Ultrafast laser excited nonlinear optics : harmonic generation and up-conversion luminescence at lanthanide doped up-conversion nanoparticles

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**ULTRAFAST LASER EXCITED NONLINEAR OPTICS:
HARMONIC GENERATION AND UP-CONVERSION
LUMINESCENCE AT LANTHANIDE DOPED UP-
CONVERSION NANOPARTICLES**

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2018

Abstract

Nonlinear optical harmonic generation and lanthanide-ion doped up-conversion (UC) luminescence have been considered as the two main promising candidates to convert low energy photons to high energy ones. Despite their attractive applications in laser development, sub-diffraction limit focusing and bio-imaging, they both suffered from low conversion efficiency. To fulfill their application potential, it is necessary to further understand these phenomena and the interaction between them. In this thesis, nonlinear optical harmonic generation from different substrates was comprehensively characterized to pave ways for precise wafer characterization; a non-invasive inspection technique for inter-layer defects in silicon (Si) wafers with high depth resolution was presented to demonstrate the significant application potential of UC processes in semiconducting industry; the interaction between lanthanide-ion based up-conversion luminescence (UCL) and third harmonic generation (THG) was investigated for coherent enhancement of optical harmonic generation, which will be beneficial in the development of highly efficient coherent UC platforms for ultrafast lasers development and deep ultra-violet (UV) ultrafast pulses generation.

This study starts from the characterization of third-order harmonics excited from crystalline sapphire wafers of different cutting planes using femtosecond (fs) laser. The efficiency, optical yield, crystalline orientation and excitation depth dependence

Abstract

were thoroughly characterized. It was found that the crystal orientation affects the THG intensity by ~20% for A, M and R-plane cut wafers, while this orientation dependency was not clear for the C-plane. The maximum excitation depth of THG was found to be 54 μm , and the propagation vectors of third harmonic (TH) and fundamental beam were found to be the same but can be separated.

Based on these findings, a demonstration was made to apply optical harmonic generation as a tool for non-contact, non-destructive detection of internal and inter-layer defects in Si wafers with high depth resolution of 121 nm, together with characterization of THG and fifth harmonic generation (FHG) from Si wafers. It was discovered that a modulation depth of 35% and 50% can be achieved for THG and FHG from Si wafers by changing the polarization state of incident laser, and the effective excitation depths of THG and FHG in Si wafer were 20 and 5 μm , respectively.

With a better understanding of nonlinear optical harmonic generation, the interaction between THG and lanthanide-ion doped UC nanoparticles (UCNPs) was studied by depositing a thin-film of UCNPs onto either amorphous or single crystalline substrates. Enhancement of THG intensity by 7.8 was discovered when UCNP thin-film was coated on top of substrate. The amplification of THG was believed to be caused by the simultaneous resonance among energy band gap in lanthanide ions, incident laser, and THG.

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Nomenclature

Nomenclature

$\tilde{E}(t)$ Optical field intensity ($V \cdot m^{-1}$)

$E^{2\omega}$ Optical field density of second harmonic generation ($V \cdot m^{-1}$)

$E^{2\omega}$ Optical field density of third harmonic generation ($V \cdot m^{-1}$)

$\tilde{F}_R$ Restoring force (N)

e Charge of an electron (C)

h Plank constant

I_n Intensity of the n^{th} -order of harmonic generation ($W \cdot m^{-2}$)

J Fundamental optical power (J)

J_a Absorbed optical power (J)

J_r Reflected optical power (J)

J_t Transmitted optical power (J)

k_ω Wave vector at optical frequency ω (m^{-1})

m Effective of an electron (kg)

N Number density of atoms (m^{-3})

Nomenclature

n Harmonic order

P Excitation laser power ($\text{W} \cdot \text{m}^{-2}$)

$\tilde{P}(t)$ Dipole moment strength per unit volume ($\text{C} \cdot \text{m}^{-2}$)

$\tilde{P}^1(t)$ First-order dipole moment strength per unit volume ($\text{C} \cdot \text{m}^{-2}$)

$\tilde{P}^2(t)$ Second-order dipole moment strength per unit volume ($\text{C} \cdot \text{m}^{-2}$)

$\tilde{P}^3(t)$ Third-order dipole moment strength per unit volume ($\text{C} \cdot \text{m}^{-2}$)

$U(\tilde{x})$ Potential energy generated by the electron displacement (J)

w_0 Beam waist diameter (m)

$\tilde{x}$ Electron displacement distance (m)

$\tilde{x}^{(1)}$ First order electron displacement (m)

$\tilde{x}^{(2)}$ Second order electron displacement (m)

$\tilde{x}^{(3)}$ Third order electron displacement (m)

γ Dipole damping rate (Hz)

Δk Phase mismatch (rad)

ϵ_0 Permittivity of free space ($\text{F} \cdot \text{m}^{-1}$)

Nomenclature

θ Azimuthal angle with respect to one of the crystal axes on the sample surface

(rad)

λ Coupling strength

Σ_3 Sum of the photons absorbed in third harmonic wavelength

Σ_5 Sum of the photons absorbed in fifth harmonic wavelength

Σ_i Sum over the material excitations created in the elementary quantum process

Σ_n Sum of the photons absorbed in fundamental wavelength

φ Polarization of incident optical field (rad)

$\chi^{(1)}$ Linear susceptibility

$\chi^{(2)}$ Second-order susceptibility ($\text{m} \cdot \text{V}^{-1}$)

$\chi^{(3)}$ Third-order susceptibility ($\text{m}^2 \cdot \text{V}^{-2}$)

Ω_i Frequency of elementary material excitation

ω_0 Atom single resonant frequency (Hz)

ω_j Optical frequency of excitation light (Hz)

Glossary of Terms

Glossary of Terms

2-D: Two-dimensional

3-D: Three-dimensional

AFM: Atomic force microscope

Ag: Silver

Au: Gold

AuNS: Gold nanosphere

AuNT: Gold nanotriangle

BF: Band-pass filter

BS: Beam splitter

CCD: Charge coupled device

Ce³⁺: Cerium ion

CR: Cross-relaxation

EMCCD: Electron multiplying charge coupled device

Er³⁺: Erbium ion

Glossary of Terms

ESA: Excited state absorption

ETU: Energy transfer up-conversion

FH: Fifth harmonic

FHG: Fifth harmonic generation

fs: Femtosecond

FWHM: Full-width-half-maximum

Gd³⁺: Gadolinium ion

Ho³⁺: Holmium ion

HRS: Hyper-Rayleigh scattering

HWP: Half-wave plate

ITO: Indium tin oxide

Li⁺: Lithium ion

LPF: Long-pass filter

LSPR: Localized surface plasmon resonance

NA: Numerical aperture

NaYF₄: Sodium yttrium fluoride

Glossary of Terms

$\text{NaYF}_4:\text{Er}^{3+}$: Erbium doped sodium yttrium fluoride

$\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$: Ytterbium/erbium co-doped sodium yttrium fluoride

$\text{NaYF}_4:\text{Yb}^{3+}:\text{Tm}^{3+}$: Ytterbium/thulium co-doped sodium yttrium fluoride

Nd^{3+} : Neodymium ion

NIR: Near-infrared

OL: Objective lens

OSA: Optical spectrum analyzer

PAA: Poly(acrylic acid)

PAMAM G1: Polyamidoamine generation 1

PD: Amplified photo-detector

PMT: Photomultiplier tube

RF: Radio-frequency

Sc^{3+} : Scandium ion

SEM: Scanning electron microscope

SHG: Second harmonic generation

Si: Silicon

Glossary of Terms

SPF: Short-pass filter

SPP: Surface plasmon polariton

TEM: Transmission electron microscope

TH: Third harmonic

THG: Third harmonic generation

Tm³⁺: Thulium ion

UC: Up-conversion

UCL: Up-conversion luminescence

UCNP: Up-conversion nanoparticle

UV: Ultra-violet

Chapter 1. Introduction

1.1 Background

Near-infrared (NIR) light is considered an excellent energy source for photoluminescence in various applications including bio-imaging¹, controllable drug delivery², and solar cell development³ due to its deep tissue-penetration depth, low phototoxicity, and culmination in solar photon flux⁴. While the common existing molecular dyes⁵⁻⁶ and quantum dots⁷ undergo “down conversion” processes in which the emitted photons have the energy lower than the pumping light, materials with the potential to generate photons with higher energy than the excitation source, or “up-conversion”, is more preferable for the better visibility of high energy photons to human eyes. As a very first observation of UC process, second harmonic generation (SHG) was discovered in 1961 by Franken *et al*⁸. In SHG, new photons having twice the photon energies are generated while maintaining the coherence with the incident light⁹. After that, higher orders of optical generations were discovered from TH¹⁰ to 13th harmonic generation¹¹, which made it possible to generate extreme deep ultra-violet (UV) light using NIR light as the energy source.

Another technique to achieve UCL utilizes lanthanide-ions, the long life and ladder-like energy levels of lanthanide-ion make it capable of absorbing two or more photons in sequence at NIR range to pump their electrons from the ground state to higher energy levels for generating luminescence at visible and UV range¹²⁻¹³. By doping trivalent lanthanide-ions into host materials and forming a diluted guest-host system, various UC materials can be fabricated including lanthanide ion doped glasses¹⁴, optical fibers¹⁵⁻¹⁶, and UCNPs¹⁷. Among them, UCNPs attract special interest due to its small size down to a few nanometers¹⁷ and the great potential to be applied in theragnostic¹⁸⁻¹⁹ and solar energy harvesting²⁰.

Although the wavelength-conversion properties of optical harmonic generation and UCL come from different energy conversion processes, they are closely related to each other. Energy band gap structure of materials plays an important role in both processes²¹. For example, similar to nonlinear optical harmonic generation, UCL from single-crystalline UCNPs also shows dependence on incident polarization states due to its reliance on the energy band gap structure²². Besides, it has been reported that in quantum dots, when the energy band gap resonates with the incident laser, optical harmonic generation can be enhanced²³. As a result, with UCNPs having energy band gap resonating with the incident laser and emission wavelength matching with the HG wavelength, nonlinear optical harmonic generation can be enhanced.

1.2 Motivation

Despite the great potential of optical nonlinear harmonic generation and UCL from UCNPs, their applications are still limited by low conversion efficiencies²⁴⁻²⁵. The need to improve the efficiency of optical nonlinear harmonic generation and UCNPs put requirements on a systematic and comprehensive understanding of these phenomena.

Optical harmonic generations have been discovered in a variety of materials²⁶⁻²⁸, several different factors including material symmetry, incident angle, and excitation depth have been proven to affect their efficiencies^{10, 26, 29}. However, there lacks a comprehensive and systematic characterization of the dependence of nonlinear optical harmonic generation on these factors. As a result, a comprehensive and thorough characterization of optimal harmonic generation was necessary in order to look for better strategies to enhance its efficiency.

Optical harmonic generation has been applied as a perfect surface imaging tool³⁰ due to its high surface selectivity. Based on the significant efficiency differences of optical harmonic generation in the bulk body and interface of materials, it also has great potential in detecting internal cracks or defects inside materials that are not conveniently detected by conventional methods. As an example, the development of single-chip based three-dimensional (3-D) integrated computing and data storage device³¹ has put an urgent need for non-contact, non-destructive detection method

for internal and inter-layer defects in Si wafer stacks. Current detection technologies based on ultrasonic probes³²⁻³³ and high energy radiation³⁴ either suffered from possible damage and contamination of sample³⁵ or handling of dangerous radioactive substances³⁴. As a result, it is beneficial to use the optical-based nonlinear harmonic generation as a tool for developing non-contact, non-destructive inspection method for internal and inter-layer defects in Si wafers with high resolution and surface selectivity.

Current techniques for enhancing optical nonlinear harmonic generation and UCNP luminescence are very similar due to their analogous nature³⁶⁻³⁷. Plasmonic resonance has been utilized to enhance the efficiencies of both optical harmonic generation³⁶ and UCL³⁷. However, the interaction between these two optical processes has not been investigated, the optical confinement effect of UCNP may be a good candidate for improving the yield and efficiency of harmonic generation. In order to pave a new road to high-efficiency UC processes, it is necessary to study the interaction between nonlinear optical harmonic generation and UCNP luminescence under ultrafast laser excitation.

1.3 Objectives of The Work

The objectives of this project are:

1. Comprehensively understanding the dependence of optical nonlinear harmonic generation efficiency on incident power density, crystalline

orientation, excitation depth, and incident angle through characterization of THG from sapphire wafers of different cutting planes.

2. Developing non-contact, non-invasive techniques to detect internal and inter-layer defects in Si wafers with high resolution and interface selectivity based on nonlinear optical harmonic generation.
3. Investigating the interaction between UCNP luminescence and nonlinear optical harmonic generation under ultrafast laser excitation, enhancing the efficiency and yield of optical harmonic generation using the coupling between UCNP luminescence and THG.

1.4 Organization of The Thesis

The organization of the thesis is as follows. In Chapter 2, the fundamental knowledge of nonlinear optical harmonic generation and UCNP luminescence will be separately reviewed first. The mechanism of optical nonlinear harmonic generation, differences between even- and odd-orders of nonlinear optical harmonic generation, up-to-date works in investigating factors that affect nonlinear optical harmonic generations will be introduced for a comprehensive understanding of nonlinear optical harmonic generation. The mechanism and energy transfer progresses in UCNP will also be discussed to compare with that of nonlinear optical harmonic generation. Then the state-of-the-art for internal and inter-layer defects inspection techniques will be summarized to convince the reader that optical

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nonlinear harmonic generation can be helpful in non-contact, non-destructive detection of internal and inter-layer defects with high resolution and interface selectivity. Strategies to improve harmonic generation and UCL efficiencies including plasmonic coupling and energy bandgap resonating will then be discussed. At last, a few pioneering works in single nanoparticle level study of nonlinear optical harmonic generation and UCL luminescence will be introduced.

In order to systematically investigate efficiency affecting factors of nonlinear optical harmonic generation from crystalline materials as the foundation of this thesis. THG is excited from crystalline sapphire wafers with different cutting planes. Incident power, crystalline orientation, excitation depth and incident angle dependence of THG efficiency from sapphire wafers are comprehensively investigated in Chapter 3. A simple demonstration of beam steering is also demonstrated as one of the potential applications of THG based on the comprehensive understanding of THG.

To further explore the potential applications of nonlinear harmonic generation, Chapter 4 shows the application of nonlinear optical harmonic generation to solve the problem of internal and inter-layer defects inspection for Si wafers discussed in Chapter 1.2. A non-contact, non-destructive detection method for inter-layer defects in Si wafer stacks with a depth resolution of 121 nm and high interface selectivity is developed, together with careful characterization of THG and FHG efficiency dependence on crystalline orientation, incident power, excitation depth, cutting

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planes and doping conditions. Our results show that nonlinear optical harmonic generation can play a significant role in not only optical industry but also in other fields like semiconductor industry.

The interaction of nonlinear optical harmonic generation and UCL from UCNPs is studied in Chapter 5. UCNP thin-film (thickness < 100 nm) is self-assembled onto nonlinear optical substrates to be excited by fs laser. It is found that through energy band resonating between the energy levels in Er^{3+} ions and the incident laser, THG can be enhanced when UCNP thin film is oriented facing towards the excitation laser. On the other hand, UCNP luminescence will be enhanced when it faces against the fs laser due to the reabsorption of THG generated from substrates. It is also found that by coupling with single crystalline substrate like Si wafer, the dependence of UCL on the polarization state of incident laser will be enhanced.

Finally, this study is concluded in Chapter 6. The future research direction to extend the current works is also recommended in Chapter 6. The content of this thesis is summarized in the flowchart as in Fig. 1.1.

Figure 1. 1 Flowchart for the overall structure of this thesis.

Chapter 2. Literature Review

2.1 Preamble

In this chapter, the background knowledge of optical harmonic generation and UCL are presented separately. The mechanism of optical harmonic generation is introduced first, followed by experimental exploration on factors that affect nonlinear optical harmonic generation efficiency. Then a brief introduction on state-of-the-art techniques to inspect internal and inter-layer defects in Si wafers is given, to show the significant potential possessed by nonlinear optical harmonic generation in non-contact, non-destructive inspection of internal and inter-layer defects in Si wafers. After that, the fundamental knowledge of UCL is introduced to show its similarities and differences with nonlinear optical harmonic generation. Finally, up-to-date experimental works on improving UC efficiencies are introduced, and their limitations are discussed.

2.2 Nonlinear Optical Harmonic Generation

In this section, the background knowledge of nonlinear optical harmonic generation is introduced. The concept of nonlinear optical susceptibility, the differences between odd- and even- order of optical harmonic generation are reviewed.

2.2.1 Mechanism

In 1961, shortly after the first demonstration of a working laser in 1960, Franken and his co-workers discovered that when intensive optical field was generated on a quartz substrate by focusing a ruby laser on it, another laser beam at half of the incident laser wavelength was detected at the output of the system⁸. This phenomenon was then found to be the first nonlinear optical harmonic generation, which is second-order harmonic generation, or SHG. After that, higher orders of optical harmonic generation such as THG³⁸ and FHG³⁹ were discovered. Due to the non-invasive, non-destructive and optical UC nature of nonlinear optical harmonic generation, they attract significant interest in different fields including laser development⁴⁰, light manipulation at the nanoscale⁴¹, highly sensitive bio-molecular detection³⁰, and deep-UV generation⁴². Up to now, high-orders of harmonics have been excited with the maximum harmonic order of 21, which generated deep-UV light at the wavelength of tens of nanometers⁴².

Despite their differences among second-, third- and other higher-order optical harmonic generation, they can all be described as a result of part of atomic response that scales exponentially with the strength of the applied optical field⁴³. When an optical field is applied on a material system, the positive and negative charges in the material will be separated by the electric field, creating an electric dipole moment⁴³. The dipole moment will oscillate due to the periodical change of electric field in a

Chapter 2

propagating light wave, the energy generated by the dipole moment oscillation is then converted to elementary material excitations in quantum process like excitons and phonons, and also photons⁴⁴. In conventional optics, the strength of dipole moment per unit volume $\tilde{P}(t)$ created by an optical field, which is also generally defined as polarization, is linearly related with its strength $\tilde{E}(t)$ following Eq. (2.1)⁴³

$$\tilde{P}(t) = \epsilon_0 \chi^{(1)} \tilde{E}(t) \quad (2.1)$$

where ϵ_0 is the permittivity of free space and the constant $\chi^{(1)}$ is known as the linear susceptibility. In nonlinear optical processes, this expression can then be generalized into Eq. (2.2)⁴³

$$\tilde{P}(t) = \epsilon_0 [\chi^{(1)} \tilde{E}(t) + \chi^{(2)} \tilde{E}^2(t) + \dots] = \tilde{P}^1(t) + \tilde{P}^2(t) \dots \quad (2.2)$$

where $\chi^{(2)}$ is known as the second-order nonlinear susceptibility, $\tilde{P}^1(t)$ and $\tilde{P}^2(t)$ are first- and second-order dipole moments, or polarizations created by the optical field. It is clear that while the intensity of first order polarization scales linearly with the optical field strength, nonlinear optical polarization intensities are related with the integer exponential of the optical field intensity, the order of the exponential relationship follows the order of nonlinear optical susceptibility. This induces the exponential relationship between the intensity of nonlinear optical harmonic generation I_n with the incident laser intensity P as expressed in Eq. (2.3)⁹.

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$$I_n = \alpha P^n \quad (2.3)$$

where α is a constant and n is the order of harmonic generation. In order to simplify the concept of nonlinear optical harmonic generation, the process can be imagined as in Fig. 2.1. An electron in materials absorbs several photons in the incident laser in sequence and being pumped to a higher “virtual state”, followed by a radiative relaxation back to the ground state, releasing a new photon at integer times of incident photon energy⁴⁵. Note that the “virtual states” are imaginary and do not really exist in the nonlinear optical harmonic generation.

Figure 2. 1 (a) Example digital photo of green THG light spot excited by fs laser at 1,590 nm. (b) Illustration of virtual energy state involved in nonlinear optical processes, second, third and fifth harmonics are presented here as examples.

2.2.2 Even- and Odd-order of Harmonic Generation

As discussed in Chapter 2.2.1, optical harmonic generation comes from the electric dipole moment excited by an applied optical field. In linear optics, the linear dipole

Chapter 2

moment excited by optical field can be well explained by Lorentz model⁴⁶. In this section, the Lorentz model is extended for the description of nonlinear optical harmonic generation by considering the possibility of a nonlinearity in the restoring force exerted on electrons in the material system. Based on the extended Lorentz model, it is found that even-orders of harmonic generation require the presence of noncentrosymmetry in the optical medium while the requirement is less strict in odd-orders of harmonic generation.

When an optical field is applied on a material, the electrons will be moved by a distance of $\tilde{x}$, which is related with the strength of the optical field $\tilde{E}(t)$ by Eq. 2.4

$$\ddot{\tilde{x}} + 2\gamma\dot{\tilde{x}} + \omega_0^2\tilde{x} + a\tilde{x}^2 - b\tilde{x}^3 = -e\tilde{E}(t)/m \quad (2.4)$$

Where e and m are the charge and effective mass of an electron, respectively, γ is the dipole damping rate, which is half of the full-width-half-maximum (FWHM) in angular frequency units of the atomic absorption profile in the limit of linear response. ω_0 is the single resonant frequency of atom, a and b are parameters that describe the strength of the material nonlinearity.

The potential energy generated by the displacement of electrons $U(\tilde{x})$ can be calculated by the integration of electron restoring force $\tilde{F}_R$ in Eq. 2.5

$$U(\tilde{x}) = -\int \tilde{F}_R dx = \frac{1}{2}m\omega_0^2\tilde{x}^2 + \frac{1}{3}ma\tilde{x}^3 - \frac{1}{4}mb\tilde{x}^4 \quad (2.5)$$

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In a centrosymmetric material, the dipole strength generated at the position and negative direction of the electron displacement should be the same, as illustrated by Fig. 2.2a, and it can be expressed by $U(\tilde{x}) = U(-\tilde{x})$, this lead to $a = 0$ and Eq. 2.4 can be simplified to Eq. 2.6

$$\ddot{\tilde{x}} + 2\gamma\dot{\tilde{x}} + \omega_0^2\tilde{x} - b\tilde{x}^3 = -e\tilde{E}(t)/m \quad (2.6)$$

Equations for each order of electron displacement can therefore be derived as Eq. 2.7 to Eq. 2.9

$$\ddot{\tilde{x}}^{(1)} + 2\gamma\dot{\tilde{x}}^{(1)} + \omega_0^2\tilde{x}^{(1)} = -e\tilde{E}(t)/m \quad (2.7)$$

$$\ddot{\tilde{x}}^{(2)} + 2\gamma\dot{\tilde{x}}^{(2)} + \omega_0^2\tilde{x}^{(2)} = 0 \quad (2.8)$$

$$\ddot{\tilde{x}}^{(3)} + 2\gamma\dot{\tilde{x}}^{(3)} - b[\tilde{x}^{(1)}]^3 = 0, \text{ etc.} \quad (2.9)$$

While Eq. 2.7 is the same equation as the classical Lorentz model⁴⁶, it can be conveniently solved to obtain the expression for the first-order electron displacement distance excited by an optical field of frequency ω_j

$$x^{(1)}(\omega_j) = -\frac{eE_j}{mD(\omega_j)} \quad (2.10)$$

where $D(\omega_j)$ is a complex denominator function as

$$D(\omega_j) = \omega_0^2 - \omega_j^2 - 2i\omega_j\gamma \quad (2.11)$$

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Since the linear susceptibility is defined through its relationship with the optical polarization in a unit volume, which is also directly related with the electron displacement distance, the first-order electron displacement distance can then be related with first-order optical susceptibility by Eq. 2.12

$$P^{(1)}(\omega_j) = \epsilon_0 \chi^{(1)}(\omega_j) E(\omega_j) = -N e x^{(1)}(\omega_j) \quad (2.12)$$

where N is the number density of atoms, and then the first-order optical susceptibility can be derived as

$$\chi^{(1)}(\omega_j) = \frac{N e^2}{m \epsilon_0 D(\omega_j)} \quad (2.13)$$

By substituting Eq. 2.13 into Eq. 2.9 and other equations for higher-order of nonlinear susceptibility, it can be found that odd-orders of nonlinear susceptibilities can be solved. However, for even-orders of nonlinear susceptibilities, since the system can be treated as damping without driven; at steady state, even-orders of electron displacement distances are 0. As a result, for centrosymmetric materials, only odd-orders of nonlinear optical harmonic generation processes can be excited when the optical field is polarized parallel with the material surface.

Things are different in noncentrosymmetric materials. Since $U(\tilde{x}) \neq U(-\tilde{x})$, a is not equal to 0 while b becomes negligible since it is a correction value and only meaningful when a equals to 0. This lead Eq. 2.6 changes to

$$\ddot{\tilde{x}} + 2\gamma\dot{\tilde{x}} + \omega_0^2\tilde{x} + a\tilde{x}^2 = -e\tilde{E}(t)/m \quad (2.14)$$

By substituting Eq. 2.6 into Eq. 2.16, different orders of electron displacement distance can be expressed as follows

$$\ddot{\tilde{x}}^{(1)} + 2\gamma\dot{\tilde{x}}^{(1)} + \omega_0^2\tilde{x}^{(1)} = -e\tilde{E}(t)/m \quad (2.15)$$

$$\ddot{\tilde{x}}^{(2)} + 2\gamma\dot{\tilde{x}}^{(2)} + \omega_0^2\tilde{x}^{(2)} + a[\tilde{x}^{(1)}]^2 = 0 \quad (2.16)$$

$$\ddot{\tilde{x}}^{(3)} + 2\gamma\dot{\tilde{x}}^{(3)} + \omega_0^2\tilde{x}^{(3)} + 2a\tilde{x}^{(1)}\tilde{x}^{(2)} = 0, \text{ etc.} \quad (2.17)$$

While Eq. 2.15 and 2.17 can be solved by a similar approach, Eq. 2.16 now possess a term containing $\tilde{x}^{(1)}$, which can act as the driving force is the Lorentz model, as a result, a non-zero solution can be obtained for the second- and other higher even-orders of electron displacement distances, which lead to the presence of even-orders of harmonic generation in noncentrosymmetric materials excited by an optical field. The differences between optical harmonic generation excited from centrosymmetric and noncentrosymmetric materials are illustrated as in Fig. 2.2.

Figure 2. 2 Nonlinear optical harmonic generation of centrosymmetric and noncentrosymmetric materials. (a) Schematic of a material with noncentrosymmetric atomic structure in the x -axis direction. Both even- and odd-orders of optical harmonic generations can be excited, SHG, THG, and fourth harmonic generations are shown as examples. (b) Schematic of a centrosymmetric material, only odd-orders of optical harmonic generation can be excited in this case, THG and FHG are shown as examples. Atomic dipole potential energy with electric fields for (c) noncentrosymmetric and (d) centrosymmetric medium.

2.3 Efficiency Affecting Factors

It has been discussed in sections 2.2.1 and 2.2.2 that incident laser power and symmetry of materials have a significant impact on the efficiency of harmonic generation. There are other factors that play important roles in determining the efficiency of harmonic generation including crystalline orientation, excitation depth and incident angle. In this section, the effect of these factors will be discussed for a comprehensive understanding on efficiency affecting factors of optical harmonic generation.

2.3.1 Crystalline Orientation

Since optical harmonic generation comes from the nonlinear electric dipole moment created by the incident optical field, it is closely related with the atomic structure of the optical medium. Soon after the first demonstration of SHG generation in 1961, Maker and Terhune predicted that TH intensity generated from a calcite was related with polarization of the incident optical field φ by a cosine function of $\cos 3\varphi$ ³⁸. An experimental demonstration was made in the same work by rotating the sample stage to change the relative alignment between calcite lattice and incident laser polarization. Similar dependence was discovered in 1968 by Blombergen *et.al* for SHG generated from Si and silver (Ag)⁴⁷, the intensity of SHG was found to be proportional to $\cos^4 \varphi$. Note that because Si and Ag have a centrosymmetric lattice structure, the incident angle was inclined to the surface of the substrate to create the

noncentrosymmetric environment required for second harmonic (SH) excitation. The polarization dependence was found to be a general case for different orders of optical harmonics generated from most of the crystalline optical medium such as Si²⁹, CaF₂⁴⁸, quartz⁴⁸ and MoS₂²⁸, while no clear dependence was found for amorphous media such as glass or amorphous fused silica due to the randomly distributed crystalline domains in amorphous materials. Fig. 2.3 shows several examples of polarization angle dependent relative harmonic generation intensities of different crystals. The dependence was found to be closely related with the crystalline structure of the optical medium due to the variation of energy bands at different electron oscillation directions along the Brillouin zone.

Figure 2. 3 Optical harmonic generation dependences on crystalline orientation. (a) Schematics for the optical dipole moment and harmonic generation intensities dependent on the angle between incident laser polarization and lattice axis of optical medium. THG is taken as the example here. Examples of harmonic generation intensities at different incident laser polarization angles for (b) (100) Si wafer, taken from reference 14. (c) C-plane sapphire wafer, and (d) M-plane sapphire wafer, taken from reference 27.

2.3.2 Surface and bulk contribution

Another important factor that affects the intensity of optical harmonic generation is surface/bulk contribution. Compared to the bulk of optical media, optical harmonic generation was believed to be more significant at the interface⁴⁸. The surface selectivity of optical harmonic generation was first discovered for SHG in 1968⁴⁷. While even-orders harmonic generation is forbidden for centrosymmetric optical media as discussed in the previous section, SHG was discovered at the interface between crystalline Si, which is a well-known centrosymmetric optical medium, and air. The unusual enhancement of the SHG intensity was then attributed to the broken of bulk symmetry at the material interface⁴⁷. However, Thsang *et.al* found that the same surface-induced enhancement of efficiency can also be detected for THG, which does not have the requirement for material asymmetry⁴⁸⁻⁴⁹. This significant THG enhancement is conveniently linked to Gouy phase shift before and after the focusing point of incident laser at first⁵⁰. When an optical field is focused in the bulk body of an optical medium, the third-order nonlinear optical polarization $\tilde{P}^3(t)$ is proportional to the cube of optical field at fundamental wavelength ($E^3(t)$)

$$\tilde{P}^3(t) \propto \chi^{(3)} E^3(t) \quad (2.24)$$

where $\chi^{(3)}$ is the third-order nonlinear susceptibility.

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If the focused beam is strongly focused in Gaussian profile, the THG power can then be expressed as a function of the incident laser power P ⁵¹

$$\tilde{P}^3(t) \propto J^2 P^3(t) \quad (2.25)$$

where

$$J = \int_{-\infty}^{\infty} \frac{\chi^{(3)}(z) e^{i\Delta k b z}}{(1 + iz)^2} dz \quad (2.26)$$

Here, z is the axial position, b is the confocal parameter, which can be described as a function of the wave vector k_ω and beam waist diameter w_0 by $b = k_\omega w_0^2$. Δk shows the phase mismatch, which is equal to $3k_\omega - k_{3\omega}$. After integration over the volume of the optical medium, results show that in a uniform medium, efficient THG can only be excited when $\Delta k > 0$ while $\Delta k \leq 0$ in common uniform medium. This means that only at the interface where the optical medium become non-uniform, efficient THG can be excited⁵².

The contribution of surface and bulk THG was then experimentally distinguished by P. N. Saeta *et.al*²⁹. In this experiment, TH was excited at the interface between ultra-thin Si films of different thicknesses and SiO₂ substrate. By measuring THG intensities at the Si-SiO₂ interfaces with different Si film thicknesses, the contributions of surface and bulk body of optical medium can be identified. The experiments show that when the thickness of the optical medium is comparable to the absorption length at TH wavelength, bulk THG plays the dominant role, while

in samples thicker than the TH absorption length, surface THG becomes significantly important. Further investigations involved the utilization of atomic-thin materials such as single layer graphene to eliminate the effect of surface THG, it was found that bulk THG is quadratically dependent on the thickness of the sample⁵³. Note that Gouy phase shift was not involved in bulk TH in thin-film samples because the thickness of the sample was thinner than the confocal length of the focused beam⁵⁴, and the resulting intensity of THG will be determined by the interference among TH excited at the top surface, bottom surface and bulk material⁵⁵, which is shown in fig. 2.4c.

Figure 2. 4 Surface selectivity of optical harmonic generation. (a) Schematic of surface dependent THG intensity, only when incident laser is focused at top and bottom surfaces of the optical medium, TH can be excited. If the focusing point is in the bulk body of the optical medium, no THG can be detected. (b) Calculated results for THG intensity (blue line and left axis) and Gouy phase shift (red line and right axis) at the shallow depth around the surface of a homogenous non-dispersive medium. Taken from reference 23. (c) When the sample thickness is smaller than the confocal length, TH can be excited at top surface, bottom surface, and bulk material, resulting in interference among them.

2.3.3 Incident Angle

Despite the requirement for noncentrosymmetric structure in even-orders of harmonic generation, second harmonic (SH) was excited at surface of centrosymmetric crystalline Si when the incident beam was inclined to the sample surface⁵⁶⁻⁵⁷. At the surface of an optical medium, the refractive indices of the two sides of the interface will be different. As a result, the inclination of the incident optical field results in the generation of asymmetric dipole moment at the surface of a centrosymmetric material (e.g. Si), as depicted in Fig. 2.5a. The intensity of SH excited in this case was found to be strongly dependent on the incident angle, as well as the polarization of incident laser⁴⁸.

Unlike even-orders of harmonic generation, odd-orders of harmonic generation can be generated at both centrosymmetric and noncentrosymmetric medium. However, the intensity of odd-orders harmonic generation is also dependent on the incident angle. The inclination of incident laser from the direction perpendicular to the optical medium surface results in a weaker electric field on the optical medium surface⁹, which is schematically depicted in Fig. 2.5b.

The incident angle can affect not only harmonic generation efficiency but also its propagation direction. As an optical process governed by the optical dipole moment oscillation, the optical field of harmonic generation maintains excellent coherence with the incident optical field⁵⁸. The high coherence of harmonic generation process

ensures that the propagation direction of harmonic generation will be kept the same as the incident laser beam. This was demonstrated by Hyunwoong Kim *et.al* using an sapphire wafer with a cut groove of inclination angle of 30° ²⁷. The incident angle dependence of harmonic generation propagation direction provides new possibilities of optical harmonic generation application in the field of beam steering.

Figure 2. 5 Incident angle impact on even- and odd-orders of optical harmonic generation. (a) Inclination of incident beam enables the generation of even-order harmonics from centrosymmetric optical medium. SHG is taken as example in the schematic. (b) Effect of incident beam inclination on the generation of odd-order harmonics. THG is taken as example in the schematic. (c) Experimental demonstration of harmonic generation propagation direction related with incident angle. Taken from reference 27.

2.3.4 Limitations of Previous Study

After a comprehensive introduction of the mechanism and efficiency affecting factors of nonlinear optical harmonic generation, it is clear that many factors including incident power density, crystalline property of sample, polarization angle of incident laser, incident angle and depth can significantly affect the intensity of optical harmonic generation. However, there has not been a comprehensive and systematic characterization of the effect of these factors based on one substrate. As a result, a thorough characterization of THG from sapphire wafers of different cutting planes is carried out under different incident intensities, polarization angles, excitation depths and incident angles. Sapphire is chosen as the substrate due to its excellent optical transmission in UV-visible range, high thermal conductance for efficient heat dissipation, and good physical and chemical stability. The results are presented in chapter 3 and we believed that this study will lead to broader use of TH for high-precision sapphire characterization, such as surface quality inspection, crystallinity determination, interfacial studies, delamination check, and real-time monitoring of crack generation and propagation.

2.4 Internal Defect Inspection for Si Wafers

Because of its optical UC nature, surface selectivity and coherence preserving ability, optical harmonic generation has been widely used in laser development⁵⁹, surface and interface probing⁶⁰ and optical beam steering²⁷ in recent years. Among

these applications, surface and interface imaging is an attractive area for the application of nonlinear optical harmonic generation due to its high surface selectivity and nonlinear incident power dependence. There have been several demonstrations about the surface probing and imaging using nonlinear optical harmonic generation⁶¹⁻⁶³. As an optical phenomenon with high coherence, optical harmonic generation-based surface probing techniques possess great virtues including non-contact, non-destruction and high temporal and spatial resolution. Which makes it a promising tool to be applied in the semiconducting industry for high-quality wafer manufacture. However, advances in current semiconducting industry put a high requirement on the inspection of internal and inter-layer quality of semiconducting wafer and wafer stacks due to the progressing 3-D integrated computing and data storage devices development³¹. The increasing needs for high quality, large-scale production of semiconducting wafers calls for an inspection technique for internal and inter-layer defects in semiconducting wafer and wafer stacks that is non-contact, non-destructive, good surface selectivity and high depth resolution.

Silicon (Si) wafer is the most widely used material in semiconducting industry, due to its low transmittance to visible light, it is not easy to use traditional optical inspection technologies for the internal and inter-layer defects inspection. In order to overcome the low transmittance of Si, several strategies have been proposed

including infrared optical based inspection⁶⁴⁻⁶⁸, ultrasonic inspection⁶⁹⁻⁷¹ and lock-in thermography inspection⁷²⁻⁷³.

2.4.1 Optical based inspection

Although Si is opaque to light at visible wavelength, it is partially transparent to NIR light of wavelength longer than 1000 nm with a transparency over 40% for a 5.0-mm-thick Si wafer. The presence of cracks and defects will scatter the transmitted light and therefore affect the transparency of Si wafer. Utilizing a NIR optical detector such as a NIR charge coupled device (CCD) camera and a board band light source, Aghamohammadi et al. proposed a technique to detect microcracks inside the Si wafer and calculate their sizes by counting the associated dark gray pixels⁶⁵.

Optical signal can be also excited from Si wafers using a forward bias voltage⁶⁷ or an incident laser beam with photon energy higher than the energy band gap of Si⁶⁸. The presence of internal cracks reduces the intensity of luminescence because more energy is lost at the cracks by non-radiative emission. These methods provide a short data acquisition time of 1 s and high resolution of several microns determined by the diffraction limit⁷⁴.

2.4.2 Ultrasonic Based Inspection

Ultrasound is another candidate for inspection of internal defects in Si wafer since it can be converted to heat when interacting with internal defects in Si wafers. By using an infrared camera to image the thermal picture of a wafer under an ultrasound probe, internal defects can be detected with a resolution of $100\text{ }\mu\text{m}$ ⁷⁵. Besides, by scanning a focused ultrasound beam across a Si wafer in a pulsed mode, the acoustic signal will transmit the Si wafer and being reflected at the top, bottom surfaces of the wafer and also the internal cracks inside the wafer. This enables the detection of internal defects at a resolution of $5\text{-}10\text{ }\mu\text{m}$ ⁶⁹.

2.4.3 Lock-in Thermography Imaging

Another potential tool for non-destructive imaging of internal defects in Si wafers is lock-in thermography imaging. In this method, photons at infrared wavelength are generated using either voltage⁷² or optical⁷³ excitation and detected by an IR camera to create a specific temperature pattern. This method provided high resolution of a few micrometers⁷⁵.

Figure 2. 6 Schematics for experimental setup of internal defects detection using (a) optical transmission, (b) electroluminescence imaging, (c) photoluminescence imaging and (d) ultrasonic imaging. Note that lock-in thermography method shares a similar experimental setup as electro and photoluminescence imaging. Taken from reference 75.

2.4.4 Limitation of Previous Study

Current technologies for non-destructive inspection of internal defects in Si wafers suffer various limitations. The resolution of optical based inspection techniques is limited by the optical diffraction limit. In ultrasonic based method, long data acquisition time of tens of minutes is required for each wafer, and immersive medium is sometimes required due to the high attenuation of acoustic signal in air, which may cause contamination to the sample. In thermography imaging, thermal blurring may also result in low resolution. Utilizing high energy radiation sources

such as X-ray or γ radiation may improve the resolution and acquisition time but high energy radiation can cause severe damage to semiconducting devices. As a result, a non-contact, non-destructive, highly resolved and interface-selective inspection method without the use of high energy radiation for detection of internal defects in Si wafers is desired for the future development of semiconducting industry. A demonstration of such inspection technique based on nonlinear optical harmonic generation will be presented in Chapter 4 to address problems mentioned above.

2.5 Lanthanide Doped Up-conversion Nanoparticles

In this section, the basics of UCL from UCNPs are introduced. Different energy transfer processes in UCNPs are presented, factors that affect the efficiency of UCNPs luminescence are discussed, efforts in optimizing these factors to improve UCL efficiency are reviewed.

2.5.1 Energy Transfer Processes in UCNPs

Lanthanide-doped up-conversion nanoparticles (UCNPs) are the most widely used UC materials. The nature of UC property of this material comes from the ladder-like energy levels of the trivalent lanthanide ions embedded in an appropriate inorganic lattice⁷⁶⁻⁷⁷. There are mainly two different classes of UC mechanisms: excited state absorption (ESA) and energy transfer up-conversion (ETU)⁷⁸.

Excited State Absorption

A typical ESA process can be illustrated as in Fig. 2.7a, in a multilevel system simplified to a three-step ladder-like structure where two pump photons are successfully absorbed by a single ion. The occurrence of this mechanism is based on both the equal separation between the multiple energy levels, ground state G to E1 and E1 to E2 in Fig. 2.7a, and the reservoir capability of the long-lived intermediate level E1. Under appropriate excitation photon energy that resonates with the transition energy from G to E1, electrons can be excited to E1, and due to the long lifetime of E1, they have a high possibility to be further promoted to higher lying state, E2, before decaying to the ground state. Consequently, emission will be upconverted to occur from E2 to G. These two requirements limited the selection of lanthanide ions to only erbium (Er^{3+}), thulium (Tm^{3+}), holmium (Ho^{3+}) and neodymium (Nd^{3+})¹³. In this type of UCNPs, low doping concentration is necessary to avoid luminescent centers' cross-relaxation (CR) resulted energy loss as well as increase the gain in the ESA process¹³. However, since the UC process with ESA mechanism involves only one single ion, the UC efficiency is independent of the doping ions concentration if it is low enough to avoid CR of luminescent centers. However, when the doping ions concentration is high and the distance between ions are close enough, CR will significantly reduce the UC efficiency. The CR process will be further explained in next section.

Energy transfer up-conversion

Another UC mechanism is illustrated in Figs. 2.7b-f. Different from ESA, two lanthanide ions are involved in this mechanism instead of one and energy is transferred between the two neighboring ions. Ion 1 in an ETU process is defined as the sensitizer, which firstly absorbs a pump photon and is promoted to the intermediate level E1; the energy reserved in E1 of ion 1 is then transferred to ion 2, which is known as the activator, and excites ion 2 to its upper emitting state. This process requires the sensitizer to relax back to ground state G twice. In contrast to ESA, the involvement of two ions cause the UC efficiency to be limited to the average distance between the neighboring sensitizer and activator, which is controlled by the concentration of dopants.

Depending on the energy transfer sequence between the sensitizer and activator, ETU can be further divided into five different types and they are illustrated as in Fig. 2.7b-f. Fig. 2.7b shows the schematic of energy-transfer followed by excitation absorption; in this process, energy from the excitation light is firstly absorbed by the sensitizer to excite electrons from G to E1, energy transfer then happens between the sensitizer and activator, following by an ESA step which excites the electrons of the activator from G to E1 and then to E2. If the activator is not able to absorb energy from the excitation light and can only be excited via the energy transfer from the sensitizer, the process is called successive energy transfer (Fig. 2.7c). When the

sensitizer and activator have similar energy states and lifetime, ETU can happen in a CR fashion as shown in Fig. 2.7d. Both the sensitizer and the activator absorb energy from the excitation source, and the relaxation of electrons in E1 in sensitizer results in the energy transfer to the activator to bring its electrons from E1 to E2, following by the relaxation to G, emitting light with higher photon energy.

There are also ETU processes that involve more than one sensitizer or activator ions in the process. For example, when more than one sensitizer takes place in the energy absorption from the excitation source (Fig. 2.7e), both sensitizer ions transfer energy to the activator cooperatively to excite electrons of the activator from G to E2 directly. On the other hand, when more than one activator ions take place in the emission process, they emit cooperatively at a photon energy higher than the excitation source (Fig. 2.7f).

Figure 2. 7 Energy transfer processes in UCL. (a) ESA, (b) Energy-transfer followed by ESA, (c) successive energy transfer, (d) CR, (e) Corporative sensitization, (f) Cooperative luminescence.

By far, ETU is considered as the most crucial UCL process since most of highest efficiency UCNPs utilize sensitizer/activator pairs of $\text{Yb}^{3+}/\text{Tm}^{3+}$ ⁷⁹, $\text{Yb}^{3+}/\text{Er}^{3+}$ ⁸⁰⁻⁸¹ and $\text{Yb}^{3+}/\text{Ho}^{3+}$ ⁸² with excitation at ~ 980 nm. Since 980 nm is considered as the “optical transparency window” for biological tissues, which has relatively less absorption and scattering, using Yb^{3+} as sensitizer provides UCNPs with high potential in biological applications. Besides, Yb^{3+} is an excellent sensitizer with relatively large absorption cross-section area in the region of ~ 980 nm⁸³ and the capability of high concentration doping (20 to 100% for fluoride nanoparticles) without evoking deleterious CR⁸⁴. Because of the advantages mentioned above, Yb^{3+} sensitized UCNPs have attracted lots of attention in this field.

It should be noted that the border between ESA and ETU is not definite. There also can be efficient ETU in the single lanthanide ion doped system where the doping ion acts both as the sensitizer and the activator⁸⁵⁻⁸⁶. The sensitizer property of these ions is utilized in enhancing certain emission bands. As an example, Nd^{3+} has been utilized to enhance emission band of Tm^{3+} ⁸⁷ in the blue range while cerium (Ce^{3+}) was found to be able to enhance the red emission band of Ho^{3+} ⁸⁸.

2.5.2 Optimizing UCNP Efficiency

In contrast to the promising development of UCNP in different applications, the real-life application of UCNP is still very limited, mainly due to the low UC efficiency. The quantum yield for even the most effective UC materials is still below 5%⁸⁹⁻⁹¹. Up to date, huge efforts have been devoted to architecting UCNPs with higher efficiencies. Generally, the optimization of UCL efficiency involves three methods: tailoring the host material property to reduce phonon induced energy loss⁹²⁻⁹⁴, adjusting doping ion concentration to avoid cross-relaxation⁹⁵, and improving surface quality to prevent energy transfer from lanthanide ions to the surface defects sites⁹⁶⁻⁹⁷. Factors that affect UCL efficiency are summarized in figure 2.8, and based on previous studies, it was found that NaYF_4 co-doped with 20% of Yb^{3+} and 5% of Er^{3+} shows the best luminescent efficiency. This is because of the low cutoff phonon energy of NaYF_4 crystals and the optimized inter-ion distance between adjacent Yb^{3+} and Er^{3+} ions that avoids cross-relaxation.

Figure 2. 8 Factors that affect the efficiency of UCNP luminescence.

2.6 Strategies to Enhance UC Emission

In this section, recent advances in improving UC emission are reviewed. Plasmonic enhancement of nonlinear optical harmonic generation and luminescence from UCNPs are introduced. Energy band gap resonance is also presented as another method to improve the efficiency of nonlinear optical harmonic generation. The limitation of current studies in UC emission amplification are discussed and the importance of studying the interaction between nonlinear optical harmonic generation and luminescence from UCNPs are addressed.

2.6.1 Enhancement of Nonlinear Optical Harmonic Generation

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Since its discovery in 1961, efforts have been made to enhance the intensity of nonlinear optical harmonic generation. However, the efficiency of optical harmonic generations is low due to the small nonlinear optical susceptibility of most materials. For example, the power conversion efficiency of THG at solid substrate surfaces are usually in the range of 10^{-8} ⁴³, the excitation of harmonic generations usually requires ultrafast lasers which provide intensive laser pulses with power density as high as 10^{11} W/cm².

One of the most commonly used strategies for improving harmonic generation efficiency is through surface plasmonic coupling. Surface plasmon is the collective oscillation of surface electrons in a metal. When the surface electrons of a metal interact with an incident optical wave which has the same frequency as its oscillation, the surface electrons resonate with the incident optical wave and enhances the local electric field significantly. Noble metals are usually used for the excitation of surface plasmon resonance because their resonance wavelengths are in the visible-NIR range⁹⁸. As the intensity of nonlinear optical harmonic generation is exponentially proportional to the incident optical field intensity, plasmonic enhancement of local electric field can greatly enhance the efficiency of optical harmonic generation.

Plasmonic enhanced nonlinear optical harmonic generation was first studied on an electrochemically roughened Ag surfaces for SHG⁹⁹. It was discovered that

compared to a reference dielectric surface, SHG was enhanced by 10^4 -fold but with certain diffusion due to the propagation of surface plasmon polariton (SPP) on the Ag film. The SPP resulted diffusion was soon resolved by replacing the Ag film with a carefully designed noble metal structured surfaces¹⁰⁰. When the noble metal structures are of size comparable to the wavelength of incident light, the enhanced electric field is tightly confined around the nanostructure due to the localizing effect of localized surface plasmon resonance (LSPR)⁹⁸, which avoid the diffusion of harmonic generation due to SPP propagation. Then, a variety of noble metal structures including L-shape¹⁰¹, U-shape¹⁰² and bowtie¹⁰³ were designed for the enhancement of SHG and THG with an amplification factor up to 2,000. More recently, plasmonic nanostructure arrays were utilized for the enhancement of high harmonic generation¹⁰⁴⁻¹⁰⁵, which makes it possible for the emission of extreme deep UV with the excitation in the NIR wavelength.

Not only plasmonic arrays, a single plasmonic nanoparticle is also able to behave as a nonlinear optical medium through hyper-Rayleigh scattering (HRS), which is a second-order harmonic scattering predicted by Mie theory¹⁰⁶⁻¹⁰⁷. Experimental demonstration was then carried out for 13-nm gold nanosphere (AuNS), showing a hyperpolarizability of $2-3 \times 10^{-27}$ e.s.u/atom, which is higher than most molecular materials¹⁰⁸. Similar findings were discovered for other plasmonic nanoparticles like 32-nm Ag nanoparticle¹⁰⁹. Noncentrosymmetric nanoparticles were utilized to

achieve even higher dipolar response since SHG is stronger when centrosymmetry is broken¹¹⁰. Higher-order of dipoles such as octupoles have been achieved by tailoring the plasmonic nanoparticles¹¹¹. Non-spherical nanoparticles were then fabricated since they have an even lowered symmetry than sphere. For example, SHG from a sharp tip of a gold (Au) nanocone was excited with intensity dependent on the polarization of incoming light¹¹². Another interesting design of non-array plasmonic structure involves an aperture in an Ag film surrounded by concentric rings. The concentric rings act as gratings and concentrate incoming light to the central aperture, and enhanced its SHG by four magnitudes¹¹³.

Another advantage of LSPR enhanced nonlinear optical harmonic generation is that the confined enhancement of electric field makes it possible to amplify optical harmonic generation in sub-wavelength size⁹⁸. A demonstration of enhanced THG from single indium tin oxide (ITO) crystal was made by Aouani *et.al* and its THG was enhanced by six of magnitude. The ability of local electric field confinement of LSPR may pave the way to sub-wavelength light manipulation¹¹⁴.

While the electric confinement effect of LSPR reduces the diffusion of enhanced harmonic generation, the effective volume of enhanced electric field is also limited, which results in less efficient optical harmonic generation enhancement. Compared to plasmonic nanoparticles of noble metals, dielectric materials with high-index resonance with the magnetic field of the incoming light and has a resonance volume

much higher than noble metal nanoparticles. Several explorations have been made to enhance THG using Si³⁶ and Ge²⁴ nanoparticles. An enhancement of THG efficiency of two magnitudes was found for Si nanoparticle amplified THG while using Ge nanoparticles, THG was enhanced by one magnitude^{24, 36}.

Intersubband transition is also found to be able to significantly enhance nonlinear susceptibility¹¹⁵. This was firstly discovered by finding that in two-dimensional (2-D) heterogenous materials, nonlinear susceptibility can be greatly enhanced. For example, in carefully designed GaAs/AlGaAs heterostructure where the quantum well of the semiconducting heterostructure matches with the incident laser, THG was found to be more than five orders of magnitude higher than that in bulk GaAs due to the resonance of incident laser with the quantum well¹¹⁵. Similar exploration was also carried out utilizing InAs/GaAs quantum dots because of the 3-D confinement of quantum well²³. In recent years, with the development of fabricating 2-D materials with the thickness of only a few atomic layers such as WSe₂¹¹⁶ and MoS₂¹¹⁷, intersubband transition becomes more attractive in improving the efficiency of nonlinear optical harmonic generation^{28, 118} due to the fact that it is responsible for the high nonlinear susceptibility of these materials.

Figure 2. 9 Examples of strategies for enhancing nonlinear optical harmonic generation. (a)-(c) Plasmonic nanostructure arrays with L-shape¹⁰¹, U-shape¹⁰² and noncentrosymmetric structure¹¹⁷ for enhancing optical harmonic generation. (d) Circular grating enhanced SHG from aperture on Ag film¹¹³. (e) THG enhanced by single Si nanoparticle³⁶. (f) THG from single ITO nanocrystal enhanced by plasmonic nanoantenna¹¹⁴. (g) High harmonics enhanced by Ag nanocone structure for deep UV generation. (h) Nonlinear optical susceptibilities enhanced by bandgap resonance in WSe₂¹¹⁹. (I) SHG enhanced by bandgap resonance in WSe₂ monolayer¹¹⁹. (j) High harmonic generation in MoS₂ due to intersubband transition¹¹.

2.6.2 Enhancement of Luminescence from UCNPs

Similar to nonlinear optical harmonic generation, luminescence from UCNPs can also be amplified by plasmonic nanostructures. With an appropriate distance between UCNPs and plasmonic nanostructures, the concentrated electric field can act as localized “hotspot”, efficiently improves the absorbance of excitation light of

the nearby UCNPs. This enhancement is also known to be the result of an increased radiative decay rate caused by the increased density of optical states due to LSPR¹¹⁹.

Despite their similarities, the long-lived intermediate states of UCNPs merit more careful consideration. These intermediate states usually have more than one competitive decay pathways. If inappropriately triggered by plasmonic nanoparticles, undesired pathway may be enhanced, resulting in non-radiative decay of excited ions and thus reducing the UC efficiency¹²⁰. Furthermore, the UCL related intermediate states are interdependent. If the population of one intermediate state changes, the other one will also change³⁷. Besides, the UC emission is highly dependent on the input power. While it shows a nonlinear behavior similar to harmonic generation at low power range, at high input power, the relationship between emission and excitation light is linear, which is known as the saturation effect¹²¹. The metallic nanoparticle can alter the transition point that separates the low- and the high-power regimes, which in turn, affects the enhancement of the UC emission.

Up to date, many plasmonic geometries have been employed to investigate plasmonic-enhanced UC. Most of the work focused on plasmonic local resonators such as core-shell particles¹²²⁻¹²⁵; or extended structures such as sphere assemblies¹²⁶⁻¹²⁸. Few pioneering and inspiring work has been done in studying

plasmonic enhanced UC in single nanoparticle level with the aid of microscopy technology¹²⁸⁻¹³⁰.

Figure 2. 10 Examples of plasmonic-enhanced UCL. (a) and (b) Core-shell structure for UCNP luminescence enhancement, the maximum reported enhancement factor was 27-fold¹²². (c) and (d) Extended structure for amplification of UCNP luminescence using lithography fabricated and self-assembled structures, up to 310-fold enhancement was achieved¹²⁷⁻¹²⁸. (e) and (f) Single nanoparticle-based study of plasmonic-enhanced UCNP luminescence, the distance between UCNP and plasmonic nanoparticles were controlled utilizing lithography fabricated well and atomic force microscope, respectively. Enhancement factor up to 110-fold was reported¹²⁹⁻¹³⁰.

2.6.3 Limitations of Previous Studies

While plasmonic enhancement plays a common strategy for improving efficiencies of both nonlinear optical harmonic generation and UCNP luminescence, the

confined mode volume of LSPR, difficulties in plasmonic nanostructure fabrication and intrinsic variations of chemically synthesized nanoparticle all limit the potential of UC emission amplification using plasmonic coupling methods. As two of the main methods to achieve optical UC, nonlinear optical harmonic generation and UCNP luminescence shares many similarities in mechanism. However, the interaction between harmonic generation and UCNP luminescence have not been investigated. The ladder-like energy levels of lanthanide ions in UCNPs may resonant well with the incident laser for the excitation of nonlinear optical harmonic generation, while the emission wavelength of UCNPs can also match that of harmonic generation, which makes it possible for new strategies to improve the efficiency of nonlinear optical harmonic generation. To investigate the interaction between nonlinear optical harmonic generation and UCNP luminescence and to explore new ways to improve UC efficiency, Chapter 5 will present a study involving coherent amplification of THG utilizing luminescence from UCNP thin-film excited by fs laser.

2.6 Summary

In this chapter, a comprehensive literature review was presented on ultrafast laser excited nonlinear optics. The existing problems and research gaps in nonlinear optical UC processes can be summarized as follows:

Despite the efforts in exploration of mechanism in nonlinear optical harmonic generation and its efficiency affecting factors, there has been no thorough characterization of the dependence of nonlinear optical harmonic generation on the incident power density, sample crystalline property, incident polarization, incident angle and excitation depth. With a comprehensive characterization, a deep insight into nonlinear optical harmonic generation can benefit future investigations in the application of nonlinear optical harmonic generation.

Nonlinear optical harmonic generation is known for its non-destructive nature, high resolution and selectivity to interfaces in the area of surface probing and characterization. However, its potential in internal defects inspection has not been fully explored yet. At the same time, current methods for internal defects inspection for Si wafers including optical transmission, ultrasonic based inspection techniques, lock-in thermography and luminescence-based techniques suffer from a variety of limitations such as low resolution, long averaging time and lack of surface selectivity. There are urgent demands in semiconductor industry for a non-contact, non-destructive inspection method for internal defects in Si wafers with high resolution and surface selectivity.

As another wavelength UC strategy, UCNP luminescence is also a nonlinear optical phenomenon that shares many similarities with nonlinear optical harmonic generation. Both of them suffer from low efficiency. Up to date, most of the efforts

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in amplification of nonlinear optical harmonic generation and UCNP luminescence are focused on plasmonic coupling, which is limited by the small mode volume of LSPR, the intrinsic variation of synthesized nanoparticles and the high expense in the fabrication of large plasmonic arrays. However, the interaction between optical harmonic generation and UCNP luminescence has not been studied. The possibility of utilizing the intersubband transition in lanthanide ions doped in UCNPs to enhance optical harmonic generation efficiency has not been investigated.

These existing problems are the main research focus of this thesis. The detailed studies for each problem are presented in the following chapters.

Chapter 3. Characterization of Nonlinear Optical Harmonic Generation at Crystalline Sapphire Wafers

3.1 Preamble

As discussed in Chapter 2.3, a comprehensive characterization of nonlinear optical harmonic generation at optical media would be helpful in further exploration of applications in nonlinear optical harmonic generation. In this research, we comprehensively studied on THG at thin air-dielectric interfaces of the sapphire wafers by controlling the wafer cutting planes, focusing depth, incident angle, laser intensity, and input polarization state of the input fs laser pulses. Sapphire is chosen as the optical medium because of its excellent optical transmission in UV-visible range, high thermal conductance for efficient heat dissipation, and good physical and chemical stability. These findings can lead to broader use of TH for high-precision sapphire characterization, such as surface quality inspection, crystallinity determination, interfacial studies, delamination check, and real-time monitoring of crack generation & propagation.

3.2 Experimental Procedure

The experimental setup was as illustrated in Fig. 3.1. A NIR fs laser with the central wavelength of 1.595 μm , repetition rate of 83.3 MHz and average power of 54 mW (Toptica FemtoFiber pro NIR) was used as the excitation light source. A half-wave plate (HWP; Thorlabs WPH10M-1550) was used to rotate the polarization state of the linearly polarized input beam. The excitation laser pulses passed through an 800 nm long-pass filter (Thorlabs FEL-800) installed before the focusing objective lens (OL) to remove the SHG and THG contributions generated in the Er-doped fiber pre-amplifier inside the laser system. fs laser pulses were then reflected by a set of mirrors and focused by a 40 $\times$ OL having a numerical aperture (NA) of 0.65. The focal spot size was 7.6 μm at a working distance of 600 μm , which corresponds to a peak power of $1.1 \times 10^9 \text{ W/cm}^2$. It is worth to note that the OL was installed on top of a 3-axis stage (Thorlabs RB13M) for adjusting the excitation depth and high-precision angular tilting mirrors were installed before the OL for testing the incident angle effect. THG spectrum generated at sapphire wafers was then collected by a 20 $\times$ OL (Olympus UPlan 20 $\times$) installed at an inverted microscope and analyzed at a spectrometer (Andor's Shamrock 193i) and an electron multiplying charge coupled device (EMCCD; Andor's IXon Ultra) as shown in Fig. 3.1a. Single crystal sapphire wafers of a 430 μm thickness were used as the measurement specimen. The atomic structure of sapphire wafer and the excitation scheme for the in-depth characterization are shown in Fig. 3.1b. The oxygen ions (shown as the blue spheres)

take the form of closest hexagonal packing, and the alumina cations (shown as the grey spheres) lie in the octahedral hollows among the closely packed oxygen ions, filling two-thirds of these hollows¹³¹. As an $R\bar{3}c$ group hexagonal crystal, the sapphire can be cut along four different planes termed as A, C, M and R-planes; the different cutting plane results in different atomic structure along with the polarization state of the incident laser electric field. For example, C-plane sapphire is cut in perpendicular to the z-axis and has a hexagonal surface atomic structure; on the other hand, R-plane is defined as the plane where the non-occupied octahedral hollows are aligned. The surface atomic structure of R-plane is of rectangular shape¹³¹. As a result, THG at the sapphires with different cutting planes will differently respond to the input polarization, excitation depth, and incident angle⁴⁸. In this investigation, we tested all the specimens with different cutting planes including A, C, M and R-planes.

Figure 3. 1 THG in crystalline sapphire. (a) Optical layout. (b) Atomic structure of C-plane sapphire as an example. Input polarization state, incident angle, and excitation depth were controlled to characterize the THG from sapphire wafers with different cutting planes. Abbreviations: HWP: half-wave plate, LPF: long-pass filter, OL: objective lens, and EMCCD: electron multiplying charge-coupled device.

3.3 Result and Discussion

3.3.1 THG Characterization: Spectral Position, Bandwidth, and Conversion Efficiency

The THG spectra from the sapphire wafers with different cutting planes are shown in Fig. 3.2a. The incident beam was aligned perpendicular to the surface of sapphire wafers and focused onto the top surface. Clear THG peaks were observed at 531 nm for all cutting planes with negligible wavelength deviations, which is in a good agreement with one-third of the input laser wavelength. In order to identify the spectral bandwidth of THG, the bandwidth of the TH was normalized here by

dividing the photon energy spread by the harmonic order, 3, and overlapped with the bandwidth of the fundamental beam as shown in Fig. 3.2c. The spectral bandwidth of the THG was 0.005 eV in FWHM, which is relatively smaller than that of the fundamental beam, 0.008 eV in FWHM. The smaller normalized bandwidth of the THG is expected to come from the material dispersions from a series of optical components in the microscope system. Imperfect dispersion compensation broadens the pulse so different wavelength portions of the pulse arrive at the sample at different timing. This results in the spectral bandwidth reduction in generated TH spectrum. All observed TH peaks were in Gaussian shape (See Fig. 3.2a). The intensity dependence of the THG yield was tested for all cutting planes as shown in Fig. 3.2b. The slopes were 3.09, 2.82, 2.93 and 2.76 with deviations of 0.016, 0.016, 0.036 and 0.040 in standard deviation for A, C, M and R-planes, respectively. These matches well with the power dependence law for nonlinear perturbative harmonic generation, $I_{THG} \propto P^n$, where n is 3 in THG. Note that second harmonic was not detected in this experiment; the THG intensity was much higher than the SHG intensity at least by 10^5 times considering the EMCCD gain. This is because the sapphire lattice has a centrosymmetric structure in all cutting planes¹³¹. When a sample excited by an external electric field (e.g. a laser pulse), the potential energy of the dipole in a centrosymmetric medium is in the form of even function without the directional sensitivity as shown in Fig. 3.2d⁴³. Since the dipole intensity corresponds to the integration of the dipole potential energy, it is comprised of the

odd functions in centrosymmetric medium¹. Therefore, the nonlinear susceptibility, which is proportional to the dipole intensity, is also odd function, so the even order susceptibilities of the sapphire are zero (including the 2nd-order susceptibility required for SHG). Second harmonic can be generated at the sapphire surfaces where the centrosymmetric geometry is broken; however, the relative SHG intensity is still much lower compared to THG¹¹.

Figure 3. 2 THG generated from sapphire wafers with different cutting planes. (a) THG spectra from A, C, M and R-plane sapphire wafers. (b) THG yield vs. pumping power density. (c) Normalized THG bandwidth compared with that of fundamental beam. (d) Atomic dipole potential energy with electric fields for noncentrosymmetric (left) and centrosymmetric (right) medium.

3.3.2 Polarization-dependent THG Spectrum: Study on Crystallographic Orientation Dependence

The THG yield dependence on crystal orientation is shown in Fig. 3.3. Because the energy band varies with the electron oscillation direction, the harmonic generation process is also dependent on the crystalline structure¹³²⁻¹³³. Fig. 3.3a shows a typical THG intensity spectrum from A-plane sapphire wafer excited by different input polarization states from 0 to 360°. Clear four-fold symmetry was observed for THG at 531 nm without any SHG signal at 775 nm for all polarization states. THG spectra at the sapphire wafers with different cutting planes are compared in Figs. 3.3b-e. Note that breaks are inserted into Figs. 3.3b-e from 540 to 760 nm for a magnified view around THG and SHG. For A, M and R-planes, four-fold symmetries were clearly observed with ~20% modulation depth. It matched well with the symmetric crystal lattice structures of A, M, and R-plane sapphires¹³⁴; it can be understood by considering the projection of a single unit cell of sapphire crystalline on to the A, M, and R-planes, which all show a four-fold symmetric rectangle. Meanwhile, the projection of a unit cell of sapphire on to C-plane forms a six-fold symmetric hexagon¹³⁴ but its THG spectrum did not show clear polarization dependency. The anisotropic nature of the energy gap along different axis in the Brillouin zone of sapphire leads to a polarization dependent third-order susceptibility, resulting in an angle-dependent THG yield²¹. However, for C-plane sapphire, the nonlinear optical dipole formed along the Γ -K axis in the Brillouin zone at 0 degree of incident

polarization and gradually changes to Γ -M axis at 60 degrees of polarization. The energy gap difference between Γ -K and Γ -M axis are very close to each other, and consequently leads to a weaker angle dependence compared to other planes^{27, 133, 135}.

Figure 3. 3 Crystallographic orientation dependence of THG from sapphires. (a) 3-D (top) and 2-D (bottom) intensity spectrum (from 500 to 850 nm) generated at an A-plane sapphire wafer under different input polarization states. Clear polarization dependence of THG was observed without SHG. (b) to (e) THG intensity spectra from A, C, M, and R-plane sapphire wafers with different incident laser polarizations, Breaks are inserted from 540 to 760 nm for a magnified view around THG and SHG. (f) Sapphire crystal cutting planes. (g) Sectioned THG intensity profile at 531 nm with different crystal cuts and incident polarization states.

3.3.3 Surface and Bulk THG: Study on Excitation Depth Dependence

THG is known to be more efficient at the interface between two materials with different refractive indices compared to the case generated inside the bulk medium^{29, 48}. However, the detailed relationship between the excitation depth and THG yield from the sapphire wafers has not been explored. To identify the relationship, the excitation depth was controlled by adjusting the height of the focusing OL installed on a three-axis micrometer translation stage; the depth of focus was 29.3 μm . A schematic of the experimental system is shown in Fig. 3.4a. Figs. 3.4c-f shows the THG intensity distribution under different excitation depths for all sapphire wafers with different cutting planes. The polarization angle was chosen to be 70° for the optimization of THG intensity. The THG intensity was strong at the top surface of the air-sapphire interface and decreased to zero inside the bulk volumetric part of the sapphire wafer. When the laser beam was focused on the bottom surface of another interface between air and sapphire, the THG intensity increased back. The lower THG intensity in the bulk part of the sapphire wafers before and after the laser focus can be explained by the Gouy phase shift which leads to the $\pi/2$ phase shift of generated THG beam¹³⁶; as the result, the two THG beams, one THG beam generated before the focal point and the other generated after the focal point, interfere with each other in destructive way so cancel out the resultant intensity to zero¹³⁶. This phenomenon commonly occurs for all cutting planes, indicating no dependence on crystal orientation. Fig. 3.4b shows the sectional THG intensity

profiles at different focusing depth. The THG intensity decreased to 50% at 23.6, 14.0, 17.2 and 13.6 μm from the air-sapphire interface (top and bottom surfaces) for A, C, M and R-planes; the intensity decreased to 0 at 51.6 μm for all sapphires with different cutting directions. With a sapphire wafer thinner than 51.6 μm , THG at top and bottom surfaces can be excited at the same time, which possibly provides a stronger THG emission by making constructive interference with the aid of phase-matching scheme. In order to realize constructive interference, the phase difference between THG at top and bottom surfaces of the sapphire wafer should be $2n\pi$ where n is an integer. As a result, the thickness of the sapphire wafer should be $1,595 \times (4n + 2) \text{ nm}$ to achieve constructive interference between TH excited at top and bottom surfaces of sapphire wafer. Note that bulk THG is not considered here, for a better understanding about surface and bulk contribution of THG in thin-film samples to achieve a higher THG efficiency, more studies are required.

Figure 3. 4 THG at different excitation depth in sapphire wafers. (a) System schematics for testing THG at different focal depths. (b) THG intensity at different focal depth in A, C, M and R-plane sapphires. (c) to (f) THG intensity map with different excitation depths for A, C, M and R-plane sapphires.

3.3.4 Sensitivity to Incident Angle Change: Study on THG's Angle Dependence and Propagation Vector

The THG intensity dependence to the incident angle was investigated by tilting the mirror located before the focusing lens, as shown in Fig. 3.5a. The input laser beam was tilted by 5.6° in 9 steps and the resulting THG intensity was measured for the sapphire wafers with different cutting planes. It was found that THG intensity decreased to 0 when the tilt angle was larger than 4° for all specimens with different cutting planes, as shown in Figs. 3.5b and c. This decrease in THG intensity is

mainly because of the weaker focused electric field on the sapphire surface to drive the atomic dipole in the horizontal plane of the crystal. This trend was similar at the bottom surface of the sapphire wafers.

Figure 3. 5 THG intensity and propagation direction with different incident angle and wafer inclination. (a) Experimental setup for THG excitation with different incident angle, the black dotted lines are guidelines to show the incident angle tilt; (b) and (c) THG intensity change with different incident angle for top and bottom generated THG, respectively; (d) and (e) Fundamental and THG beam location for top and bottom surface excited THG with different incident angle; (f) and (g) Fundamental and THG beam location for top and bottom surface excited THG with different wafer inclination. The fundamental and THG beams are coloured red and green respectively for clear identification, the dotted lines are guidelines to show the differences in beam location for top and bottom surface excited THG, scale bar stands for 20 μm .

The propagation directions of THGs in and out of the sapphire were finally tested. The position of the fundamental and THG beams were taken by a CCD camera with the tilt of the incident angle and sapphire wafers. To visualize THG beam without the fundamental beam, a short-pass filter (SPF) was installed in the illumination beam path. The resulting images of THG and fundamental beam on top and bottom surfaces of C-plane sapphire with different tilt angles from 0 to 1.8° are shown in Figs. 3.5d and e. When the input beam was focused onto the bottom surface of the sapphire with a 1.8° tilt angle, both the fundamental and THG beams were shifted by $\sim 15.6 \mu\text{m}$, which meets well the theoretical value of $15.4 \mu\text{m}$ based on geometrical calculation. Meanwhile, when the input beam was focused onto the top surface, the optical refraction of the focused beam inside the sapphire induced an extra shift of the beams. As the result, both fundamental and THG beams were shifted by $18.3 \mu\text{m}$ with the same tilt angle of 1.8° , which is also close to the theoretical value of $19.3 \mu\text{m}$. This shift was 26% larger than that of THG at the bottom surface. When the input beam was focused to the bottom surface, TH is generated in the shallow depth near to the bottom surface and propagate along the same propagation vector as the fundamental beam; therefore, the fundamental and THG beams were almost overlapped with each other without obvious chromatic beam split. On the contrary, when the input beam was focused onto the top surface of the sapphire, the fundamental and THG beams were separated by $1.7 \mu\text{m}$ at an incident angle 1.8° . It is caused by the wavelength-dependent refractive indices

(1.74 at fundamental and 1.78 at TH wavelength)¹³⁷, which leads to the chromatic separation of THG and fundamental beam at the top surface of sapphire wafer. The THG beam can be also steered by tilting the target specimen, the sapphire wafer, which is shown in Figs. 3.5f and g. The global beam shift was 11.6 μm for an incident tilt angle of 3.6° , which is close to the calculated value of 11.5 μm ; this is smaller than the case of tilting the input beam. The beam separation could not be clearly detected due to lower angular dependence. These results suggest that the fundamental and THG beams can be simply split or steered for a series of applications, such as multi-colour beam separation and combination in pump-probe experiment or THG efficiency improvement by angular phase-matching.

3.4 Summary

To summarize, we generated TH at both the top and bottom air-dielectric interfaces of sapphire with different crystalline cutting planes by focusing intense NIR fs laser pulses. The crystal orientation was found to affect the THG intensity by $\sim 20\%$ for A, M and R plane wafer, while this orientation dependency was not clear for the C-plane. The THG intensity was highest at the top and bottom surface and decreased by half when focal depth was over 18 μm from the interface. This suggests that THG conversion efficiency can be improved by generating THG from the top and bottom interfaces at the same time by selecting the sapphire thickness to be less than 51.6 μm and phase-match the generated THGs. When THG was at the top surface, the

propagation vectors of the fundamental beam and TH beam were different due to refraction; which was not conceivable at the bottom surface when THG was generated within the shallow depth around the bottom surface. The fundamental and THG beams were split by controlling the incident angle; when the incident angle of the input beam was adjusted by 1.8° , the relative position shift was $15.6\text{ }\mu\text{m}$, but when the sapphire wafer was tilted by 3.6° , the position shift was about $11.6\text{ }\mu\text{m}$. These findings will enable simple and efficient in-depth characterization of sapphire wafers for monitoring surface quality, crystallinity, interfacial uniformity, inter-layer delamination, and crack propagation.

Chapter 4. Surface Third and Fifth Harmonic Generation at Crystalline Si for Non-invasive Inspection of Si Wafer's Inter-layer Defects

4.1 Preamble

As discussed in Chapter 2.4, Detection of inter-layer and internal defects in semiconductor Si wafers by non-contact, non-destructive and depth-resolving techniques with a high lateral and depth resolution is one of the challenging tasks in modern semiconducting industry. In this research, we report that nonlinear optical harmonic generation can be of great value therein because it enables non-invasive inspection of inter-layer defects with sub-micrometer depth resolution in extensive penetration depth over several millimeters. Compared with existing inspection methods for inter-layer defects, such as ultrasound, photoacoustic and photothermal imaging, the proposed technique provides higher lateral and depth resolution as well as higher interfacial selectivity. For in-depth understanding of nonlinear harmonic generation at Si wafer surfaces, the spectral power distributions of third and fifth harmonics from Si wafers with various crystal orientations and dopants were carefully analyzed under different incident polarizations and excitation depths using a NIR fs laser as the excitation light source. We finally demonstrated that stacked Si

wafers' inter-layer defects, such as delamination or stacking faults, can be inspected with high lateral and depth resolution in a non-contact and non-destructive way. These findings will pave the way to the potential applications of nonlinear optical harmonic generations in the fields of interfacial studies of crystalline materials, high-resolution detection of sub-diffraction-limit surface defects, and high-resolution imaging of internal structures in stacked semiconductor devices.

4.2 Experimental Procedure

Semiconductor Si wafers are opaque because they have low optical transmittance of less than 0.0001% due to high linear absorption over the whole visible wavelength from 400 to 850 nm, where the photon energy is higher than the band gap of Si (~ 1.10 eV) (See Figs. 4.1a and b). Therefore, the internal and inter-layer defect inspection of semiconductor products has been difficult with conventional optical inspection systems. If we shift the spectral range of our interest to NIR regime having longer wavelengths than 1,100 nm where the photon energy is lower than the energy band gap, Si wafers are partially transparent; the transmittance through a 5.0 mm Si wafer is about 52% (See Fig. 4.1b), which is high enough for efficient inspection of internal structures and defects. The other remaining inspection issue is the depth selectivity when measuring stacked multi-layer wafers. The NIR light transmits through the stacked wafers, which makes all the layer images being overlapped. Thus, in order to check the inter-layer stacking faults, depth selectivity

is essential, which cannot be realized with traditional optical inspection methods. Therefore, we newly introduced nonlinear THG and FHG here for depth-resolved and layer-sensitive multi-layer inspection.

Figure 4. 1 Nonlinear optical processes in single crystalline Si and its application for internal or inter-layer defects detection. (a) Digital image of stacked Si wafers, scale bar stands for 1 cm. The insets show the schematics of perfect interface between stacked wafers and possible inter-layer defects including bumps, sub-wavelength dust, and delamination. (b) Wavelength-optical transmission spectrum of a 5.0 mm Si wafer. (c) Optical setup for the experiment. (d) Atomic structure of intrinsic (100) crystalline Si as an example. Input polarization state and excitation depth were controlled to characterize the nonlinear optical processes from Si wafers with different doping and cutting planes. The presence of internal defect will induce nonlinear optical harmonic generation and results in lower incident laser transmission. Abbreviations: BS: beam splitter, SPF: short-pass filter and PD: amplified photo-detector.

Fig. 4.1c shows the optical layout for Si wafer characterization and defect inspection. A NIR mode-locked Er-doped fiber fs pulse laser (Toptica, FemtoFiber Pro NIR) having a central wavelength of 1,595 nm was selected as the inspection light source considering the high NIR transmittance of Si wafer and high optical power required for efficient THG and FHG. The pulse repetition rate and the pulse duration were set to ~83.3 MHz and ~400 fs, respectively. For in-depth characterization of THG and FHG at Si wafers, five Si wafers having different crystal orientations and doping conditions were tested, including intrinsic, P-doped and N-doped ones with either (100) or (111) crystalline orientation. All Si wafers utilized here had the same thickness of 500 μm and diameter of 4 inches. The detailed information of Si wafers used in the experiment can be found in Table 4.1. An HWP (Thorlabs WPH10M-1550) rotated the polarization state of the linearly polarized input laser beam. Before the focusing OL, the laser beam was firstly long-pass-filtered to remove the background noise at shorter wavelength range than 1,200 nm. This is because the short wavelength noise can be generated during the power amplification in an Er-doped fiber amplifier and the power delivery through the optical single mode fiber. The laser beam was then focused into a small spot of a 7.6 μm diameter using a 40 $\times$ OL (Newport LI-40X) having an NA of 0.65; the power density at the focus was $1.1 \times 10^9 \text{ W} \cdot \text{cm}^{-2}$. Nonlinear optical harmonics generated from the Si sample were collected by another 40 $\times$ OL (Olympus UPlan 40X) with the same NA. They were delivered to a broadband spectrometer (Andor's Shamrock

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193i) with a highly-sensitive EMCCD (Andor's IXon Ultra) for the spectral analysis and an amplified photo-detector (PD; Thorlabs, PDA10CF) for the power analysis in the frequency domain. For highly sensitive detection of relatively weak fifth harmonic (FH) pulses, a 400 nm SPF (Ruiqi Optoelectronics SPF-400) was installed to suppress the relatively strong background noise at longer wavelengths.

Table 4.1 Characteristics of Si wafers used in the experiment.

Name	Doping	Doping concentration (cm ⁻³)	Energy bandgap (eV)	Size (inch)	Thickness (μm)	Crystal orientation	Resistance (Ω·cm)
Un-(100)	Intrinsic	None	1.13	4	500 ± 10	<100>	>5000
Un-(111)	Intrinsic	None	1.13	4	500 ± 10	<111>	>5000
N-(100)	Phosphorus	4.5×10 ¹⁴	1.129	4	500 ± 10	<100>	10
P-(100)	Boron	1.4×10 ¹⁵	1.129	4	500 ± 10	<100>	10
P-(111)	Boron	1.4×10 ¹⁵	1.129	4	500 ± 10	<111>	10

When the intense NIR laser pulses are focused onto the internal or inter-layer defects in Si wafers, TH and FH are generated at the defects; this energy conversion to shorter wavelength induces the optical power decrease at the fundamental NIR wavelength due to energy conservation law. Because TH and FH generated inside the wafers are directly absorbed back to Si, they cannot be detected by the EMCCD nor photodetector; therefore, TH and FH cannot be used for Si wafer inter-layer inspection. Instead, we monitored the transmitted optical power at the fundamental NIR wavelength over different focal lengths to reconstruct the interfaces among different layers, and also to detect the internal defects with a high lateral and depth resolution.

Fig. 4.1d shows the conceptual diagram for THG and FHG at an intrinsic (100) Si wafer. Because Si is a typical face-centered diamond cubic crystalline material, the atomic structures of the Si along with the polarization states of the incident laser beam should be different with different crystalline faces⁹. For example, while the (100) plane of single crystalline Si has a 90° symmetry cell with the edge length of 0.54 nm¹³⁸, the (111) plane has a hexagonal bi-dimensional cell having the edge length of 0.76 nm¹³⁹. The cell's edge length affects the dipole strength, which determines THG and FHG efficiencies under different polarization states of the incident laser beam⁴³. The different cell symmetry also results in the difference in harmonic spectrum^{9, 43}. Because the doping rate changes with the energy band structures, its variation also changes the power conversion efficiencies in harmonic generation¹⁴⁰⁻¹⁴¹.

4.3 Result and Discussion

4.3.1 THG and FHG: Spectral Peak Position, Conversion Efficiency, and Spectral Bandwidth

TH and FH were generated at the lower surfaces of the Si wafers as shown in Fig. 4.2a. Fig. 4.2b shows the energy diagram involved in THG and FHG. Three photons at the fundamental wavelength are combined at the Si wafer into one new photon having three times higher photon energy in THG, while five photons are involved in FHG resulting in five times higher photon energy. The typical output spectra

including the fundamental laser beam, TH, and FH are shown in Fig. 4.2c. Figs. 4.2d and g show the experimental spectra of third and fifth harmonics from various sets of Si wafers with different doping and crystalline axis. Clear TH peaks are observed at ~531 nm as in Fig. 4.2d with minor deviation of less than 3.2 nm for different samples; these minor deviations could come from the imperfect optical alignment during the sample unloading and reloading. It is worth to note that the fundamental laser's NIR spectrum around 1,595 nm was measured using an optical spectrum analyzer (OSA, Yokogawa AQ6370D) instead of the EMCCD due to the low spectral sensitivity of Si-based detectors at longer wavelength than 1,000 nm. The absolute power of TH was measured to be 1.54×10^{-6} mW at the maximum average pump power of 56.3 mW using a high-sensitivity photomultiplier tube (PMT; Thorlabs, PMT1001M); the measured THG power was then normalized by the transmittance and reflectivity of the lens and mirrors along the optical pathway. The normalized power of THG was determined to be 5.57×10^{-6} mW, which leads to the conversion efficiency to be 9.9×10^{-8} . FH peaks are observed around 330 nm, which is slightly higher than one-fifth of the excitation laser wavelength, ~319 nm. This deviation comes from the contribution of multiphoton luminescence at high pumping peak intensity. Multiphoton luminescence also results in higher emission yield and boarder spectra as in Figs. 4.2h and i, which will be discussed in the following paragraphs of this Chapter. The absolute power of FH could not be directly measured due to the low signal level even with the high quantum efficiency

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of a PMT; the conversion efficiency was indirectly estimated using the relative power ratio of fifth- and third-order harmonics detected by EMCCD. The intensity ratio between THG and FHG detected by the EMCCD at maximum pumping power density was 114.7. Because THG was at 531 nm while the wavelength of FHG was 330 nm, this ratio should be normalized by the transmittance and quantum efficiencies of all optical components, spectroscopy, and EMCCD, which lead to a THG/FHG intensity ratio of 82.5. The FHG efficiency can be then estimated to be around 1.2×10^{-9} .

Figure 4. 2 Characterization of third and fifth harmonic generations from Si wafer at different crystalline orientation and doping conditions. (a) Schematic for the experimental setup for TH and FH excitation. (b) Energy diagram for THG and FHG. (c) Representative normalized spectra of incident laser, THG, and FHG. Normalized spectra, intensity-pumping power density plot, bandwidth and photon energy spectra of THG (d) to (f) and FHG (g) to (i) from Si wafer.

The emission yields of TH and FH are evaluated by the linear-fitted slopes of the harmonic-intensity vs. pump power density relations as shown in Figs. 4.2e and h. For THG, the slopes are 2.94, 2.92, 2.93, 2.96 and 2.86 for intrinsic-(100) (hereafter, this will be abbreviated to un-(100)), P-(100), N-(100), intrinsic-(111) (hereafter, this will be abbreviated to un-(111)) and P-(111) Si wafers with standard errors of

0.028, 0.034, 0.029, 0.026 and 0.024, respectively. All these slopes are very close to 3.0 within 3% deviation, which agrees well with the nonlinear power dependence, $I_{THG} \propto P^n$ in nonlinear perturbative harmonic generation, where n is 3 for THG and 5 for FHG. FH slopes are 7.16, 7.15, 7.38, 7.67 and 6.54 with standard errors of 0.26, 0.75, 0.76, 0.90 and 0.18 for un-(100), P-(100), N-(100), un-(111) and P-(111) Si wafers. These emission yields are higher than 5.0 for all wafers, suggesting that there are additional power contributions from other mechanisms, such as multiphoton luminescence¹⁴²⁻¹⁴³. There has not been a report about the multiphoton luminescence from bulk Si but it was reported in Si quantum dots and similar semiconducting materials such as GaAs¹⁴³⁻¹⁴⁴. The relatively larger standard errors are expected to come from the low power conversion efficiency of FHG; because of this lower efficiency, FH is more vulnerable to spectral background noise than TH.

The spectral bandwidths of TH and FH are analyzed as in Figs. 4.2f and i. The bandwidths of TH and FH are converted from wavelength domain to photon energy domain, then, normalized by dividing the photon energy spectra by harmonic orders, which is 3 for TH and 5 for FH. The resulting spectra for both TH and FH make good agreement with the original spectral profile in the fundamental wavelength (See Figs. 4.2f and i); theoretically, the normalized harmonic spectral bandwidth is the same with that of the fundamental beam. The bandwidths of TH spectra with different wafers are all ~0.005 eV in FWHM, slightly smaller than that of fundamental laser spectrum of 0.008 eV. This smaller TH bandwidth is expected to

come from the spectral characteristics of the optical components in the imaging path, spectrographs, and EMCCD. The material dispersions of all focusing and imaging optical components could also contribute to this spectral bandwidth reduction. For FHG, the normalized spectra show ~ 0.021 eV bandwidths in FWHM, which is wider than that of the fundamental laser (0.008 eV). This broader bandwidth and its different spectral shape (See Fig. 4.2i) cannot be simply explained by the harmonic generation mechanism; this peak broadening could come from weak multiphoton luminescence from Si¹⁴⁴⁻¹⁴⁵. It should be noted that the spectral resolution of the EMCCD-based spectrograph system is 0.47 nm (this corresponds to 0.005 eV in photon energy), so the wider FH bandwidth does not come from the spectral resolution. The spectral power of the multiphoton luminescence around TH is much weaker compared to TH, so we could not observe this trend in TH. However, FH has two orders of magnitudes lower power conversion efficiency than TH at the pump power density of 187 kW/cm², which makes the multiphoton luminescence more significant at FH.

4.3.2 Polarization-dependence of THG and FHG: Crystallographic Orientation Effect

The yield dependence of THG and FHG to different incident polarization states was tested as shown in Fig. 4.3a. The conversion efficiency of nonlinear perturbative harmonic generation process is strongly dependent on the crystalline structure due

to the variation of energy bands at different electron oscillation directions as shown in Fig. 4.3b²⁹. Normalized THG and FHG spectra at different incident polarization states from 0 to 360° for un-(100), P-(100), N-(100), un-(111) and P-(111) wafers are shown in Figs. 4.3c-l. At all polarization states, THG shows a distinct peak around 531 nm with the deviation of less than 3.2 nm; this deviation is expected to come from the optical axis misalignment in the excitation pathway. Note that breaks are inserted to the horizontal axis of Figs. 4.3c-g to clarify that SHG signal was not observed in all polarization and doping conditions. For all the samples except P-(111), clear four-fold symmetry is observed with ~35% modulation depths. No clear polarization dependence is observed in P-(111) Si wafer, which is because the P-type ions are randomly doped into Si crystal so break the symmetric structure of Si lattice. The longer atomic distance between nearby Si atoms in the <111> crystal plane results in weaker electric dipole formation when exposed to the laser field¹⁴⁶. As a result, the dopants play a crucial role in determining the dipole strength when excited by the polarized light²⁶. Due to the random distribution of the dopants in Si crystal, the overall intensity of electric dipoles is not dependent on the polarization state of the excitation laser field²⁶. This explains the weaker polarization dependence of THG yield for P-(111) Si wafer. In (100) Si wafer, the shorter distance to nearby Si atoms on the lattice plane creates a stronger electric dipole when exposed to the polarized laser field and it also weakens the counter effect made by randomly distributed dopants in Si crystal. These lead to the stronger polarization dependence

of THG in doped (100) Si wafers. Similar trends are observed in FHG. For Si wafers other than P-(111), clear four-fold symmetry is observed with a modulation depth of $\sim 50\%$, which confirms the presence of FHG. This higher polarization dependence for FHG can be explained by higher sensitivity of the electron restoration forces in higher-order nonlinear optical processes^{27, 43}.

Figure 4. 3 Crystallographic orientation dependence of third and fifth harmonics from Si wafers. (a) Experimental setup for measuring crystalline orientation dependent THG and FHG intensity. (b) Schematics for the dependence of nonlinear optical dipole and THG intensity on the polarization state of incident laser. (c) to (g) THG intensity spectra from Si wafers of different doping and crystal orientation with varying incident laser polarizations. Breaks are inserted from 550 to 750 nm for a magnified view around THG and possible SHG. (h) to (l) FHG intensity spectra from Si wafers of different doping and crystal orientation with varying incident laser polarizations.

4.3.3 Surface THG and FHG: Study on Excitation Depth Dependence

THG and FHG are both surface phenomena so they provide higher power conversion efficiency selectively at the interfaces between two materials having different refractive indices²⁹. In-depth studies on this excitation depth effect have been addressed as shown in Fig. 4.4. A high-resolution 3-axis translational stage (Thorlabs RB13M) was used to adjust the height of a focusing OL with a step size of 5.0 μm as shown in Fig. 4.4a. Figs. 4.4c-g show the resultant TH intensity distribution at different excitation depths for all five Si wafers with different doping concentrations and cutting planes. The polarization angle was chosen to be 280° for the optimization of TH and FH intensity. The TH intensity reaches its maximum at the Si-air interface and drastically decreases at both the air and bulk Si part. In the air side, TH cannot be excited due to the low density of molecules in atmospheric air. In the bulk Si side, the lower TH intensity can be explained by the Gouy phase shift which leads to $\pi/2$ phase shift of the generated TH beam³⁰; as the result, the two TH beams, one generated before the focal point and the other generated after the focal point, interfere with each other in destructive way so as to decrease the resultant intensity to zero³⁰. This occurs at all cutting planes, indicating no dependence on crystal orientation. Sectional TH intensity profiles at different focal depths are shown in *Appendix A*. By fitting the TH intensities at different focusing depths using Gaussian profile, it was found that FWHM of TH intensity decreases to 50% at 23.4, 20.1, 15.6, 18.5 and 12.3 μm from the air-Si interface for un-(100),

P-(100), N-(100), un-(111) and P-(111) wafers, respectively; the intensity decreases to zero at 52.1 μm for all Si samples. This suggests that the simultaneous excitation of TH at both top and bottom surfaces of Si would be possible for the wafers thinner than 52.1 μm . Compared to THG, FHG was found to be more sensitive to the excitation depth. The FH spectra from different excitation depths are shown in Figs. 4.4h-l. The maximum FHG is also found to be located at the exact excitation depth for maximum THG. The full-widths FH intensity decreases to 50% are 6.1, 5.5, 5.2, 5.0 and 5.4 μm , respectively. The FH intensity decreases to zero at the excitation depth of 34.6 μm away from the Si-air interface to both bulk Si and air side.

Figure 4. 4 Third and fifth harmonics at different excitation depth in Si wafers. (a) and (b) Isotropic and front view of the excitation depth depended THG and FHG from Si wafer. THG (c) to (g) and FHG (h) to (l) intensity map with different excitation depths for Si wafers with different crystal cuts and doping. White dotted lines are guidelines for the location of the Si-air interface.

4.3.4 Non-contact, Non-destructive, and Interface-selective Detection of Inter-layer Defects in Si Wafers

Because nonlinear optical phenomena are highly selective to the presence of interfaces, THG and FHG can be promising tools for efficient detection of the internal and inter-layer defects in Si wafers. When the intense fs pulses are focused to internal or inter-layer defects in Si wafers, the resulting TH and FH intensities increase significantly due to the breakage of local symmetry at boundary atoms and end unit cells. This process is governed by the energy conservation law in nonlinear optical processes, which is described by the equation,

$$J_t = J - J_r - J_a, \quad (4.1)$$

where J_t , J , J_r and J_a are the energies of transmitted, incident, reflected, and adsorbed photons, respectively. The absorbed photon energy can be described as

$$J_a = h \sum_n \omega_n = h(\sum_3 \omega_3 + \sum_5 \omega_5) + h \sum_i \Omega_i, \quad (4.2)$$

where h is the Planck constant, $\sum_n$, $\sum_3$ and $\sum_5$ are the sum of the photons absorbed in fundamental, TH, and FH wavelengths; ω_n , ω_3 and ω_5 are the optical frequencies of the fundamental beam, TH and FH; $\sum_i$ is the sum over the material excitations created in the elementary quantum process; $h\Omega_i$ describes the energy of an elementary material excitation, for example, a phonon or an exciton⁴⁴. This equation on energy conservation implies that TH and FH generated at the defects with energy

of $h \sum_3 \omega_3$ and $h \sum_5 \omega_5$ will result in the decrease of the transmitted intensity at the fundamental wavelength, J_t , which newly enables the efficient inspection of internal and inter-layer defects of Si wafers. Although TH and FH are at visible and UV wavelength regime where Si has low transmission of around 0.0001%, the intensity decrease at the fundamental NIR wavelength can be efficiently monitored using amplified InGaAs photodetectors thanks to the high transmission of Si wafers in the NIR range. Besides, the presence of material excitations in the elementary quantum process make the power decrease at the fundamental wavelength even larger than the simple sum of the energies of TH and FH, and therefore, improves the inspection resolution. Based on this energy conservation law in nonlinear harmonic generation, we demonstrated non-contact, non-destructive, and interface-selective detection of internal or inter-layer defects in stacked Si wafers with high resolution as shown in Fig. 4.5. Three un-(100) Si wafers of $280 \pm 10 \mu\text{m}$ thickness were stacked together to imitate a stacked Si wafers with a thickness of $\sim 840 \mu\text{m}$ and two inter-layer defects, one at $\sim 280 \mu\text{m}$ and the other at $\sim 560 \mu\text{m}$, respectively (See Figs. 4.5a-b). The focal depth of a NIR fs laser was scanned along the depth direction over the stacked Si wafers to measure TH intensity profile for the reconstruction of the inter-layer structures; the focusing OL was gradually shifted up with a $5 \mu\text{m}$ step size. At the interface between Si wafers, TH and FH are generated, which leads to sudden power decreases at fundamental wavelength (See Fig. 4.5c). The location of the interfaces can be calculated from the focusing depth by considering the refractive index of Si

at 1,595 nm, which was 3.47 in this experiment¹⁴⁶. For highly sensitive signal detection with minimal background noise, we introduced frequency-selective signal detection which is generally used in the field of optical communication. For the purpose, the intensity of incident beam was detected by a PD and analyzed by a radio-frequency (RF) spectrum analyzer (Rigol DSA875) with a resolution bandwidth of 1 kHz and a span from 83.3345 to 83.3350 MHz. A distinct RF peak is identified at 83.33 MHz, which matches well with the repetition rate of incident fs laser beam; this indicates that the coherence, linewidth, and mode spacing of the fs laser is successfully maintained during THG without been disturbed by the inter-layer defects (See the TH RF spectrum in linear and logarithm scale in Figs. 4.5d-e). The signal-to-noise ratio is higher than 55 dB, which means the signal strength is ~320,000 times higher than the background noise thanks to the frequency selective nature of RF spectrum analyzer; this is significantly higher than traditional non-frequency-sensitive analyzers such as oscilloscope, data analyzers, or EMCCD. The background noise was further suppressed to 0.36 mV by optimizing the data averaging time, which leads to an even higher depth resolution of 121 nm; the noise level at different data averaging time is shown in *Appendix B*. The accumulated RF spectrum along the depth scanning shows the interior interfacial structure of the stacked wafers as shown in Fig. 4.5f. Three clear gaps can be recognized around 287.3, 652.4, and 926.5 μm from the back surface of the overall stacked wafers, indicating the precise locations of the two Si-Si interfaces between stacked Si wafers

intimating the inter-layer delamination and the top Si-air interface of the Si wafer stack. The yellow dots on the right side of Fig. 4.5f show the peak intensity of RF spectra at different Si wafer depths, three clear dips can be clearly identified and match well with the positions of the interfaces. Note that these dips are created by the nonlinear optical absorption not by other linear optical phenomena such as multiple reflections at the Si-air-Si interfaces. This is experimentally evidenced by the dip at the excitation depth of 926.5 μm at the Si-air interface (See Fig. 4.5f), where multiple reflection does not take place. Theoretically, the intensity decrease made by the multiple reflections was calculated to be about 0.05% based on the Fresnel equations¹⁴⁷, which is two orders of magnitude lower than the experimental result of 3%; the detailed calculation is shown in *Appendix C*. Besides, linear absorption was also negligible in the experiment due to the low absorption coefficient of Si at 1560 nm ($\sim 10^{-9} \text{ cm}^{-1}$).

This proposed method provides a non-contact, non-destructive inspection technique for internal defects in Si wafers with a high depth resolution of 121 nm, which is higher than that of current standard methods such as ultrasonic and photothermal based techniques⁷⁵. The data acquisition time was 1 s, which is comparable to that of photoluminescence method, which is the fastest method to date not utilizing high energy radiation sources⁷⁵. It still does not meet the demands for on-line inspection of Si wafers, the data acquisition time can be further suppressed by replacing current free-space optical setup to fiber-coupled one, which can significantly reduce the

noise introduced by environmental light change and floor vibration. With the system improvement by adopting a shorter pulse duration laser, higher resolution translational stage for the focus scanning, and highly sensitive detector to FH, we believe this nonlinear harmonic generation can become a promising tool to achieve non-contact, non-destructive, on-line inspection of internal defects in Si wafers with high lateral and depth resolution.

Figure 4. 5 Detection of inter-layer defects in Si wafer stack using energy conservation in nonlinear optical harmonic generations. (a) and (b) Isotropic and side view of experimental setup for detection of inter-layer defects in Si wafer stacks. Spectra in (b) show the intensity of fundamental laser detected by the PD at the corresponding focusing depth. (c) Relative power diagram for fundamental laser focused at the bottom surface of Si wafer for TH and FH excitation. (d) and (e) Representative linear and logarithm spectra of fundamental laser detected by the PD. (f) Incident laser intensity map at different excitation depth of Si wafer, the yellow dots show the peak intensity of incident laser detected by the PD at different focusing depth inside Si wafers.

4.4 Summary

To summarize, we demonstrated depth-selective optical inspection of stacked Si wafers using nonlinear THG and FHG at interfacial surfaces. In-depth optical characterization was firstly addressed for understanding THG and FHG in crystalline Si wafers by focusing mode-locked fs pulses to the Si wafers with different crystalline orientation, doping ratio, and excitation depths. With different crystalline Si of intrinsic, P-doped, and N-doped wafers, TH and FH intensities were changed by 35% and 50%, respectively, whereas the crystalline intensity dependence was much weaker in P-doped (111) wafer. For non-contact, non-destructive, interface-selective detection of inter-layer defects inside the opaque Si wafers over the visible wavelength range, the focal depth the incident NIR laser beam was scanned along the depth direction of three stacked Si wafers and detected the Si-Si interfaces intimating the internal defects at the depth of 290 and 650 μm by monitoring the power decrease at the fundamental wavelength based on energy conservation in nonlinear optical harmonic generation. By introducing frequency-selective RF peak detection method and background noise suppression at the averaging time of 1 s, the depth resolution was improved to 121 nm. This scheme can serve as an excellent tool for surface and inter-layer studies in material sciences and nonlinear photonics as well as mass production of semiconductor devices.

Chapter 5. Interaction Between Nonlinear Optical Harmonic Generation and Luminescence from UCNPs

5.1 Preamble

As discussed in Chapter 2.5, The ladder-like energy steps in lanthanide ions may provide intersubband transitions that resonant with the incident and emission light of optical harmonic generation, while the interaction between luminescence from UCNPs and optical harmonic generation remains less investigated. In this research, we demonstrate the first coherent amplification of third-order harmonic fs pulses at multi-layered UCNP thin-film with an amplification factor of 7.8. This amplification was made by the resonance interaction of incident fs laser field, generated third-order harmonics, and the electric band gaps of UCNPs. The power contribution of the third-order harmonic and the UCL was strongly dependent on the sample geometry due to the reabsorption effect. For in-depth understanding of the emission characteristics, spectral-domain, time-domain, RF domain, and polarization-dependence analysis has been addressed. This coherent amplification of TH at UCNP thin-films enables us to attain higher power, shorter wavelength, and ultra-short fs pulses generated from simple thin-film structure near to the target samples,

which will pave a way to an ultrafast short-wavelength laser platform for material characterization, sub-wavelength photonics, and biomolecular detection.

5.2 Experimental Procedure

Fig. 5.1 illustrates the experimental setup for power amplification of TH at thin-film UCNPs. A mode-locked Er-doped fiber fs laser (Toptica FemtoFiber pro NIR) was used as the excitation light source with central wavelength of 1,560 nm, pulse duration of 200 fs, and repetition rate of 83.3 MHz. The UCNP thin-film was deposited on top of two substrates, a fused silica glass coverslip, and a crystalline intrinsic (100) Si wafer. An HWP (Thorlabs WPH10M-1550) was utilized to control the polarization state of the excitation laser beam. The SH and TH generated from the fs fiber laser and power amplifiers were removed by a 1,200 nm long-pass filter (Thorlabs FEL-1200). The excitation beam was focused onto the interface between substrate and UCNP thin-film by a 40× OL (Newport LI-40X) of a 0.65 NA; the resulting output TH and UCL were collected by another 40× OL (Olympus UPlan 40X) with a 0.65 NA. The collected light was then delivered to a broadband visible spectrometer (Andor's Shamrock 193i) in combination with an EMCCD (Andor's IXon Ultra) for the spectral domain analysis and a PMT (Thorlabs PMT1001M) for the time- and frequency-domain analysis. A series of optical band-limiting filters (Thorlabs FES-550 and FEL-600) were utilized with the PMT when measuring the rise and decay time of green or red emissions from the sample.

Figure 5. 1 Ultrafast laser excited self-assembled UCNP thin-film emission. (a) Schematic for the optical setup. (b) THG enhanced by UCL through ultrafast laser excitation. (c) TEM image for synthesized UCNP. (d) SEM image for self-assembled UCNP thin-film. (e) and (f) Schematics and normalized intensity for incident laser, THG and UCL across the sample with different geometry. Abbreviations: BF: band-pass filter; PMT: photomultiplier tube.

Erbium-doped sodium yttrium fluoride ($\text{NaYF}_4:\text{Er}^{3+}$) UCNP was chemically synthesized following the procedures reported Saboktakin¹²⁷. The self-assembled UCNP thin-film was then fabricated by the interfacial assembly method¹²⁷. Figs.

5.1c and d show the synthesized NaYF₄:Er³⁺ UCNP thin-film measured by a transmission electron microscope (TEM) and a scanning electron microscope (SEM). The mode-locked fs laser pulses were tightly focused onto the UCNP-substrate interface. The resulting beam diameter was $\sim 7.6\ \mu\text{m}$ and the power density at the focal spot was $\sim 4.4 \times 10^9\ \text{W}\cdot\text{cm}^{-2}$. As a surface phenomenon, the THG intensity at the interface between the substrate and UCNP is significantly higher than the bulk body by more than 10^5 times²⁹. Due to this high peak power of the fs pulse laser, both THG and UCL signals were clearly observed. The TH and UCL had a good spectral overlap at $\sim 531\ \text{nm}$, which enabled the efficient power amplification (See Fig. 5.1b). Interestingly, TH amplification factor was found to be strongly dependent on the excitation sample geometry. When the UCNP thin-film is placed facing towards the excitation laser beam (laser-UCNP-substrate geometry as shown in Fig. 5.1e), UCL gets strongly coupled to TH, resulting in TH yield enhancement. When UCNP thin-film is placed facing against the excitation laser beam (laser-substrate-UCNP geometry as shown in Fig. 5.1f), TH at 520 nm is generated firstly at the substrate-UCNP interface, then passes through the UCNP thin-film, which leads to reabsorption of TH by Er³⁺ ions in UCNP¹⁴. This reabsorption does not occur in the laser-UCNP-substrate geometry since the propagation direction of TH remains the same with fundamental laser beam⁹. While the absorption peak of Er³⁺ at 1,560 nm significantly enhances the absorption of fundamental laser beam at the interface between UCNP thin-film and substrate¹⁴⁸,

the nonlinear optical dipoles at the UCNP-substrate interface make resonance with the energy gap between the excited states and ground levels, which triggers the energy transfer from the excited electrons to TH²³. This effect results in the power amplification of TH and, in turn, the power reduction of UCL. Meanwhile, in laser-substrate-UCNP geometry, TH is firstly generated at the substrate-UCNP interface and propagates along with the fundamental laser beam; here, the absorption peak of Er³⁺ at 520 nm¹⁴ allows for the reabsorption of TH at the UCNP thin-film, which leads to less efficient TH amplification. The reabsorbed TH then acts as secondary excitation source for UCNP thin-film, resulting in higher intensity at UCL. The excitation geometry-dependent enhancement of THG demonstrated in this experiment can be applied for the development of tunable ultrafast light sources with high power, short wavelength and ultra-short pulse duration.

5.3 Result and Discussion

5.3.1 Spectral Domain Analysis of The Output Emission from Thin-film UCNPs

Fig. 5.2a shows the energy diagram of NaYF₄:Er³⁺ UCNPs. The one-third of the central wavelength of the fs laser matches well with one of the UCNP emission peaks, formed by the electron relaxation from ⁴H_{11/2} to ⁴I_{15/2}. This enables the resonance of the incident NIR fs laser (working as the fundamental pump light), its TH (working as the seed light), and UCL (working as the secondary pump light).

The emission spectra from two different sample geometries are shown in Figs. 5.2b and e. The emission from the laser-UCNP-substrate geometry contains a narrow peak at 536 nm with a 3.7 nm bandwidth and two relatively broader UCL peaks at 551 and 661 nm. The narrower THG peak at 536 nm here matches well with one of the UCNPs emission peaks, made by the electron relaxation from $^4H_{11/2}$ to $^4I_{15/2}$. Compared to the reference THG measured with a bare glass substrate without the UCNPs thin-film (See the blue curve in Figs. 5.2b and e), the spectral intensity ratio of the two peaks, one at 536 nm and the other at 516 nm is 4.9-times higher than the ratio in the laser-UCNP-substrate geometry, suggesting more efficient THG amplification at 536 nm while maintaining the original spectral bandwidth of TH. The detailed TH pulse characteristics will be verified further in subsequent sections. This power amplification mainly comes from the resonance between the $^4H_{11/2}$ - $^4I_{15/2}$ energy gap and the nonlinear electron dipole oscillation at the UCNPs-substrate interface excited by the fs pulse laser¹⁴⁹⁻¹⁵⁰. The amplification mechanism was further evaluated by the emission yield calculated from the linear-fit slope of the emission-intensity vs. pump-power-density plot as shown in Figs. 5.2c and f. A 7.8-times higher TH intensity was detected at 536 nm from the sample with UCNPs thin-film compared to bare glass slide. The THG emission yield from the reference bare glass slide was 2.85, while the emission yield from the UCNPs thin-film reaches 3.51, which is higher than the predicted value by the power dependence law for nonlinear perturbative harmonic generation ($I_{THG} \propto P_n$, where n is 3 in THG). Meanwhile, the

linear-fit slopes for UCNP emissions at 551 nm and 664 nm were 0.51 and 0.57, respectively; these are far lower than 3 (which is the case for THG) due to the strong scattering of UCL, high beam divergence due to the low coherence, and the limited collection angle of the imaging OL. The electrons of Er^{3+} are excited to $^2\text{H}_{11/2}$ following the three-step excitation process through $^4\text{I}_{13/2}$ and $^4\text{I}_{9/2}$. Due to the resonance between TH and $^2\text{H}_{11/2}$ - $^4\text{I}_{15/2}$ energy gap, the major portion of the electrons in $^2\text{H}_{11/2}$ move through the radiative pathway and enhance THG process, while the minor part of the electrons decay to $^4\text{S}_{3/2}$ non-radiatively for further relaxation to the ground state, resulting in the minor peak at 551 nm. At $^4\text{I}_{9/2}$, some part of the electrons also decay non-radiatively to $^4\text{I}_{11/2}$ due to the relatively higher stability of $^4\text{I}_{11/2}$ Ref [17]⁷⁷; then, these electrons are pumped to $^4\text{F}_{9/2}$, followed by relaxation to the ground state and emit photons at 661 nm.

Figure 5. 2 Comparison of THG and UCL in different geometries. Energy diagram, representative spectra for sample emission and reference THG from bare glass, emission intensity-pumping power density plot for (a) to (c) laser-UCNP-substrate geometry and (d) to (f) laser-substrate-UCNP geometry.

In the laser-substrate-UCNP geometry, TH was also excited at the glass-UCNP interface. However, due to the absorption peak of Er^{3+} ions located at 520 nm¹⁴, the generated TH are reabsorbed by UCNPs multilayers and utilized to pump Er^{3+} electrons to $^2\text{H}_{11/2}$; this results in weaker and broader TH spectrum as shown in Fig. 5.2e. Due to the presence of the board UCL, the detected spectrum at the green region is wider than the reference TH. The emission intensities at different pumping power densities for both TH and UCNPs emission peaks are plotted in Fig. 5.2f. The linear-fit slopes are 2.59 for the THG peak at 536 nm, 0.81 for the UCNPs emission

at 661 nm, and 0.89 for the other UCNPs emission at 551 nm, respectively. The lower slope of this TH yield can be also explained by the reabsorption by thin-film UCNPs. The minor increase of the UCL yield is mainly due to the fact that the absorbed TH acts as a second excitation source for UCNPs, overcoming the small absorption cross-section area of UCNPs at 1,560 nm⁷⁷.

5.3.2 Radio-frequency Domain Analysis of The Output Emission from Thin-film UCNPs

Because the TH and UCL are near to each other, it is difficult to analyze their contributions separately in the wavelength domain. Therefore, in order to confirm the TH contribution, RF domain analysis was additionally introduced here using a PMT as the high-speed photo-detector. A mode-locked fs pulse laser emits a repetitive pulse train with the same pulse-to-pulse time spacing; the time spacing between the pulses in this investigation is 12 ns, which corresponds to 83.3 MHz in the pulse repetition rate, which is the reciprocal of the time spacing. THG is a coherent photon conversion process having a time constant significantly shorter than a nanosecond, so preserves the original repetition rate of the excitation fs laser. Whereas, the UCL is governed by the relaxation time constant of UCNPs, which is longer than a microsecond. Therefore, the very ultra-short pulse duration and the high repetition rate of the excitation fs laser cannot be preserved in UCL but in THG. The experimental setups are configured as shown in Figs. 5.3a and b. A train of fs

pulses of 83.3-MHz repetition rate was focused onto the interface between the thin-film UCNP and the substrate via the two sample geometries. The fundamental wavelength (1,560 nm) was filtered out using a short-pass filter (Thorlabs FES 1000) so as to detect the TH and UCL only without the background noise. A high-speed PMT with the radiant sensitivity of 78 mA/W was utilized to detect the pulse train with a 0.57 ns time resolution using a 10^6 -amplification ratio. The detected electric signal was analyzed by an RF spectrum analyzer (Rigol DSA875) with a resolution bandwidth of 10 Hz from 83.333 to 83.335 MHz. Fig. 5.3c shows the RF spectra of the PMT signals from the two geometries, laser-UCNP-substrate and laser-substrate-UCNP. The RF spectra from the laser-UCNP-substrate geometry clearly shows strong peak at the repetition rate with a signal-to-noise ratio higher than 50 dB, which indicates that the signal is more than 100,000 times stronger than the background noise. These results confirm that the TH contribution is 2,240 times stronger in laser-UCNP-substrate geometry than the contribution in laser-substrate-UCNP geometry, which can be identified by the 33.5 dB spectral power difference at the RF peaks as shown in Fig. 5.3c. This deviation comes from the difference in the excitation pathways in the two experiment geometries as explained in Chapter 5.3.2.

Figure 5.3 RF spectrum analysis for different excitation geometry. (a) and (b) Experimental setups for laser-UCNP-substrate geometry and laser-substrate-UCNP geometry. (c) RF spectra of emission from laser-UCNP-substrate and laser-substrate-UCNP geometries.

5.3.3 Time-domain analysis of THG and UCNP Emissions

To analyze the time response of UCL in more detail, time-domain analysis was carried out with a long time-span over 3,000 μs . The RF-domain analysis in Section 3 is more appropriate for testing TH characteristics requiring an ns-level time resolution, which, however, does not work well for UCL having much longer time constants. Figs. 5.4a and b show the system configuration for the time-domain analysis. An optical chopper (Stanford Research Systems SR540) was additionally installed in front of the laser in order to modulate the intensity of the excitation laser beam at 100 Hz. A fiber-coupled continuous-wave laser diode at 635 nm wavelength was used as the reference laser for system characterization without UCNP samples.

The time-domain analysis provided the rise and decay times which are shown in Figs. 5.4c and d with the UCNPs samples. In the laser-UCNP-substrate geometry, the rise times of both green and red emissions to 50% from their maximum intensities are 190 μ s, which indicates that UCNPs are mainly excited by the three-photon absorption process (See Fig. 5.4c). The green emission decays to 50% from its maximum within 30 μ s, while the red emission does within 290 μ s (See Fig. 5.4c); this faster decay of the green emission indicates that THG is significantly enhanced with the aid of thin-film UCNPs. It should be noted that the long rise time of the electron population at $^2H_{11/2}$, resonant with TH, is mainly responsible for the slow rise of green emission. Although THG itself is an ultrafast phenomenon, the power amplification inside UCNPs takes longer time due to the slow absorption process in UCNPs. Once the electron population at $^2H_{11/2}$ becomes high enough for the power amplification, the time response is dominated by THG itself; thus, the pulse duration and repetition rate of the excitation pulses can be maintained thereafter. When UCNPs are excited in the laser-substrate-UCNP geometry, the rise time of the red emission is 290 μ s, which is similar to the typical rise time of UCL excited by continuous-wave lasers¹⁵¹. The rise time of the green emission around 550 nm is only 60 μ s, 230 μ s faster than the UCL at 661 nm. This shorter rise time of the green emission indicates that TH at 516 nm plays the major role in the excitation of UCL. THG, as a ultrafast phenomenon, excites the UCNPs by a single-photon process, which does not involve any intermediate energy level, which results in the short rise

time. Meanwhile, the UCL at red emission coming from the electron relaxation from $^4F_{9/2}$ is governed by three-photon excitation process, which results in a long rise time. The decay times of green and red emissions are 90 and 340 μs , respectively. While the red emission at 661 nm follows with the decay time of UCL, the decay time of the green emission is relatively shorter due to the presence of remaining TH that is not absorbed by UCNP.

Figure 5. 4 Time-domain analysis. (a) and (b) Schematics for experimental setups to measure rise and decay time for laser-UCNP-substrate and laser-substrate-UCNP geometries, respectively. (c) and (d) Rise and decay time for emissions from laser-substrate-UCNP and laser-UCNP-substrate geometries, respectively.

5.3.4 Power-amplified TH and UCNP Emission from Thin-film UCNP on A Single Crystalline Si Substrate

A single crystalline Si wafer was tested as the second substrate for thin-film UCNPs instead of the glass as shown in Fig. 5.5a in order to study how the TH seed power affects to TH amplification in terms of the emission spectrum, yield strength, rise time, and decay time. Si wafers provide ~50 times higher THG efficiency than glass^{9, 48}. Besides, as a single crystalline material, Si wafer shows a clear crystalline orientation dependency in TH; this provides a deeper insight to the polarization coupling between TH and UCL, which will be dealt in detail in Section 6. The emission spectrum from the Si-UCNP is compared with the one from the glass-UCNP sample as shown in Fig. 5.5b. Note that the sample was excited only via the laser-substrate-UCNP geometry due to the limited spectral transmittance of Si; Si has less than 0.00001% optical transmittance over the whole visible spectrum. Despite the 50-times higher THG efficiency at Si substrate, the intensity ratio between TH at 536 nm and UCL at 661 nm from thin-film UCNPs deposited on Si is only 2 times higher than the case supported by glass substrate, which indicates the saturation of Er^{3+} absorption level at 520 nm. As a result, the slope of UCNP emission peak at 536 nm is 2.7, 1.1 times higher than that of glass substrate coupled UCNPs as shown in Fig. 5.5c. Highly doped UCNPs could provide higher TH energy without the gain saturation. The emission yield of UCL at 661 nm is 0.91, which is also slightly higher than the case with the glass substrate. With a stronger green TH seed light from Si substrate, the rise time in the green band was shortened to 12 μs as shown in Fig. 5.5d, which is 18 μs shorter than that from the glass-

5.3.5 Polarization-dependence in Power-amplified TH and UCNP Emission

The emission intensity dependence on input polarization state was finally tested (See Figs. 5.6a and c. While the input polarization was rotated from 0 to 360°, the emission TH and UCL spectra from thin-film UCNPs on Si and glass substrates was recorded and mapped into 2-D diagram as in Figs. 5.6b and d, respectively. As a face-centered crystalline material, the seed TH from the intrinsic (100) Si substrate provides a four-fold symmetry⁹. Following this polarization state of the seed TH, the spectral peak at 536 nm in Fig. 5.6b shows a clear four-fold symmetry. This result confirms that the spectral emission at 536 nm is from the amplified TH. UCNP emissions were reported to have a two-fold symmetry due to their non-uniform dipole orientations along the certain axes within the anisotropic nanocrystal²². The spectral UCL peak at 661 nm in Fig. 5.6b also shows clear two-fold symmetry. Different from the polarization dependence of TH from a bare Si wafer, the green spectral peaks from thin-film UCNPs on the Si substrate are more than 20% stronger at 120 and 300°. This spectral power redistribution is expected to come from the coupling between TH and UCL, which indicates that the power amplification of TH is more efficient when TH seed and UCL are stronger (like 120 and 300° in Fig. 5.6b). This can be explained by the alignment of the dipole orientation of UCNPs to the dipole in the Si crystal, which results in the resonance between UCNP absorption and TH emission. On the other hand, TH from the glass substrate is independent

from the incident polarization state due to its amorphous nature. No clear polarization dependence was observed with the glass substrate as shown in Fig. 5.6d.

Figure 5. 6 THG enhanced UCNP emission with different excitation incident laser polarization. (a) and (c) Experimental setup for incident laser polarization dependence of UCNP thin-film emission supported by Si and glass substrate. (b) and (d) 2-D mapping of polarization dependent spectra for UCNP thin-film supported by Si wafer and glass substrate. Note that the solid filled arrows show the change of polarization states of fundamental laser, and the gradient filled arrows show the incident polarization dependent THG and UCL intensities from Si wafer supported UCNP thin-film.

5.4 Summary

To summarize, we demonstrated the coherent power amplification of TH fs pulses by a factor of 7.8 at multi-layered thin-film UCNPs. This power amplification was enabled by the resonance of incident fs laser field, its TH, and the electric bandgaps of UCNPs. The amplification factor was strongly dependent on the sample orientation; the TH emission yield was 3.5 in the laser-UCNP-substrate geometry

and 2.5 in the laser-substrate-UCNP geometry. The RF spectral analysis at the pulse repetition rate of 83.3 MHz confirmed that TH portion is 2,240 times stronger in the laser-UCNP-substrate geometry than the laser-substrate-UCNP geometry. In addition, the laser-UCNP-substrate geometry also preserved the repetition rate and pulse duration better. Time domain analysis revealed the power dominance of TH over UCL through the rise and decay times. By testing two different substrates, one amorphous glass and the other crystalline Si, seed power and polarization dependencies were revealed. The power amplification ratio at thin-film UCNP can be maximized by coupling a stronger TH seed light, aligning the incident polarization state to the dipole orientation UCNP, and optimizing the doping rate. This coherent amplification of TH at thin-film UCNP provides higher power, shorter wavelength, and ultra-short pulse duration at simple thin-film geometry, which will contribute to realizing efficient test platform for material sciences, nano/micro integrated photonics, and biomedical diagnosis.

Chapter 6. Conclusions and Recommendations for Future Work

In this chapter, the key conclusions, derived from the present research work, are highlighted. A brief outlook of potential future research works to be carried out is presented and their significance is also introduced.

6.1 Conclusions

As two main methods to achieve UC emission, nonlinear optical harmonic generation and luminescence from UCNPs have attracted significant research interest in recent years, but their low efficiencies limited their applications. In this thesis, we aim to develop a method to amplify optical harmonic generation. In order to achieve the target, we started with a detailed characterization of THG from sapphire wafers to comprehensively understand the dependence of THG on the incident power density, crystalline structure of the substrate, excitation depth, and incident angle in Chapter 3. TH was successfully excited from both top and bottom surfaces of A, C, M, and R-plane sapphire wafers, evidenced by the cubical dependence of THG intensity on the pumping power density. When the incident polarization angle was rotated, THG intensities from A, M, and R-plane sapphire wafers can be modulated by 20% while the polarization dependence of C-plane

sapphire wafer is much weaker. This is because of the variation in energy band gap at different axis in the Brillouin zone. The dependence of THG on excitation depth was also investigated, THG was found to decay rapidly when the focusing point of the incident beam moved from the surface to the bulk sapphire wafer due to the Gouy phase shift, and it was found that THG intensity decreased by more than 99% when the incident beam was focused 52.6 μm below the surfaces. Another factor that affects THG intensity was found to be incident angle, THG intensity was found to decrease by more than 99% when the incident angle was tilted by more than 4 degrees due to the decrement in the focused electric field on the sapphire surface to drive the atomic dipole in the horizontal plane of the crystal.

The strong emission of THG at the surfaces of sapphire wafers found in Chapter 3 suggested that nonlinear optical harmonic generation can be a great candidate tool for the non-invasive inspection of internal defects in semiconducting wafers. As a result, a proof-of-concept demonstration was carried out in Chapter 4, where nonlinear optical harmonic generation was utilized to detect internal defects in Si wafers. The result shows that due to the higher THG and FHG efficiency at defects inside Si wafers, clear reduction in the fundamental laser intensity can be detected at the defects by frequency selective method using PD and RF analyzer. The demonstration showed that the proposed method can detect internal defects in Si wafers with a depth resolution of 121 nm at a data acquisition time of 1 s, making

nonlinear optical harmonic generation to be a promising tool for non-contact, non-invasive inspection tool for internal defects in semiconducting wafers with high lateral and depth resolution.

With the comprehensive understanding of optical harmonic generation in Chapter 3 and 4, a method was developed in Chapter 5 to amplify THG using UCNPs. Based on the dependence of THG on energy band gap of substrates, UCNPs thin-film with the energy band gap resonates with the fundamental wavelength and the emission wavelength coincides with THG was used. By utilizing NaYF₄ nanoparticles co-doped with Yb³⁺ and Er³⁺, TH intensity was successfully enhanced by 7.8 times with an improved emission efficiency of 3.5 since the coupling of UCL to the TH. Besides, the amplification was found to be dependent on the excitation geometry due to the re-absorption effect of UCNPs. The results provided a brief insight into the interaction between nonlinear optical harmonic generation and UCL, which can lead to further development of novel methods in the amplification of UC emission.

In summary, this thesis improved the understanding of nonlinear optical harmonic generation processes by comprehensive characterization of THG from sapphire wafers (Chapter 3). Based on the findings during the characterization, a non-contact, non-invasive technique for inspection of internal defects in Si wafers with high depth and lateral resolution was demonstrated, achieving a depth resolution of 121 nm (Chapter 4). With the understanding of THG dependence on the material's

energy band gap in Chapter 3 and 4, UCNP thin-film was used to coherently amplify THG by 7.8 times in Chapter 5. This study paves new ways for the development of highly efficient UC platforms that possess great potential in material sciences, nano/micro integrated photonics, and biomedical diagnosis.

6.2 Contribution of This Thesis

In this thesis, a systematic characterization of THG from sapphires was carried out for the first time. The dependence of THG on incident polarization, excitation depth, and incident angle was comprehensively investigated to get a better understanding of the underlying mechanisms. During the study, the energy band gap structure of materials, surface and bulk contribution of THG, and the nonlinear optical dipole moment strength were found to be closely related to THG. The improved understanding of THG at sapphire wafers does not only pave the way to the development of optical tools for quality and crystallinity monitoring in sapphire wafers but can also be applied in the inspection of surface and internal qualities of all crystalline and non-crystalline wafers.

To prove the fitness of THG in non-invasive inspection of internal defects in crystalline wafers, a proof-of-concept demonstration of non-invasive inspection of internal defects in Si wafers was carried out and a depth resolution of 121 nm was achieved with a data acquisition time of 1 s. The platform proved that with nonlinear optical harmonic generation, internal defects in semiconducting wafers can be

detected with a much higher depth resolution than current methods. It has great potential to be applied in in-line scanning of semiconducting wafers to produce high-quality wafers, which is highly demanded in the next generation 3-D mass data storage devices.

The understanding about the relationship between THG and energy band gap structure of materials enabled us to develop a UCNP thin-film based platform to amplify THG from glass surface by 7.8 times while maintaining its coherence. It provides higher power, shorter wavelength, and ultra-short pulse duration laser at simple thin-film geometry, which will contribute to the realization of efficient test platform for material sciences, nano/micro integrated photonics, and biomedical diagnosis; and may also find its applications in the miniature of compact optical systems and devices.

6.3 Current Limitations and Recommendations for Future Work

The author would like to recommend the following future directions to extend and supplement the current research work.

6.3.1 Current Limitations

In the current study, the characterization of THG from sapphire is based on bulk substrates. THG at the bulk body of sapphire wafers will be under destructive interference which greatly limits its visibility. As a result, the contribution of surface and bulk optical harmonics should be further investigated.

The nonlinear optical harmonic generation based non-contact, a non-destructive inspection method for inter-layer defects remains in the principle demonstration stage. The free-space optical setup utilized in this research introduced systematic noises through platform vibration and minor misalignment among optical components during sample loading and unloading. It greatly limited the resolution and scanning time of the platform. Currently, the data acquisition time for one point is 1 s, obviously does not meet the requirement for industrial on-line inspection. Further efforts are required to develop a prototype for on-line inspection of internal defects in Si wafers.

The interaction between nonlinear optical harmonic generation and UCNP luminescence was also carried out using bulk UCNP thin-film instead of single UCNP nanoparticle. The study of their interaction in single nanoparticle will be interesting due to the intrinsic variation of the synthesized nanoparticle. The coherent amplification factor of THG still can be improved. The including of plasmonic nanostructure in current setup may significantly improve the enhancement factor.

6.3.2 Recommended Future Directions

In future work, optical harmonic generation from surface and bulk substrates will be distinguished to get a further understanding about optical harmonic generation. This can be achieved by monitoring THG from thin-film samples with different

thicknesses. When the sample thickness is comparable or smaller than the wavelength of fundamental laser, the effect of Gouy phase shift will be reduced and bulk THG can be excited and detected if the wavelength of TH is in the transmission window of the sample. However, since the thickness of the sample is small, surface TH and interference among TH excited at the top, bottom surfaces and bulk substrate will also play an important role in the overall intensity of THG detected. The interference will be dependent on the optical path length of different TH beams, which will be determined by the thickness of the sample. Figure 6.1 shows the schematic of TH excited at thin-film samples with different thicknesses, which can be used to distinguish the contribution of surface and bulk THG.

Figure 6. 1 THG from thin-film samples of different thicknesses. THG can be excited from top, bottom surfaces and bulk body of the sample, which leads to interference among them.

It has been mentioned in Chapter 6.3.1 that current data acquisition time of the Si wafer internal defect inspection platform is much slower than the requirement of on-

line inspection application. The long data acquisition time is mainly due to the interruption coming from the free-space optical setup. In the current free-space optical setup, environmental vibration, surrounding light fluctuation and minor misalignment among the optical components during sample loading and unloading introduce noises that result in the long data acquisition time. This can be avoided by substituting the free-space based optical setup to fiber-coupled one. Theoretically, a stabled fiber-coupled optical platform can reduce the data acquisition time to less than 1 ms, which is suitable for on-line inspection application. The detailed calculation for the theoretical data acquisition time is shown in *Appendix D*. A lock-in amplifier can also be utilized to further improve the SNR ratio to achieve better resolution and faster data acquisition time; besides, to enable precise 3-D inspection of semiconducting wafers, higher resolution automated translation stages, high-speed scanners and shorter pulse duration laser should be adopted.

Single UCNP excited by fs laser can also be studied to investigate the interaction between UCNP luminescence and nonlinear optical harmonic generation, and plasmonic nanostructure can be integrated into the system to push the limit of optical harmonic generation efficiency. Due to the intrinsic variation of synthesized nanoparticles, a platform should also be developed to statistically study the nonlinear optical UC emission from single nanoparticles excited by ultrafast laser. A primary system for the purpose has been developed and UCNP monolayer coupled by single AuNS and gold nanotriangle (AuNT) has been studied statistically

Chapter 6

using the system, the detailed experimental setups and results are introduced in *Appendix E*.

Publications Arising from This Thesis

Journal papers:

GAO, Y.; Moon, B. S.; Xu, W.; Kim, Y.-J.; Kim, D., Systematic Investigation of the Wavelength-Dependent Upconversion Enhancement Induced by Single Plasmonic Nanoparticles. *Journal of Physical Chemistry C*. 2018, Accepted.

GAO, Y.; Lee, H.; Jiao, J.; Chun, B. J.; Han, S.; Kim, H.; Kim, Y. W.; Kim, D.; Kim, S.-W.; Kim, Y.-J., Nonlinear third harmonic generation at crystalline sapphires. *Optics Express*. 2017, 25 (21), 26002-26010.

GAO, Y.; Lee, H.; Jiao, J.; Chun, B. J.; Kim, S.; Kim, D.; Kim, Y.-J., Surface third and fifth harmonic generation at crystalline Si for non-invasive inspection of Si wafer's inter-layer defects. *Optics Express*. 2018, 26 (25), 32812-32823.

GAO, Y.; Lee, H.; Xu, W.; Jiao, J.; Kim, D.; Chen, P.; Kim, Y.-J., Coherent power amplification of third-order harmonic femtosecond pulses at thin-film up-conversion nanoparticles. *Scientific Reports*. 2019, Under review.

Conference paper:

GAO, Y.; Kim, Y.-J., Enhanced up-conversion emission by plasmonic nanoparticle with femtosecond laser excitation. Pacific Rim Conference on Lasers and Electro-Optics, CLEO-PR 2017, Singapore, 2017.

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Appendix

A. Sectional profile of THG, FHG dependence on incident laser polarization and excitation depth.

Figure A1 Sectioned intensity profiles at (a) TH and (b) FH spectral peaks with different crystal cuts, doping concentrations, and incident polarization states for Si wafers.

Figure A2 Intensity profiles at different focal depths in Si wafers with different crystal planes and doping concentrations for (a) TH and (b) FH.

B. Derivation of resolution for non-contact, non-destructive inspection of inter-layer defects in Si wafer stack

To determine the depth resolution of the Si wafer internal defect inspection system, the data points around the dips in Fig. 4.5f are fitted to the Gaussian profile. The peak of the profile is the position of the Si-air interface. When the excitation depth deviates from the Si-air interface by a distance, d , the detected signal intensity increases by ΔI due to the reduced intensity of optical harmonic generation. ΔI is only meaningful when it is equal to or larger than the noise level N of the signal detected by the amplified photodetector. As a result, the depth resolution can be defined as the value of d when $\Delta I = N$. From Fig. B1, the lowest noise level, N can be determined to 0.36 mV, when the data acquisition time is 1 s. To make $\Delta I = N = 0.36$ mV, the second dip at excitation depth 652.4 μm in Fig. 4.5f as an example.

Figure B1 Base noise level at different averaging times for inter-layer defect inspection. This noise level was calculated based on the standard deviation of 20 data points acquired at the same focusing depth.

The first dip in Fig. 4.5f can be fitted with Gaussian profile expressed as

$$I = 864.51 - \frac{566.78}{25.78 \cdot \sqrt{\pi/2}} e^{-2 \frac{(d-652.43)^2}{25.78^2}} \quad (B1)$$

where, I is the transmitted fundamental laser intensity detected by the amplified photodetector and d is the excitation depth from the bottom surface of the Si wafer stack. The dip of the fitted curve was located at $d_{dip} = 652.43 \mu\text{m}$, where the signal detected by the amplified photodetector $I_{dip} = 826.13 \text{ mV}$. When $\Delta I = 0.36 \text{ mV}$, the signal detected at the minimum excitation depth difference $I_{res} = I_{dip} + \Delta I = 826.49 \text{ mV}$, taking the value of I_{res} into equation 1, it can be obtained that $d_{res} = 652.55 \mu\text{m}$, which resulted in the resolution of the system to be $R_1 = d_{res} - d_{dip} = 121 \text{ nm}$.

C. Multiple reflectance at Si-air-Si interface

Except for nonlinear absorption, multiple reflectance could be one of the possible reasons which is responsible for the decrease of transmitted incident laser power when the beam is focused at the Si-air interface. In this section, we theoretically calculated the transmittance level based on Fresnel's equation. We could conclude that the intensity decrease made by the multiple reflection was very two orders of magnitude weaker than the measured value so that can be ignored in nonlinear optical harmonic generation for internal defect inspection for Si wafer stacks.

Figure C1 Schematics of Gaussian beam focused at the (a) Si-Air-Si interface and (b) bulk body of Si wafer in a two-layer Si wafer stack. The red ellipses indicate the focusing spot of the Gaussian beam.

The schematics of Gaussian beam focused on the Si-air-Si interface and the bulk body of Si wafer are illustrated in Fig. C1. When the fundamental laser beam is focused to the Si-air-Si interface, the incident beam at the interface can be assumed as a plane wave, which propagates perpendicular to the surface of the Si wafer.

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There are two possible considerations: (1) simple linear summation of a series of intensities made by multiple reflection and (2) optical interference of a series of wavefronts made by the multiple reflection. Regarding the optical interference, the Si-air-Si structure can be taken as a plane-parallel Fabry-Perot optical cavity, where the gap between two wafers determines the relative phase difference between the wavefronts. However, the interference effect could not be made here due to the unstable plane-parallel Fabry-Perot cavity structure and the high NA of the focused beam. In a plane-parallel Fabry-Perot cavity, a small beam divergence or structural tilt deteriorates the interference so very dedicated alignment is requested; therefore, the small spot size at focus with high NA of our focused beam in our system makes the interference not possible. Therefore, the simple summation of a series of intensities made by multiple reflections can be considered here. In the case of normal incident to the Si-air interface, the reflected light power I_R can be expressed as a function of the total incident laser power I as

$$I_R = \left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2 I \quad (C1)$$

Where n_1 and n_2 are the refractive indices of Si and air at 1,595 nm, which are 3.472 and 1.000, respectively. Based on these number, $I_R = 0.3059I$.

Due to the presence of Si-air-Si interface, multiple reflections can occur at the interfaces. As a result, the total transmission through the Si-air-Si system can be calculated by

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$$I_{interface} = \sum_{n=1}^{\infty} 0.3059^{2(n-1)} (1 - 0.3059) I = 0.7658I \quad (C2)$$

On the other hand, when incident laser is focused on the bulk body of Si wafer as shown in Fig. C1b, the beam incident at the Si-air interface can be taken as an inclined incident beam with an incident angle equal to the divergence angle θ of the Gaussian beam, which is 4° in this case. In this situation, I_R can be calculated to be

$$I_R = \left| \frac{n_2 \cos \theta - n_1 \sqrt{1 - \left(\frac{n_2}{n_1} \sin \theta\right)^2}}{n_2 \cos \theta + n_1 \sqrt{1 - \left(\frac{n_2}{n_1} \sin \theta\right)^2}} \right|^2 I = 0.3050I \quad (C3)$$

When the Si wafer is of infinite size, the total transmission can be then calculated to be

$$I_{bulk} = \sum_{n=1}^{\infty} 0.3050^{2(n-1)} (1 - 0.3050) I = 0.7663I \quad (C4)$$

The differences between the two cases are $0.05\%I$, which is much smaller than the signal difference measured at the Si-air interface and bulk body of Si ($\sim 3\%$). As a result, the dips measured in Fig. 4.5f are created by nonlinear absorption instead of multiple reflectance.

D. 2-D profile of Si wafer stack

The lack of fiber-coupled high power ultrafast light source and motorized translational stage limited the demonstration of 3-D mapping of Si wafer stacks at current stage. However, a brief 2-D mapping of transmitted power of fundamental laser when it was focused on different locations in the x-z plane of the Si wafer stack was shown in figure D1. The fs laser was scanned across the z-direction of a double-layer Si wafer stack at four different points in a line with a separation of 10 μm between each spot. The figure shows clear two dips of transmitted fundamental laser power at around 280 and 580 μm in the Si-wafer stack, matched well with the location of the Si-air-Si and Si-air interfaces in a double layer Si stack.

Figure D1. 2-D mapping of the x-z plane in a double-layer Si wafer stack.

E. Systematic Investigation of the Wavelength-Dependent UC Enhancement Induced by Single Plasmonic Nanoparticles

A convenient method was developed to systematically study the wavelength-dependent UC enhancement induced by single plasmonic nanoparticles to overcome unavoidable variations of nanoparticle geometry in practical synthesis techniques. AuNSs and AuNTs coupled to a UCNP monolayer were selected to compare emission and excitation resonance couplings, respectively. The emission intensity of a UCNP monolayer coupled with AuNSs (i.e., emission coupling) was found to be slightly lower than that of a reference UCNP monolayer, independent of pumping power.

E1. Dark-field image and spectrum collection for UCNPs and Au nanoparticles

The dark-field images for AuNPs and UCNPs were taken by an optical dark-field microscope system (Olympus IX71) coupled to a motorized stage (Ludl Flat-top inverted stage 96S106-N3-LE2, BioVision Technologies). A line-imaging spectrometer (Acton Research SpectraPro2150i) was used to collect spectra information for AuNP scattering and UCNP luminescence. The spectral data of the $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$ area was scanned by the motorized stage and reconstructed into a pseudo image to investigate the spectrum of a specific area, following previous work published by our group¹⁵².

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The optical images for AuNP and UCNP luminescence were collected by a color digital camera (DS-Fil-U2, Nikon). A 100 W halogen source (IX2-ILL100, transmitted light illuminator, Olympus) was used for the excitation of LSPRs of AuNPs. The white light from the halogen source passed through an ultra-darkfield condenser (IX-Aducd U-DCW, NA 1.2–1.4, Olympus) to excite the sample, and the scattering light of the sample was collected by a 100x oil-immersed objective (Uplfln 100-OI, NA 1.30–0.6, Olympus). The UCNPs were optically pumped with a continuous 980 nm laser with switchable power from 0 to 10 W (Model: MDL-N-980nm-10W-15070147), and the laser source was directed using a 400 μm optical fiber to pass through the objective and excite the sample. The luminescence light was collected and analyzed using the same system mentioned above.

E2. Experimental Sample Setup and Characterization

The experimental setup and dimensions are shown in Figs. E1a and b. AuNSs with 50 nm diameter and AuNTs with an edge length of 140 nm were used to match the 543 nm emission and 980 nm excitation wavelength of UCNPs, respectively. The density of plasmonic nanoparticles on the substrate was controlled to avoid undesired coupling effects from neighboring plasmonic nanoparticles. UCNPs (20 nm in diameter) were synthesized using a previously published method¹²⁴ and self-assembled onto plasmonic nanoparticles as a uniform monolayer using an interfacial assembly method¹²⁷ to provide a homogeneous coupling system as shown in Figs.

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E1c and d. The overall population densities for AuNTs and AuNSs in the homogeneous coupling system are $2.4 \times 10^6 \text{ mm}^{-2}$ and $3.7 \times 10^7 \text{ mm}^{-2}$, respectively. The LSPR peak wavelength of individual plasmonic nanoparticles and the enhanced UCL were investigated simultaneously using a dark field optical microscope equipped with a 980 nm laser.

Figure E1 Experimental setup and sample characterization. (a) Experimental setup and (b) investigation scheme of the UCNP monolayer coupled with a Au plasmonic nanoparticle. SEM images of the UCNP monolayer coupled with (c) AuNTs and (d) AuNSs. (Inset: SEM images of synthesized AuNTs and AuNSs). UV-Vis/NIR spectra of (e) AuNTs matched with the UCNP excitation wavelength and (f) AuNSs matched with the UCNP emission wavelength.

The spectra of the solutions of as-synthesized AuNSs and AuNTs were measured by a UV-Vis/NIR spectrometer (Figs. E1e, f). The LSPR peak of AuNS is well matched with the UCNP emission peak at a wavelength of 543 nm while the LSPR peak of AuNT encloses the excitation wavelength of 980 nm. Therefore, we used AuNS for emission coupling and AuNT for excitation coupling, respectively. The shoulder peak of AuNT around 650 nm was neglected due to the small contribution compared to the main peak at 980 nm despite a spectral overlap with $^4F_{9/2} \rightarrow ^4I_{15/2}$ UC emission peak.

E3. Dark-field imaging and spectroscopy for UCNP monolayer covered single AuNT and AuNS

Figures E2a and b show dark field scattering images of plasmonic nanoparticles coupled with the UCNP monolayer. Even though the peak positions of ensemble LSPR, i.e., the averaged LSPR peak of many plasmonic nanoparticles in a solution, are well matched with the excitation and the emission wavelengths of UCNPs (Figs. E1e and f), the individual plasmonic nanoparticles have an apparent variation in the LSPR peak positions due to their geometric inhomogeneity (Figs. E2c and d), shown as the various colored spots in dark field images under white light illumination (Figs E2a and b).

Figure E2 Dark field image of (a) AuNT and (b) AuNS coupled with the UCNP monolayer. Scattering spectra of selected (c) AuNTs and (d) AuNSs identified by white circles in (a) and (b), respectively. luminescence spectra of a UCNP monolayer coupled with (e) AuNTs and (f) AuNSs. The green curves show the reference spectra.

The scattering spectra of individual plasmonic nanoparticles and the luminescence spectrum of the UCNP monolayer were collected from 50 coupling spots. To investigate how the LSPR peak variation of plasmonic nanoparticles affects the enhancement of the luminescence spectrum of UCNPs, the collected data points were divided into 5 groups based on the degree of mismatch between the LSPR peak and the luminescence spectrum of UCNPs for both excitation and emission cases. Group 1 contains the plasmonic nanoparticles exhibiting LSPR peaks that deviated by 10 nm or less from the peak for the ensemble as-synthesized solution (their scattering spectra are shown in Figs. E2c and d for excitation and emission coupling,

respectively). For AuNTs, due to the limit of quantum efficiency of the CCD camera beyond 900 nm ($< 50\%$), the shoulder peak of AuNT at around 661 nm was used to identify the LSPR peak wavelength deviation from the excitation wavelength. Similarly, groups 2, 3, 4, and 5 contain plasmonic nanoparticles with LSPR peak variations within 10–20, 20–30, 30–40, and 40–50 nm from the excitation or emission wavelengths. The obtained luminescence spectra of the UCNP monolayer coupled with plasmonic nanoparticles were compared with that of a reference UCNP monolayer. Representative spectra of group 1 are shown in Figs. E2e and f for excitation and emission coupling, respectively. It can be seen that the UCNP luminescence intensity was enhanced by 3–4 times for the excitation wavelength coupling while it is slightly quenched for the emission wavelength coupling.

E4. Statistical investigation of UCL from UCNP monolayer enhanced by single AuNT and AuNS

Figures E3a and b show the dependence of the luminescence enhancement factor on the deviation of the LSPR peak wavelength from the excitation and emission wavelengths. The enhancement factor was calculated by dividing the luminescence intensity of the UCNP monolayer coupled with plasmonic nanoparticles by the intensity of the reference UCNP monolayer. For excitation coupling, the enhancement factor decreases from 3.26 to 1 along groups 1 to 5. The linear fit of the enhancement factor indicates that the enhancement factor decreases by 0.052

fold with every 1 nm shift of LSPR wavelength. In the case of group 5, the plasmonic effects are diminished so the spectrum becomes almost equivalent to that of the reference UCNPs. The R-squared factor is 0.92, suggesting that the descending tendency of the enhancement factor along the deviation of the AuNT LSPR peak wavelength is highly reliable. Compared to a previous report that used a thin film system composed of multi-layered nanoparticles¹⁵³, the plasmonic wavelength dependence of the luminescence enhancement factor in this study is more substantial, probably due to the elimination of the averaging effect in the single particle level coupling system. On the other hand, for emission coupling, a slight decrease of UCL is observed. This is most likely attributed to a quenching effect between plasmonic nanoparticles and UCNPs; when a luminophore contacts a metal surface, quenching occurs due to energy transfer and non-radiative relaxation¹⁵⁴. The linear fit of the enhancement factor exhibits a slope of 0.003 with an R-squared factor of 0.19, showing that the quenching process is not linearly dependent on the LSPR peak deviation in this coupling system. Interestingly, the most significant quenching takes place in group 2, which is deviated from the UCNP emission wavelength by 10 to 20 nm. Plasmonic enhancement is highly sensitive to the electric field intensity at an emission peak of fluorophore whereas FRET quenching is proportional to the overlapped area of spectra of donor and acceptor¹⁵⁵. Therefore, at on-resonance, the plasmonic enhancement and the quenching are compensated each other¹⁵⁶ but quenching takes place at 10-20 nm off-resonances. Note that, for

the case of excitation coupling, due to the absence of spectral overlap¹⁵⁵, quenching is not as effective as for the emission coupling, resulting in significant UC enhancement. Our results show that the LSPR peak wavelength deviation significantly affects the enhancement factor of the UCNP luminescence and, as a result, plasmonic nanoparticles with even small spectral variations are required to be precisely controlled for reliable investigation and practical applications. To prove the concept, we investigated further the coupling spot of group 1 (group 2 for the quenching case).

Figure E3 Enhancement factors of the intensity for the (a) excitation coupling and (b) the emission coupling depending on the LSPR peak wavelength variation from the excitation and emission wavelengths (groups 1 to 5).

E5. Pumping power dependence of plasmonic coupled UCNP luminescence

Next, the dependence of the intensity of UCL on the pumping power was investigated. The emission intensity at different pumping powers is plotted for all

samples in Figs. E4a-c. In a typical two-photon UC process of NaYF₄: Yb³⁺/Er³⁺ UCNP, the UC emission intensity is related to the pumping power as $I_{\text{up}} \propto P^n$, where n is the number of photons required to populate the emitting state¹⁵⁷. The slopes of the log-log plots in Figs. E4a-c are consistent with $n=2$ for 544, 656 nm (1.82-2.27) and 3 for 556 nm (2.39-2.70) at low pumping power. At high pumping power, due to the saturation of intermediate energy states, the slopes of the curves decrease¹⁵⁸. For the reference and the emission coupled UCNP monolayer, the saturation points are seen at around 22 kW/cm², while the excitation coupled UCNP monolayer has a saturation point of around 15 kW/cm². The early saturation of the excitation-coupled UC indicates that AuNTs successfully enhance the local field intensity of the 980 nm pump source, resulting in a faster pumping rate¹²⁹. The emission intensity of the UCNP monolayer coupled with AuNTs collapses at a pumping power above 50 kW/cm². At high pumping density, the increase of the temperature causes a deformation of AuNTs and results in an LSPR peak shift of AuNT¹⁵⁹. The shift of the LSPR wavelength from the 980 nm pumping laser is responsible for the decrease of the plasmonic enhancement.

Figure E4 Power dependence of the (a) UCNP monolayer without AuNPs and the UCNP monolayer coupled with (b) an AuNS and (c) an AuNT. The insets show schematics for the side views of the corresponding samples. (d) Emission ratio of 556 nm and 544 nm intensities at different pumping power densities. e. Energy transfer UC process of NaYF₄: Yb³⁺/Er³⁺.

In Fig. E4d, the ratio between the emission intensities at 556 nm and 544 nm is compared among the three samples. This ratio could reveal the saturation of intermediate states. At low pumping power, the emission at 544 nm ($^4S_{3/2} \rightarrow ^4I_{15/2}$) is higher than that at 556 nm ($^2H_{9/2} \rightarrow ^4I_{13/2}$)¹⁶⁰⁻¹⁶¹. With the increase of pumping power, the lower intermediate state becomes saturated and more electrons are pumped to a higher energy state, leading to the intensity increase of 556 nm light emission (Fig. E4e). It is clearly seen in Fig. E4d that the $I_{556\text{ nm}}/I_{544\text{ nm}}$ ratio of a UCNP monolayer coupled with AuNTs is higher than the other ratios displayed in

the figure, indicating that the pump light source is significantly boosted in the presence of AuNTs.

E6. Enhancement factor dependence on pumping power

Figure E5a shows the enhancement factors as a function of pumping power. The luminescence emission of UCNPs does not show any enhancement irrespective of pumping power for emission coupling. However, the luminescence emission of UCNPs for the case of excitation coupling is amplified by around 3.26-fold at low pumping power and decreases to 0.48 at a high pumping power of 82 kW/cm^2 . The higher enhancement factor of the intensity for excitation coupling with low pumping power can be explained by the locally boosted excitation intensity in the vicinity of plasmonic nanoparticles. However, due to the early saturation of intermediate states, the enhancement factor generally decreases at high pumping power density, which is in good agreement with a previous report¹⁵⁸. In the present study, we observed a continuous exponential decrease of the enhancement factor when the pumping power changes from 10 to 80 kW/cm^2 . As with the intrinsic behavior of plasmonic coupled UCNPs, the enhancement factor could be decreased by the heat generated in the plasmonic structure. Heat generated by plasmonic resonances increases the local temperature and results in temperature quenching of UCNPs¹⁶². At high pumping power above 50 kW/cm^2 , the enhancement factor decreases below 1, indicating that significant quenching takes place. The local temperature of UCNPs

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was calculated by the ratio between the emission intensity at 544 nm and 523 nm (Fig. E5b), which is commonly used as a temperature indicator since it is related to the temperature by the equation $I_{544 \text{ nm}}/I_{523 \text{ nm}} = A \exp(\Delta E/k_b \cdot T)$, where ΔE is the energy separation between the $^2H_{11/2}$ and $^4S_{3/2}$ states, k_b is Boltzmann's constant, and T is the absolute temperature¹⁵⁹. Based on the above equation, the intensity ratio was converted to the absolute temperature by using the emission spectrum of UCNP solution as a reference of room temperature. Fig. E5c confirms that the temperature increases with the pumping power density and also shows that the local temperature of the UCNP monolayer coupled with AuNTs was around 140 °C higher than that of the reference and the UCNP monolayer coupled with AuNSs. The high local temperature is attributed to the decrease of the intensity enhancement in the excitation coupled UCNPs.

Figure E5 (a) Enhancement factors of the excitation and emission coupled UCNP luminescence at various pumping power densities. (b) Ratio between the UC emission intensities at 544 nm and 523 nm. (c) Calculated temperature of UCNPs as a function of the power density.

E7. Summary

In summary, we demonstrated that the plasmonic enhancement of UC is highly dependent on the LSPR peak variation. To reveal this relationship, 50 coupling spots were studied systematically for both excitation and emission coupled UCNPs monolayers. The experimental results revealed that the intrinsic variation of as-synthesized plasmonic nanoparticles has a significant impact not only on the excitation resonance coupled UCNPs but also on the emission resonance coupled UCNPs. To overcome the intrinsic variations, the most effective groups of nanoparticles were selected carefully and used for further investigations. As a result, the excitation resonance coupling displayed up to a 3.26-fold enhancement of the intensity while the emission resonance coupling resulted in a slight quenching of the UCNPs intensity. However, the enhancement effect decreases for increasing pumping power due to the early saturation of the intermediate states and the local temperature effect. Our method could provide a convenient strategy for massive data collection involving plasmonic nanoparticles in a single nanoparticle level. Further, our strategy may provide a guideline for single-nanoparticle investigations involving plasmonic nanoparticles that essentially include plasmonic variations inevitably occurring between individual nanoparticles in practical synthesis techniques.