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Second harmonic generation as a surface probe

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Second harmonic generation as a surface probe

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San Jose State University, 1990

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**SECOND HARMONIC GENERATION
AS A SURFACE PROBE**

A Thesis

Presented to

The Faculty of the Department of Physics
San Jose State University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

By

Heung-Rae Lee

August, 1990

APPROVED FOR THE DEPARTMENT OF PHYSICS

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ABSTRACT

SECOND HARMONIC GENERATION AS A SURFACE PROBE

by Heung-Rae Lee

As the need to characterize surfaces under various conditions continues to be significant, new and improved techniques are continuously being developed. The second order nonlinear optical techniques have gained attention during the past few years in addressing the above need.

This thesis embodies the experimental studies of the optical second harmonic generation (SHG) reflected from a y-cut crystalline quartz surface and from titanium (Ti) and titanium nitride (TiN) thin film surfaces. The quartz crystal was rotated about its surface normal and SHG was measured for various angles of orientation of the crystal under different input and output polarizations. The results show the basic symmetry of the crystal surface reflected in the second harmonic intensity variations. The data not only indicated the C_2 symmetry of the crystal surface but also the interference structure due to the birefringence of the crystal and the interference between the free and bound waves.

The experimental considerations are the sensitivity of the reflected SHG generated from solid Ti and TiN thin films and the dependence of that from TiN thin film on the thickness of deposition on aluminum and silicon substrates. The former measurement shows that SHG generated from TiN surface was significantly larger than from Ti surface and the latter does that the difference in increment of SHG with the thickness of TiN deposition is due to the different substrates.

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Chapter 1. Introduction

One of the most interesting applications of lasers is the investigation of nonlinear interaction with matter. This was the first demonstration in a set of experiments performed, soon after the invention of laser, by Franken et al.¹ and Kaiser and Garret.² These so called nonlinear optical effects were observable owing to the high power density of laser. When the electric field of radiation interacting with matter is comparable to "atomic fields" of the matter, the interaction leads to nonlinear effects. These effects include a wide range of phenomena, as we know it today, like second harmonic generation,¹ two-photon absorption,² third harmonic generation,³ and many other interesting diverse effects.⁴ Generally speaking, the nonlinear effects could be due to light induced population effects such as saturation or could be due to nonlinear response of individual molecules or unit cell. While the saturation effects are interesting and have a wide range of applications, it is the second category that is of interest to work reported in this Thesis.

Nonlinear interaction of molecules can be modeled classically as the result of anharmonicity in the restoring force experienced by electrons attached to the nuclei (or lattice). Quantum mechanically this process is described by the need to include higher order terms in the time dependent perturbation calculation. In simple terms, the incident radiation induces dipoles in the medium which are expressed in terms of induced polarization being proportional to the inducing field in linear optics. This induced polarization in turn leads to refractive index and absorption coefficient of

the medium in which the radiation is propagating. Equation 1-1 shows this relationship

$$\mathbf{P}^{(1)} = \mathbf{X} : \mathbf{E} \quad \text{-----} \quad (1-1)$$

where $1 + \mathbf{X} = \boldsymbol{\epsilon} = \mathbf{n}^2$ (refractive index). $\mathbf{X}$ is called the first order susceptibility of the medium. As the incident field strength is increased, Equation 1-1 is no longer appropriate to use and instead one should consider that the induced polarization is expandable in Taylor series as a function of the field strength. This expansion, of course, assumes that the series is convergent and successive terms are smaller compared to preceding ones. Some of saturation effects, for example, do not satisfy this requirement.⁵ Therefore, one can write

$$\begin{aligned} \mathbf{P}_{\text{total}} &= \mathbf{P}^{(1)} + \mathbf{P}^{(2)} + \mathbf{P}^{(3)} + \dots \\ &= \mathbf{X} : \mathbf{E} + \mathbf{X}^{(2)} : \mathbf{E} \mathbf{E} + \mathbf{X}^{(3)} : \mathbf{E} \mathbf{E} \mathbf{E} + \dots \quad \text{-----} \quad (1-2) \end{aligned}$$

for the induced polarization, and $\mathbf{P}_{\text{total}}$ thus calculated is used as the source term in the wave equation to complete the calculation of radiated fields which are related to observed signal. The effects attributable to the second term in Equation 1-2 are called second order nonlinear optical effects (SNLO). These include second harmonic generation (SHG) where twice the incident frequency is generated; sum-frequency generation (SFG), difference-frequency generation (DFG) where sum and difference between two incident frequencies are observed. The effects attributable to the third term are referred to as third order nonlinear effects. Raman scattering, optical phase conjugation, and self-focusing are examples for this category.

Symmetry considerations show that while $X^{(3)}$ is always non-zero, $X^{(2)}$ is non-zero only when the medium lacks inversion symmetry (this conclusion is strictly correct in the electric dipole approximation; all even order terms in expansion should vanish in this approximation). A large class of crystals do lack such inversion symmetry, thus are utilized in applications dealing with second harmonic generation and parametric conversion.^{6,7} On the other hand, the fact that $X^{(2)}$ is zero in the centrosymmetric media can be effectively exploited in the surface sciences, where surfaces and interfaces necessarily lack inversion symmetry. The first experimental observation emphasizing this aspect were reported in 1960's⁸⁻¹¹ while the mathematical formulation of SNLO was given by Blembergen and Pershan in 1962.^{12, 13} With the need to develop techniques which are non-destructive, in situ, in surface science studies, SNLO techniques have become very useful surface probes during the past several years.¹⁴ The advantages of SNLO techniques in the study of surfaces are surface specificity, mono-layer sensitivity, spectroscopic capability, and high spatial and temporal resolution.

SNLO techniques have been successfully used in studies of electro-chemical process,¹⁵ adsorption-desorption kinetics of molecules on clean surfaces^{16, 17} and in solid-liquid interfaces,¹⁸ reconstruction of crystalline solid surface after laser-damage,¹⁹ and in studies of organization of assemblies of molecules on liquid surfaces,²⁰ spectroscopy of molecules adsorbed on solid surfaces,²¹ molecular vibrational relaxation at metal surfaces,²² and many more.

This Thesis embodies experimental results of second harmonic generation studies performed on single crystal quartz surface and thin film samples as described in the subsequent chapters. Experimental details are described in Chapter 2 followed by quartz crystal measurements and thin film measurements presented in Chapter 3 and 4, respectively.

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Chapter 2. Experimental Methods and Apparatus

2-1. Introduction

The experimental work presented in this Thesis consists of measurement of second harmonic radiation generated (SHG), mainly in reflection mode, by solid materials that are either crystalline or thin films. As discussed in the introduction, the SHG signals are generally weak when the contributions are strictly from surface and as such a measurement of SHG involves careful selection and arrangement of apparatus. In any nonlinear optical experiment, the signal generated is proportional to some power of the incident field intensity; for example, SHG signal is proportional to square of input intensity at the fundamental frequency. On the other hand a given material surface has a certain damage threshold which is proportional to fluence (energy per unit area) of the incident radiation.¹ An order of magnitude estimate of the signal levels expected in an experiment can be made easily with the help of the relation

$$S(2\omega) = \frac{32\pi^3\omega \sec^2 \theta_{2\omega}}{\left(\frac{h}{2\pi}\right)C^3 \epsilon_1^{\frac{1}{2}}(2\omega)\epsilon_1(\omega)} |e(2\omega) \cdot \chi^{(2)}:e(\omega)e(\omega)|^2 I^2(\omega) AT \quad -- (2-1)$$

where θ is the angle of reflection for SH signal, h is Plank's constant, $\epsilon_1(2\omega)$ and $\epsilon_1(\omega)$ are dielectric constants of a medium at the frequency 2ω and ω , respectively, $S(2\omega)$ is the number of photons at the second harmonic frequency generated per pulse, $I(\omega)$ is the incident field intensity, A and T are the excitation beam area and pulse width, and $\chi^{(2)}$ is the second order susceptibility tensor characterized by the medium.² The vectors $e(\omega)$ and $e(2\omega)$ are related to the unit polarization vectors

coefficients determined by continuities of electric and magnetic fields at the boundary. On the assumption that the surface contribution to $X^{(2)}$ is dominant, the strength of SH signal $S(2\omega)$ can be estimated with known values of $X^{(2)}$, $I(\omega)$, A , and T . If $X^{(2)}$ is known as $\sim 10^{-14}$ esu, $I(\omega) \sim 10$ MW/cm², $A \sim 0.03$ cm², $T \sim 10$ nsec, and $\theta \sim 45^\circ$, then $S(2\omega)$ is of the order of 10^3 photons/pulse.

The experimental arrangement is depicted schematically in Figure 2-1. The optical alignment was optimized to generate and detect SHG, to prevent the target samples from being damaged, and to keep the consistent relationship among the input power, the characteristics of samples, and the detected SH intensity. To avoid the damage on the sample surface, the reduced and collimated beam was used. The desired polarizations of the input fundamental beam and of the output SHG were selected with Glan-Taylor polarizers. The incident angle of the fundamental beam on the sample surface was 45° and SHG was measured at an angle of 45° , collinear with the fundamental, because dispersion of air is negligible. The measurements were performed by rotating the sample about the axis normal to the surface. SHG was filtered by a monochromator and detected by a photo-multiplier tube (PMT). The output of PMT was fed into a gated integrator controlled by a computer. The instrumentation and the optical assembly will be described in detail in Section 2-2 and the experimental consideration be narrated in Section 2-3. Table 1 (page 30) shows the summarized details of experimental apparatus and optical assembly.

2-2. Experimental Apparatus

2-2-1. Q-switched YAG Laser

The technique of Q-switching is used to obtain intense and short bursts of oscillation from lasers. If the active medium is continuously pumped keeping the shutter closed, the population inversion in the cavity keeps on increasing and reaches a high value.³ If now the shutter is suddenly opened, the inversion would correspond to a value much above the threshold and the energy stored in the cavity will be released in the form of a short pulse of light with a high peak value of intensity. The laser was a Q-switched Nd:YAG oscillator delivering over 320 mJ at 1,064 nm. The system can operate at several repetition rates with a nominal pulse length of approximately 12 ns. Figure 2-2 shows the laser layout. The oscillator consists of several optical and electrical components: hard coated flat and convex mirrors, an electro-optic Q-switch, a quarter-wave plate, 7 mm aperture, and laser head. The electro-optic Q-switch consists of a KDP longitudinal field Pockels Cell, a coated Glan-Taylor polarizer and high voltage power supply board.

Figure 2-3 schematically describes the principle of operation of Q-switch.³ Depending on its orientation, the polarizer is highly transparent to one component of the laser light (typically horizontal) when no voltage is applied to the Pockels Cell. A beam propagating within the oscillator cavity makes a double pass through the quarter-wave plate for a net rotation of 90° in polarization. Thus rotated, the beam is rejected by the polarizer and no lasing occurs. When a high voltage (about 3600 V) is applied to the Pockels Cell, the Pockels Cell acts as a quarter-wave plate.

A further rotation of 90° takes place in the polarization of the beam. Thus the beam is free to propagate and Q-switched lasing occurs.

2-2-2. Optical Assembly

Optical alignment is shown in Figure 2-1. To control the polarization and intensity of the laser beam, two Glan-Taylor polarizers were used. The orientation of the polarizer-2 as an analyzer determines the polarization of the laser beam available for experiments and that of the polarizer-1 varied the intensity of the beam. An IR beam splitter separated the polarized laser beam into two. The reflected beam was used for the reference signal to normalize SHG signal which was generated on the surface of the target sample by the transmitted beam. The purpose of using a Galilean telescopic optical alignment was to reduce the diameter of the beam from 1 cm to 0.2 cm, and to collimate the laser beam. The optical elements used to make the telescope were a 250 mm focal length positive lens and a 50 mm negative lens. While the beam passed through a low pass filter, the filter removed from the laser beam any green light which could contaminate the experimental results. After passing through the filter, the power of the collimated beam is reduced to 4.4 % of that measured before the beam collimator. Thus, the actual peak intensity range to generate SHG is 6.4 MW/cm^2 to 64 MW/cm^2 .

The reflected SHG propagated in the same direction as the reflected fundamental beam.⁴ The IR reflector dumped out the reflected fundamental beam from the reflected beam arising from the target sample to prevent the reflected fundamental beam from generating SHG in the

optical materials. To increase the collecting efficiency of the monochromator, a lense imaged the SH source on the surface of the sample on the entrance slit of the monochromator which had been previously tuned to the desired wavelength of 533 nm. The effect caused by the angular deviation in incident angle was minimized with this optical alignment. After the desired polarization of SHG was selected by the analyzer, SHG passes through a monochromator for spectral filtering and is finally detected by a PMT. The output signal of the PMT was fed into a gate integrator and processed by a computer.

2-2-3. Gated Integrator/ Boxcar Averager

A gated integrator was used to recover fast and short pulsed signals from noisy background.⁵ The gated integrator consists of a gate generator, and an exponential averaging circuit. The gate generator is externally triggered by TTL pulse coming from the electro-optical Q-switch. Figure 2-4 shows the schematic function of the gate integrator with the pulse intensity of a repetitive train of light pulses.⁶ When triggered, the unit generates a gate and the input signal is sampled and integrated while the gate is on. In practice, the capacitor in the exponential averaging circuit charges up and holds the input signal until the next sample is taken. This signal will leak away due to the finite time constant of circuit. Thus the voltage on the capacitor after n samples is

$$V_C = V_i \{ 1 - \exp(-nT_s/\tau) \} \quad \text{----- (2-2)}$$

where n is the number of samples, T_s is the gate width of the sampling pulses, and τ is the time constant to charge up the capacitor. The averaged

output provides an exponentially moving average over the number of samples specified by the samples selector. The delay from the input trigger to the start of the sample gate is set by the delay control for the exact timing relation of the sample gate with respect to the signal.

2-3. Experimental Methods

2-3-1. Confirmation of SHG

To confirm that SHG is selectively detected, the shape of, the tunability of, and the input-intensity dependence of the detected signals are considered.

Since a coherent input field generates the second harmonic pulse, the detected pulse should have the same shape as the input pulse whose pulse width is not more than 12 ns and be also coherent and highly tunable. Figure 2-5 shows the high tunability of SHG arising from the quartz surface. The δ -function-like peak at the wavelength of 533 nm is the expected result for SHG. As shown in Figure 2-5, however, the peak has the band width of 4 nm which is produced by the size of slits of the monochromator. It is necessary to widely open the slits to enclose the full image of the SH source on the sample target.

The intensity of SHG is proportional to the squared value of the nonlinear polarization $P^{(2)}$, and thus expressed as

$$I(2\omega) \propto [P^{(2)}]^2 \quad \text{-----} \quad (2-3).$$

Since $P^{(2)}$ is also proportional to $[E(\omega)]^2$ as shown in Equation 1-1, $I(2\omega)$ can be rewritten as⁷

$$I(2\omega) \propto [E(\omega)]^4 \propto [I(\omega)]^2 \quad \text{-----} \quad (2-4).$$

Figure 2-6 shows the linear relationship, called the sensitivity of SHG, between the square of input power and the SH intensity. The high correlation coefficient greater than 0.99 proves that the detected signal has the linear functional dependence.

2-3-2. Sample for Experiments.

The target quartz crystal sample was cut along a (010) crystallographic orientation in order to have the optic axis parallel to the crystal faces. The dimensions of the thin quartz plate were 2.540 ± 0.001 cm in diameter and 0.100 ± 0.001 cm in thickness. A mount was constructed for the quartz element to provide complete 360° of rotational freedom along an axis perpendicular to the crystal surface, as shown in Figure 2-7. Measurements were made with selected polarizations of excitation beam and SHG signal. Four combinations of polarizations of input and output field are possible, p- and s- polarized input $E(\omega)$, and p- and s- polarized output $E(2\omega)$.

The thin film samples are titanium (Ti) and titanium nitride (TiN) wafers and the wafers of TiN thin film on different substrates, silicon (Si) and aluminum (Al). The solid wafers are of dimensions 10.00 or 15.00 ± 0.01 cm in diameter and 0.030 ± 0.001 cm in thickness for different film. The range of film thickness used is 45 to 450 Angstroms. Since Ti and TiN have low resistivities of 45 and 150 m Ω cm, respectively, the s-polarized input beam cannot generate SHG nor can s-polarized SHG be generated on the surface. Therefore, the combination of p-polarized input $E(\omega)$ and p-polarized output $E(2\omega)$ is chosen for the experiment.

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Chapter 3. SHG Arising from Quartz Crystal

3-1. Introduction

As indicated in the introduction in Chapter 1, second order nonlinear optical (SNLO) techniques are very powerful in the studies of surface science owing to their surface specificity and mono-layer sensitivity. More appropriately, the SNLO signal measured is due to several contributions. The total signal measured could be thought of arising from an effective second order susceptibility given by

$$\chi_{\text{eff}}^{(2)} = \chi_{\text{bulk}}^{(2)} + \chi_{\text{surf}}^{(2)}$$

and the corresponding nonlinear polarization $\mathbf{P}^{(2)}$ can be expressed as

$$\mathbf{P}^{(2)} = \mathbf{P}_{\text{bulk}}^{(2)} + \mathbf{P}_{\text{surf}}^{(2)}$$

where $\mathbf{P}_{\text{surf}}^{(2)}$ is the polarization produced by the surface or interfacial region and $\mathbf{P}_{\text{bulk}}^{(2)}$ is due to the bulk material. The bulk contribution may be due to the bulk having no inversion symmetry as is the case for the quartz experiment reported in this chapter. The surface term which invariably has some bulk contribution comes from structural and field discontinuity at the surface as well as due to the adsorbates which may have no inversion symmetry by themselves on the surface.

Generally speaking, this surface term, even in the absence of adsorbates, will have contribution from dipole allowed processes as well as a quadrupolar type contribution due to the field variation near the surface. These two surface and bulk contributions cannot, in general, be separated.¹⁻³ Recently, several experimental studies showing the relative contributions of various terms discussed above have been performed.⁴⁻⁶ While the above studies are concerned with bulk materials with no

inversion symmetry (hence with no dipole allowed in bulk), SHG from noncentrosymmetric media was used as a surface probe reported in experiment of GaAs crystal which is cubic and noncentrosymmetric.⁷ The experimental work reported in this chapter was done on quartz crystal which is noncentrosymmetric as well as birefringent. The object of the experimental work is to compare the bulk and the surface contributions from noncentrosymmetric birefringent crystalline surface.

3-2. Experimental Results

The basic experimental setup for SHG in reflection from the quartz single crystal was shown in Figure 2-7. The quartz crystal supplied by CVI Lasers has a measured thickness of 1.00 mm and is y-cut (the crystal z-axis called c-axis is in the plane of the reflecting surface). SHG measurements were performed as a function of the angle of rotation about the axis perpendicular to the reflecting surface (x-z plane of the crystal) in step of 2° with a resolution of 1° .

Figures 3-1 a) to d) show the measurements of the reflected SH signal for four combinations of input-output polarization. It is clear from the data that the angular distribution of SHG from y-cut quartz crystal surface has 180° symmetry. This is consistent with the C_2 symmetry of the surface normal to y-axis ((010)-plane). Such a type of study for surface symmetry using SHG was reported by H.W.K. Tom et al.⁶ and it is one of the main advantages of SNLO techniques for surface sciences. While the two-fold symmetry in the data can be easily understood, the additional structure still needs to be accounted for. Because quartz is

noncentrosymmetric, bulk quartz produces a large SHG in the dipole approximation. In view of this, it is natural to speculate that what is observed in reflection is a fraction of SHG generated in the bulk. Such SHG measurements in transmission were also performed as a function of the angle of rotation about the surface normal. The experimental setup for these transmission measurements is shown in Figure 3-2; the angle of incident of the fundamental beam was kept at 45° corresponding to the same angle in reflection measurements. Figures 3-3 a) to d) show the results of these experiments which are very similar to the reflection data. Clearly, these data also reflect two-fold symmetry with the additional interference structure as the reflected SHG measurements do. While there are similarities in the reflected and transmitted data, there are also clear differences. In particular, p-polarized excitation by the fundamental beam produces very different structure in output of reflection and transmission measurements as indicated in Figures 3-1 d) and 3-3 d). The only clear similarity in data is two-fold overall symmetry.

Structure in SHG was observed in very early development of nonlinear optics,⁸ and was well investigated with a view to utilize the structure as a method of precise evaluation of relative nonlinear susceptibility of material.⁹ The basic reason for the structure in these studies was the interferences between the bound and free SH waves traveling in the medium. That is to say, owing to the dispersion of the medium, the bound and free waves in general travel with different velocities giving rise to periodic phase differences producing the

interference. These fringes are known as "Maker's fringes"⁹ and are used in many applications involving nonlinear optics.

3-3. Discussion

The basic formulation of description of Maker's fringes, in non-birefringent materials was well documented.⁹ Figure 3-4 shows the propagation of the fundamental and second harmonic wave. In a nonlinear material, the nonlinear polarization is given by

$$\mathbf{P}_{2\omega}^{(2)}(\mathbf{r}, t) = \frac{1}{2} [\mathbf{P}_{2\omega} \exp(i\mathbf{k} \cdot \mathbf{r}) \bullet \exp(i\omega t) + \text{c. c.}]$$

where $\mathbf{P}_{2\omega}$ is the amplitude vector independent of time. Since this nonlinear polarization acts as a source term in the wave equation expressed as

$$\left[\nabla \times (\nabla \times) + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right] \mathbf{E}(\mathbf{r}, t) = - \frac{4\pi}{c^2} \frac{\partial^2}{\partial t^2} \mathbf{P}^{(2)}(\mathbf{r}, t) \quad \text{----- (3-1),}$$

then the solution of Equation 3-1 for electric field is given by

$$\mathbf{E}_{2\omega} = \mathbf{e}_f E_f \exp(i\mathbf{k}_f \cdot \mathbf{r}) + \frac{4\pi \mathbf{P}_{2\omega}}{(n_{\omega}^2 - n_{2\omega}^2)} \times \left[\mathbf{p} - \frac{\mathbf{k}_b (\mathbf{k}_b \bullet \mathbf{p})}{|\mathbf{k}_f|^2} \right] \bullet \exp(i\mathbf{k}_b \cdot \mathbf{r})$$

where $\mathbf{e}_f$ is field unit vector, $\mathbf{p}$ is that of the nonlinear polarization $\mathbf{P}^{(2)}$, $P_{2\omega}$ is magnitude of $\mathbf{P}^{(2)}$, and $\mathbf{k}_f$ and $\mathbf{k}_b$ are the wave vectors for the free and bound waves respectively. The first term of the solution is the "free wave" solution when $P_{2\omega}=0$, and the second term is the "bound wave" as a particular solution. The reflected harmonic wave in air is given by

$$\mathbf{E}_{2\omega}^R = \mathbf{e}_r E_R \exp(i\mathbf{k}_2^R \cdot \mathbf{r}).$$

$\mathbf{k}_f$, $\mathbf{k}_b$, $\mathbf{k}_2^R$, $\mathbf{e}_f$, $\mathbf{e}_r$, E_f , and E_R have to be determined from the boundary conditions at the input face of the crystal, i.e., continuity for the tangential and normal components of the electric and magnetic fields, respectively.

For simplification of the mathematical manipulation, the definitions as follows are used;

$$\mathbf{e}_b = \mathbf{p} - \left[\frac{\mathbf{k}_b(\mathbf{k}_b \cdot \mathbf{p})}{|\mathbf{k}_f|^2} \right] \quad \text{and} \quad Q = \frac{4\pi P_{2\omega}}{(n_{\omega}^2 - n_{2\omega}^2)}$$

According to the crystal coordinate system (X, Y, Z) shown in Figure 3-4, the continuity relations are expressed as

$$R_x E_R = f_x E_f + b_x Q$$

$$R_y k_{Rz} E_R = f_y k_{fz} E_f + b_y k_{bz} Q$$

$$R_y E_R = f_y k_{fz} E_f + p_y k_{bz} Q$$

$$(R_x k_{Rz} - R_z k_{Rx}) \times E_R = (f_x k_{fz} - f_z k_{fx}) \times E_f + (p_x k_{bz} - p_z k_{bx}) \times Q$$

where $\mathbf{e}_f = (f_x, f_y, f_z)$, $\mathbf{e}_b = (b_x, b_y, b_z)$, $\mathbf{e}_r = (R_x, R_y, R_z)$, and $\mathbf{p} = (p_x, p_y, p_z)$. After mathematical manipulations, the amplitude of reflected SHG E_R and the corresponding field vector $\mathbf{e}_r$ can be determined with the above continuity relations.

An explanation of the experimental results reported in this chapter would require a generalization of the above formalism. This is because a single fundamental beam, in general, excites two transmitted waves at the fundamental frequency owing to double refraction characterized by the birefringence of the crystal. These two transmitted waves of wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ will, in general, create three polarization waves of wave vector

$2\mathbf{k}_1$, $2\mathbf{k}_2$, and $\mathbf{k}_1+\mathbf{k}_2$.¹⁰ Because the medium is birefringent, there will also be, in general, two free waves propagating in the medium. This situation is to be contrasted with single bound and free wave interference described in conjunction with Maker's fringes. Because of the presence of five harmonic waves propagating in the medium, the mathematical formulation is very complicated and is not attempted here.

After a complete calculation of bulk contribution is performed, one can subtract that contribution from the total to see the role of surface contribution. The difference between transmitted and reflected SHG structures can clearly be understood only after such a complete analysis. Further studies incorporating the above idea, in future, will provide a deeper understanding of the role of surface structure in complicated systems like quartz.

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Chapter 4. SHG Arising from Metal Thin Films

4-1. Introduction

Thin metal films, especially of noble metals and aluminum, have long been used as reflective surfaces in optics. With the advent of micro-electronics and optical coatings for modern optical systems, the significance of thin film coating of different materials on variety of substrates has become very important.^{1,2} For example, thin films are used as protective optical coatings, selective membranes, thermal transfer layers, metallization of semiconductor micro-electronic devices, and large area of energy conversion devices. Clearly, it is important to understand the interfacial region between film and the substrate because this region ultimately determines adhesion, diffusion, corrosion, and electrical properties of the films. The growth of epitaxial films of III-V, II-VI, and IV-VI materials such as GaAs, CdSe, and HgTe is another area which is widely used to the advancement of both optical and micro-electronic technologies. At the present time, there are no reliable techniques to probe this interfacial region. Optical techniques to probe this interfacial region are very attractive because of their non-intrusive nature. Of course, this fact requires that either the film or the substrates be transparent to the probing light beam. SNLO techniques, in particular SHG, have been used recently for this purpose.³⁻⁶ These studies include investigations of nucleation and growth of silver layers and clusters, long range surface plasmons, spatial and frequency dependence of local fields, and structural symmetry of interfacial region.

The work reported in this chapter is a preliminary effort to study thin film deposition and interfacial properties via optical SHG. The thin films studied were of titanium (Ti) and titanium nitride (TiN). The industry of Ti and its alloys has been a part of high technology owing to their usefulness in a variety of applications such as multilevel metallization schemes and protective coatings. As the cost declines and the available supply increases, the application of Ti and TiN will surely expand because of their light weight, high strength and hardness, and corrosion resistance. Titanium's density is about 60 % of that of steel and its modulus is 55 % of that of steel.⁷ Titanium is exceptionally corrosion resistant which often exceeds that of stainless steel in most environments. Since it is joinable, formable, and readily machinable, Ti is available in a wide variety of types and forms. Titanium like other metals in the IV group is an allotropic transition metal between the low temperature hexagonal close-packed (hcp) α -phase and the high temperature β -phase. At room temperature, Ti has a hcp crystal structure, which is referred to as "alpha" phase. This structure transforms to a body-centered cubic (bcc) crystal structure called "beta" phase, at 883 °C.⁸ TiN is an interstitial alloy in which the interstitial nitrogen stabilizes the α -phase at high temperature.⁹ Alloying elements generally can be classified as α or β stabilizers. Alpha stabilizers increase the temperature at which the α phase is stable while beta stabilizers result in stability of the β phase at lower temperature. The interstitial elements, oxygen, nitrogen, and carbon, are alpha stabilizers which raise the transformation temperature. In an interstitial alloy, the metal-metal atom bond remains the dominant one and the non-metal atoms are sufficiently

small to be accommodated with the lattice without distortion from metal type symmetry.¹⁰ Thus, the essential feature of interstitial alloys are their metallic properties (conductivity, opacity, etc.) implied by the predominant metal-metal bond.

TiN thin films have extreme hardness and high temperature stability as well as aesthetic qualities of a golden color. These properties are primarily exploited in hard and well-resistant metallurgical and decorative coatings. On the other hand, the thermodynamical and electrical properties of TiN films make them the primary candidates in micro-electronic industry. TiN has been found to be the most promising diffusive barrier material in applications both to Si and III-V compound device technology in multilevel metallization schemes involving Al as second layer.¹¹⁻¹³

4-2. Experimental Results and Discussion

The experimental setup used is the same as the reflection measurement of quartz shown in Figure 2-7. The samples used were provided by Intel Corporation, Santa Clara, CA and were made by the method of sputtering and reactive sputtering. The thickness of the solid Ti and TiN wafers used is 0.30 mm and the diameter is 10.00 cm. For the investigation of the interfacial characteristics, the wafers of TiN thin film on different substrates Al and Si were used with different thicknesses of 45, 100, 200, and 450 Angstroms of TiN deposition and their diameter is 15.00 cm.

Figure 4-1 shows SHG from thick (bulk-like) film of Ti and TiN, respectively, as a function of square of input power. That the curve in the

graph is a straight line is evidence that the signal measured is indeed SHG and no laser damage to the film was observed. As shown in Equation 2-1, the SH signal generated is given by

$$S(2\omega) = \frac{32\pi^3\omega \sec^2 \theta_{2\omega}}{\left(\frac{h}{2\pi}\right)C^3\epsilon_1^{\frac{1}{2}}(2\omega)\epsilon_1(\omega)} |e(2\omega) \cdot \chi^{(2)}:e(\omega)e(\omega)|^2 I^2(\omega) AT \quad \text{--(2-1)}.$$

From this equation, SH signal should vary linearly with square of input power and the slope of the straight line is proportional to the square of the second order susceptibility of the medium, as well as inversely proportional to linear dielectric constant. From Figure 4-1, it is clear that SHG from TiN film is much larger than from Ti film. This may be due to the structural difference between Ti and TiN. Titanium in the single crystal form is centrosymmetric and so SHG from Ti is due to metallic character of free electron contribution as a first approximation. On the other hand, TiN is less metallic (more of semiconductor nature), and more importantly has a GaAs type crystal structure which lacks a center of inversion. Thus, it is expected that dipole allowed strong SH signal from TiN is observed even though the material is in polycrystalline form.

Figures 4-2 a) and b) show SHG from TiN films of different thickness on Al and Si substrates. The input power used in the measurements is as shown. The behavior of SHG as a function of film thickness is the same for all the powers. These results show clearly that SHG from TiN film varies significantly with thickness and they indicate that SHG from TiN film is different for Al metal substrate and Si

semiconductor substrate. The films used are sufficiently thin so that the bulk TiN behavior cannot be expected to influence SHG. However, it should also be noticed that the skin-depth of TiN, corresponding to the bulk conductivity, is about 190 Angstroms and that the range of variation of film thickness ranges up to twice the skin-depth. At present, no definite conclusions can be drawn about TiN/Al and TiN/Si interfaces from our preliminary results. These experimental results indicate the fact that SHG is indeed sensitive to film thickness.

The fact that SHG from TiN films of same thickness but different substrate is different is a clear suggestion that the interfacial region influences the SH generation. Thus, SHG can be useful in probing interfacial region between substrate and very thin film (of the order of skin depth). A complete understanding of these results can be obtained from complete modeling studies that could be used as the basis for future investigations.

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Chapter 5. Conclusion

The experimental work reported in this Thesis consists of SHG from birefringent noncentrosymmetric single crystal quartz and thin films of TiN.

The SHG in reflection from quartz shows the structure in which the broad variation is attributable to the symmetry of the crystalline surface. The additional finer detail is presumably due to interference between bound and free waves in the bulk of crystal. In order to completely understand the contribution due to the surface structure as opposed to the bulk of the crystal, a more detailed calculation of SHG from such a crystal must be undertaken. If the bulk contribution is completely calculated, then one can subtract this contribution from experimental data to see any residual information which could be attributed to the surface structure.

The experimental results of SHG from thin film samples show that one can clearly distinguish Ti and TiN samples even if these samples have the same metallurgical properties and that SHG is very sensitive even to small structural change. SHG is also found to be dependent of TiN film thickness. Further studies involving thicker film will verify whether the limiting value of signal for thicker films is due to bulk behavior. In addition, further experimental studies of films of various thickness on the substrate together with linear optical measurements will be valuable to an understanding of this phenomenon. The theoretical work characterizing such thin films, whose thickness is much smaller than the wavelength of radiation, is also necessary for a complete understanding these results. One

can use SHG as a probe for thin film characterization if such an understanding of the process involved is available.

**Table 1. Description of Experimental Instrumentation
Used in Experiments**

Nd:YAG pulsed laser:

Company: Quantel International
Model: YG 480
Wavelength: 1,064 nm
Maximum Energy per pulse: 400 mJ
Pulse width: 13 ns

Monochromator:

Company: Bausch & Lomb
Model: F/3; 50 cm focal length
Spectral range: 0.0 to 1,000 nm

Photomultiplier (PMT):

Company: Hamamatsu
Model: R262 (multi-alkali dynode)
Spectral range: 450 to 800 nm

Filter:

Corning Color Filter 7-54 and Total IR reflector at 1.064 m

Gated Integrator/Boxcar Averager:

Company: Stanford Research Systems
Models: SR 250 - Gated Integrator & Boxcar averager
SR 235 - Analog Processor
Sr 250 - Display Modulus
SR 245 - Computer Interface with an RS-232 Connection
Operated Sampler Module: Gate Width - 60 ns
Sensitivity - 10 mV
Number of Samples - 1000 samples

Computer:

Company: Eltech Corporation
Model: 286
Software Package: SR 265

Figure Captions

- Figure 2-1. Experimental Setup: The experimental setup was optimized to generate and detect the reflected SHG. The incident angle of the fundamental beam and the reflected angle of SHG are 45° .
- Figure 2-2. Laser Layout: The oscillator consists of several optical systems; hard coated flat and convex mirrors, a quarter-wave plate, a 7 mm aperture, a KDP longitudinal field Pockels cell, a coated Glan-Taylor polarizer. The Pockels cell and the polarizer constitutes an electro-optical Q-switch with a high voltage power supply.
- Figure 2-3. Q-switching Diagram: A principle of operation of Q-switch is schematically described; a) a closed cavity and for b) an open cavity.
- Figure 2-4: Schematic Function of Gated Integrator: When triggered, the unit generates a gate and the repetitive train of input signal is sampled and integrated while the gate is on.
- Figure 2-5: Tunability of SHG: The δ -function-like shape prove that SHG has a high tunability.
- Figure 2-6: Proportionality of SHG: The intensity of SHG is linearly proportional to the square value of the peak intensity of the fundamental input beam.
- Figure 2-7: Orientation of Target Sample for SH Measurement in ` Reflection: A mount was constructed for the samples to

provide complete 360° of rotation freedom along an axis normal to the sample surface.

Figure 3-1: Variation in Intensity of Reflected SHG for Y-cut Quartz with Angle of Rotation about Axis Normal to Surface.

- a) : S-polarized reflected SHG generated by s-polarized input beam.
- b) : P-polarized reflected SHG generated by s-polarized input beam.
- c) : S-polarized reflected SHG generated by p-polarized input beam.
- d) : P-polarized reflected SHG generated by p-polarized input beam.

Figure 3-2: Orientation of Target Sample for SH Measurement in Reflection

Figure 3-3: Variation in Intensity of Transmitted SHG for Y-cut Quartz with Angle of Rotation about Axis Normal to Surface.

- a) : S-polarized transmitted SHG generated by s-polarized input beam.
- b) : P-polarized transmitted SHG generated by s-polarized input beam.
- c) : S-polarized transmitted SHG generated by p-polarized input beam.
- d) : P-polarized transmitted SHG generated by p-polarized input beam.

Figure 3-4: Propagation of the Fundamental and SH Waves.

Figure 4-1. Sensitivity of Reflected SHG to Titanium and Titanium

Nitride: SH sensitivity to TiN is higher than that to Ti.

Figure 4-2: Variation in Intensity of Reflected SHG Arising from TiN

Thin Film with Thickness of deposition on Aluminum and Silicon Substrates respectively: The consistent relationship between the SH intensity and the thickness of TiN deposition is shown with different input powers.

a) : Aluminum substrate.

b) : Silicon substrate.

Figure 2-1

Figure 2-2

Figure 2-3

Figure 2-4

Figure 2-5

Figure 2-6

Figure 2-7

Figure 3-1 a)

Figure 3-1 b)

Figure 3-1 c)

Figure 3-1 d)

Figure 3-2

Figure 3-3 a)

Figure 3-3 b)

Figure 3-3 c)

Figure 3-3 d)

FIGURE 3-4

Figure 4-1

Figure 4-2 a)

Figure 4-2 b)