the azimuthal angle defined as being between plane of incidence and the

[100] crystal direction. The SH intensity is proportional to the magnitude square of the SH field. The coefficients a_0 and a_4 are the isotropic and anisotropic contributions to the RA-SHG signal, respectively. They are functions of the relevant susceptibility elements, Fresnel factors, and dielectric functions, as shown in Chapter 2. Here, a_4 is chosen to be real and positive (its phase is in δ), then a_0 is complex in general and can be split into real and imaginary parts, written as $a_0 = a_{0,r} + ia_{0,i}$.

We fit the measured (p, p) and (p, s) RA-SHG signals from the series of differently thermally oxidized Si(001) samples to Eqs. (6.1) and (6.2), respectively, and obtain the isotropic and anisotropic coefficients. Figure 6.1 shows $a_{0,r,(p,p)}/a_{4,(p,p)}$ and $a_{0,i,(p,p)}/a_{4,(p,p)}$ (upper panel), and $a_{4,(p,s)}$ (lower panel) as a function of oxide thickness at different two-photon energies: 3.44 eV, 3.40 eV, and 3.26 eV. For the (p, p) polarization, the multiple reflection effect is cancelled out by dividing the isotropic coefficient by the anisotropic coefficient. This is the reason for using the ratios $a_{0,r,(p,p)}/a_{4,(p,p)}$ and $a_{0,i,(p,p)}/a_{4,(p,p)}$ to characterize the SiO₂-Si interface. As shown, the coefficient $a_{4,(p,s)}$ increases with increasing oxide thickness, which is consistent with the prediction that the oxide layer functions as an antireflection coating. At a two photon energy of 3.26 eV, the magnitude of $a_{0,r,(p,p)}/a_{4,(p,p)}$ decreases with decreasing interface width. Note that thinner interface width corresponds to larger oxide thickness [57, 93]. Such a trend does not hold for all photon energies. As shown, at a two-photon energy of 3.44 eV, $a_{0,r,(p,p)}/a_{4,(p,p)}$ changes from negative to positive as the oxide thickness increases, which means that its magnitude is not a monotonic function of oxide thickness any more. For all these

photon energies, the magnitude of $a_{0,i,(p,p)} / a_{4,(p,p)}$ is relatively flat with increasing interface width, except that it drops to lower values when the oxide is very thin. The strength of the anisotropic and isotropic contributions to the total SH signal also varies with photon energy, as shown Fig. 6.1.

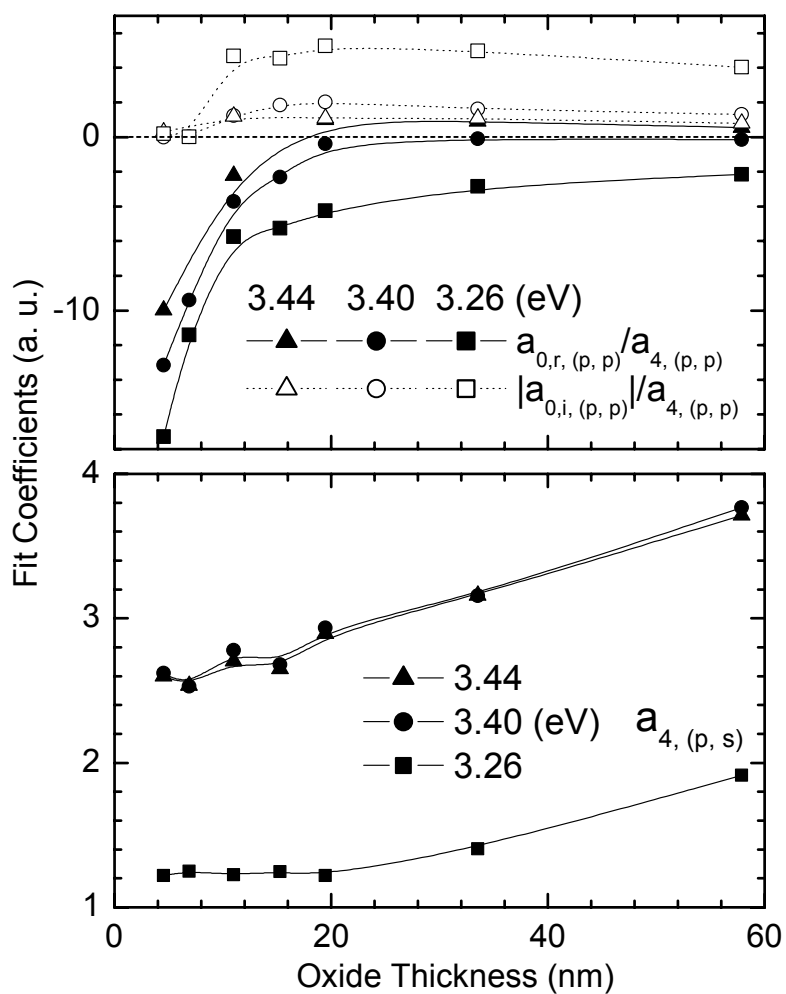


Fig. 6.1. Ratio of the isotropic to anisotropic SHG components for the (p, p) polarization (upper panel) and anisotropic SHG components for the (p, s) polarization (lower panel) as a function of oxide thickness at several two-photon energies: 3.44 eV, 3.40 eV, and 3.26 eV.

6.3.2 Phase inversion photon energy

The critical two-photon energy at which RA-SHG shows eightfold symmetry differs for different interfaces. For the (p, p) polarized RA-SHG, we observe that $a_{0,r,(p,p)}$ can be either positive or negative depending on the sample and on the photon energy. For a given sample, it is possible to find a critical photon energy, at which $a_{0,r,(p,p)}$ is zero, in other words, the RA-SHG signal shows eightfold symmetry. We name the critical photon energy as the phase inversion photon energy. As we showed in Chapter 4, phase inversion by varying photon energy happens for the (s, p) polarization. We show here that it happens for the (p, p) and (q, s) polarizations as well. In Fig. 6.2, the upper panel shows the variation of the phase inversion photon energy with oxide thickness for (p, p) , (s, p) , and (q, s) polarizations, and the lower panel shows the (s, p) RA-SHG curves from a 57.9 nm thick oxide covered Si(001) sample at different photon energies. The appearance of eightfold symmetry in RA-SHG curves is significant. A small deviation of photon energy from the phase inversion photon energy leads to a large change in the relative height between two adjacent peaks, which can be easily detected by eye. Therefore, the phase inversion photon energy can be accurately determined. Combining with the fact that it is sensitive to interface conditions (rather than oxide thickness), we can use it as a reliable probe for interface identification.

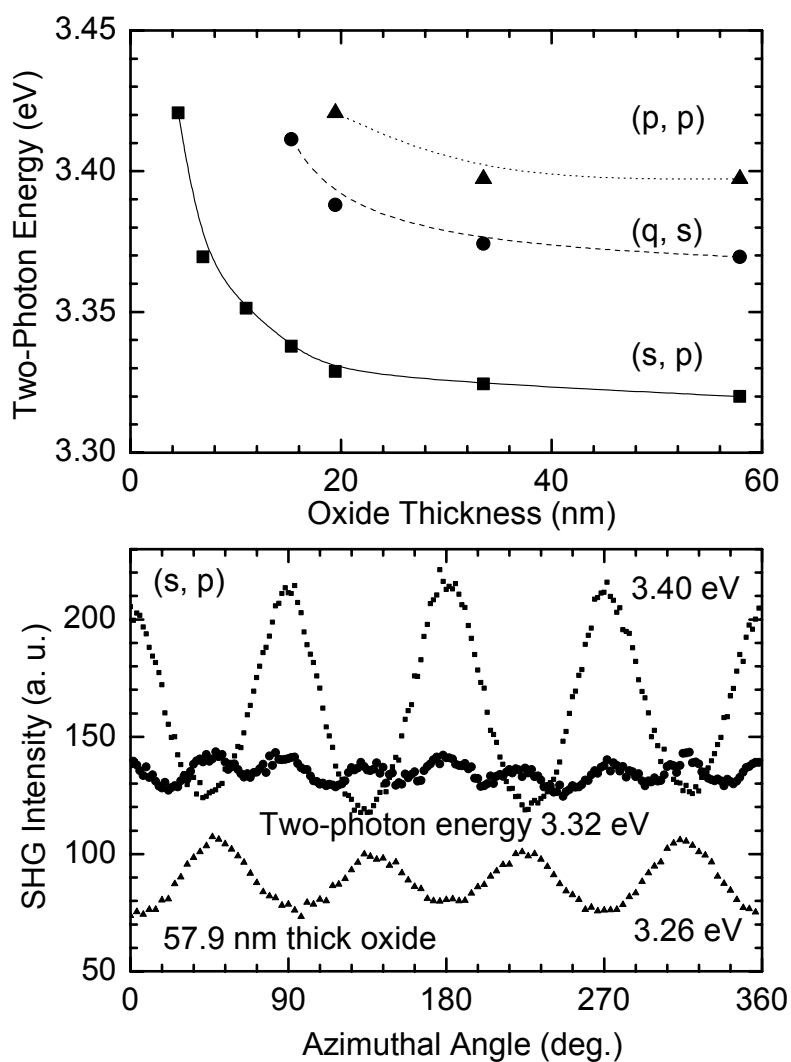


Fig. 6.2. Upper panel: oxide thickness dependence of the two-photon energy at which the RA-SHG signal shows eightfold symmetry for (p, p) , (q, s) , and (s, p) polarizations. Lower panel: RA-SHG signals from a thermally oxidized Si(001) sample with 57.9 nm thick oxide for the (s, p) polarization, showing either eightfold or fourfold symmetry.

6.3.3 Time-dependent SHG

Thermal oxidation greatly affects the time-dependent SHG (TD-SHG) signal, as shown in Fig. 6.3 for the (*p, p*) polarized TD-SHG signals from several Si(001) samples with different thicknesses of thermally grown oxide (and different interfaces) at a two photon energy of 3.26 eV. During the measurement, the azimuthal angle was fixed at a peak the RA-SHG signal. Before the TD-SHG measurement, the samples were fully discharged by leaving them in a dark environment for a long time. The fundamental beam started to continuously illuminate the sample at time zero. The SH signal was taken with a counting gate time of 0.5 sec. As shown, the TD-SHG signal increases rapidly with time and gradually saturates for samples with thin oxide layers, but it stays about the same value for samples with thick oxide layers. The saturated SH signal decreases with increasing thickness of the oxide layer, consistent with previous results [66]. The TD-SHG signal was measured in a N₂ (research grade purity) ambient, but no noticeable difference in the TD-SHG response was observed when the ambient was changed from N₂ to O₂. This suggests that the ambient-oxide interface is not likely responsible for the charge trapping, which makes the SH signal time-dependent. The stronger time-dependence of SHG from thinner oxide covered Si samples can be attributed to more charge traps at the SiO₂-Si interface. The number of charge traps is reduced by conducting high temperature oxidation for longer time. The observation of the time-dependence in SHG response indicates that the SH susceptibility at the SiO₂-Si interface is a dynamic rather than a static value for thin oxide covered samples. In addition, the measured SH signal depends on the charging history and the gate time of the counting system.

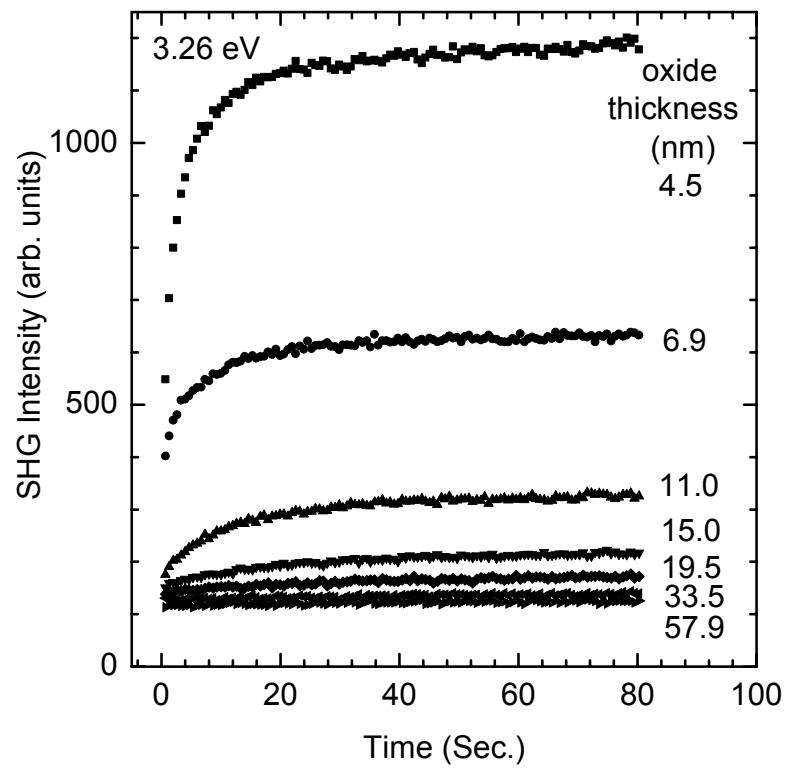


Fig. 6.3. Time-dependent SHG signal for the (p, p) polarization at a two-photon energy of 3.26 eV for several thermally oxidized Si(001) surfaces with different thicknesses of the oxide layer.

6.3.4 Effect of thermal oxidation on SHG spectroscopy

To systematically study the effect of thermal oxidation on SH spectra, we compare SHG from different samples. The SH spectrum is expected to change with interface conditions if the interface SH contribution dominates. Figure 6.4 shows the SH spectra from a Si(001) sample with 57.9 nm thick thermally grown oxide at a fixed azimuthal angle of 22.5° for different polarization configurations: (p, p) , (s, p) , and (q, s) . By choosing this azimuthal angle, the anisotropic SH signal is eliminated totally for the (p, p) and (s, p) polarizations and mostly for the (q, s) polarization. However, the measured SH signal still includes both bulk and surface contributions. Combining the SH spectra results in Chapters 3 and 4, we find that the resonant energy of 3.27 eV for the (p, p) polarization for the thick oxide sample is significantly red shifted from that for thin oxide samples, thus thicker oxide leads to a larger red-shift. This resonance is known as E_1 resonance because its energy is close to the E_1 critical point of the band-gap of bulk Si [68]. The directions of the observed strong energy and intensity variations of this resonance as a result of the different oxidation procedures are consistent with previous results [59]. The redshift in resonant energy was previously explained by oxide-induced lattice strain in the Si layers near the interface, leading to weakening of Si-Si bonds in these layers [33]. This explanation in terms of strain sounds reasonable, but it is probably hard to convince that it is the main effect because methods of direct measurement of the interfacial strain are very limited. The measured SH signal consists of bulk and surface contributions. In the case that there is charging effect, the electric-field-induced SHG should also be included and can be treated as an effective surface SHG. The bulk SH contribution

increases with increasing oxide thickness, but the measured total SH intensity drastically decrease with increasing oxide thickness. Therefore, the relative strength (including phase) between bulk and surface SH contributions varies strongly with oxide thickness. Interference between these two SH contributions can shift the measured resonant energy, as shown in Chapter 3.

In addition to the dependence of SH spectra on thermal oxidation, we find that resonant behavior of SHG depends strongly polarization configuration, as shown in Fig. 6.4. For the same sample, resonant energies and SH intensities clearly differ between polarizations. For the (p, p) polarization, the resonance energy is 3.27 eV, but for the (q, s) polarization, it is 3.33 eV. It is interesting to notice that this resonance almost disappears for the (s, p) polarization. At higher photon energies, the SH intensities for the (q, s) and (s, p) polarizations are much stronger than that for the (p, p) polarization. If the SH response is described by susceptibility tensors, polarization selection helps in discriminating among tensor elements. These results indicate that different tensor elements may have different spectra, and the relative importance of tensor elements depends strongly on photon energy. SHG responses for different polarization configurations represent different types of excitation and bond orientation. In addition, different orientation of the excitation field may have different ability on charge injection across the SiO₂-Si interface, which causes different band bending at the interface. For example, electrons can be excited more easily across the angstrom scale interface by an out-of-plane excitation field than an in-plane excitation field. Moreover, the relative strength between bulk and surface SH contributions may shift the apparent resonance.

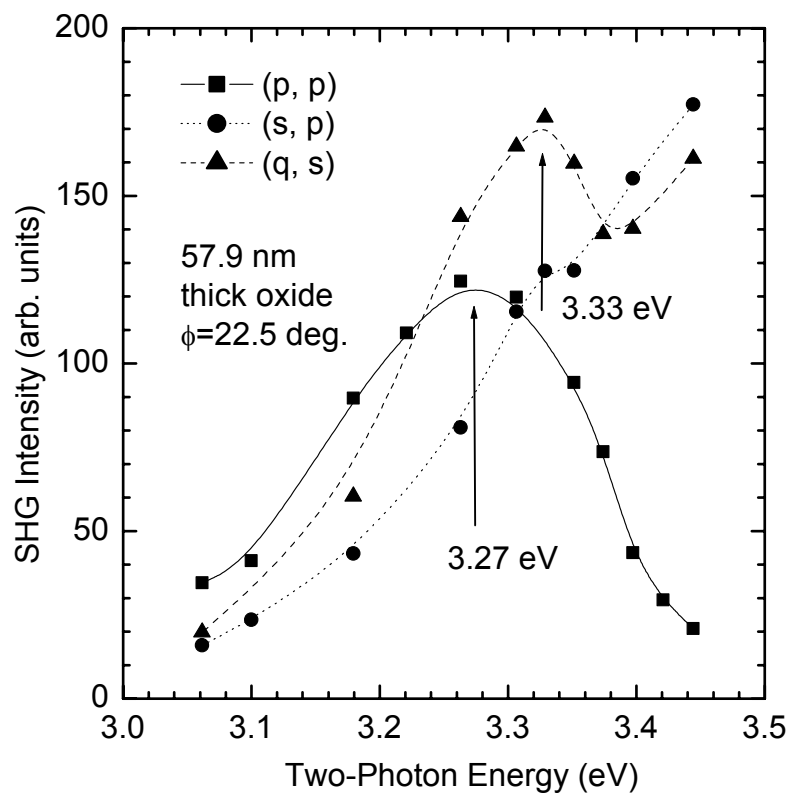


Fig. 6.4. SH spectra from a thermally oxidized Si(001) sample with 57.9 nm thick oxide at a fixed azimuthal angle of 22.5° for different polarization configurations: (p , p), (s , p), and (q , s).

6.4 Discussion

To explain the apparent discrepancy in the dependence of SHG on interface width between the new results and previous results [57, 58], we need to investigate the differences in experimental conditions and characterization variables used in these studies. The tunable photon energy used in this research is larger than the previous used the value of two-photon energy 2.92 eV [57]. However, photon energy in the vicinity probably does not affect the direction of variation of SHG with interface width because some photon energies used in this work are detuned from the resonance and no considerable variation with photon energy in the band from the present and previous photon energies is expected for linear and nonlinear optical properties. The observed trends of the SHG signal varying with interface width are similar for several photon energies, as shown in Fig. 6.1. The pulse spectral widths here are much narrower than the previously used pulse. The fit equations of the RA-SHG data are slightly different for the two studies. Using real isotropic fit coefficient for a_0 in the previous studies [57, 58] is apparently a crude approximation. When the (p, p) polarized RA-SHG signal shows eightfold symmetry at a certain photon energy, the isotropic and the anisotropic coefficients are 90° out of phase. This is a clear evidence of the phase issue in SHG. Taking into account the complex property of a_0 would be closer to the physical reality. We also notice that the anisotropic coefficients a_4 should increase with increasing thin oxide thickness because of the multiple reflection effect, but it was assumed previously to be independent of surface

preparation. These considerations may account for the discrepancy on whether the ratio $|a_{0,(p,p)}|/a_{4,(p,p)}$ increases or decreases with interface width.

The time dependence of SHG can be related to the interface width. Macroscopically, the volume of the medium with broken symmetry affects the SH intensity. Thermal oxidation performed with shorter time leaves more defects in the transition region, which can cause stronger charging effect. However, even the TD-SHG signal is taken with very short gate time so that the charging effect is negligible at the initial stage, the initial SH signal from samples with thinner oxides is still stronger than that from samples with thicker oxide. This is qualitatively understood in terms of the fact that the mobility of interfacial electrons is greater for thicker interface width than for thinner interface.

In the future work, we hope to study how the TD-SHG signals change with oxide thickness while the SiO₂-Si(001) interface stays the same. This can be done by using a series of samples prepared by etching a very thick thermally grown oxide on the Si(001) surface to various thicknesses. If the SH signal decreases with decreasing oxide thickness and the TD-SHG signal shows similar behavior of negligible time-dependence for different samples, our results in this chapter will be further confirmed.

6.5 Summary

We have studied the effect of thermal oxidation on SHG by using a series of Si(001) samples with different oxidation conditions. By comparing the (p, s) polarized RA-SHG, we found that multiple reflection in the oxide film enhances the measured SH signal. By comparing the (p, p) polarized RA-SHG, we found the

interface condition can be characterized by the ratio of the isotropic coefficient to the anisotropic coefficient (multiplication effect is cancelled out). Through spectroscopic studies, we found that the RA-SHG signal can be either fourfold symmetric or eightfold symmetric depending on photon energy. This leads to the important issues of the relative phase between the isotropic and anisotropic SH contributions. Eightfold symmetric RA-SHG signals were found for all the (p, p) , (s, p) and (q, s) polarizations, and the corresponding photon energy varies monotonically with interface width, thus it provides a reliable way for interface identification. We showed that the time-dependence of the SH signal is stronger for a larger interface width. Thermal oxidation affects SH spectra and the resonant behaviors for the same sample are significantly different for different polarization configuration. These results suggest that surface SHG is a sensitive probe for oxidized Si interfaces, but a probe with multiple effects.