Analytical and Device-Related Applications of Nonlinear Optics

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Nonlinear optics is a broad field of research and technology that encompasses subject matter in the fields of physics, chemistry, biology, and engineering. The diversity of nonlinear optics stems, in part, from the need for all-optical and electro-optical devices for applications in telecommunications, optical storage, and all-optical computing. In addition, many nonlinear optical effects have proved to be versatile probes of fundamental issues such as interfacial adsorption, the electronic structure of compound semiconductors, and phase transitions in liquid crystal films. This article discusses analytical and device applications that are based on second-order nonlinear interactions of light with matter. Particular attention is given to the exciting technique of infrared–visible sum-frequency generation, which illustrates the capability of the second-order nonlinear response in probing surface and interfacial phenomena. The connection between nonlinear optics and optical waveguides is discussed to demonstrate the potential of thin semiconductor films for efficient second-harmonic generation in the ultraviolet region of the spectrum.

INTRODUCTION

With the invention of the laser nearly 35 years ago, a fascinating new field of research termed "nonlinear" optics was introduced to the scientific and engineering community. Historically, nonlinear optics originated with the experimental work of P. A. Franken, who in 1961 noticed that a weak optical signal at 3471 Å could be generated in a quartz crystal when the material was illuminated with a high-power ruby laser at 6942 Å.[1] Franken quickly surmised that this new light source was due to the coherent mixing of two optical electric fields in the quartz so as to produce a "second harmonic" response in the bulk region of the material. Soon after this discovery, N. Bloembergen and his group at Harvard University formulated many of the theoretical foundations of nonlinear optics, both classically and quantum mechanically, showing that the basic physical laws and principles of the nonlinear response of matter were simple extensions of the conventional or "linear" optical interaction.[2] The landmark work of Bloembergen and his co-workers provided a useful bridge between the world of nonlinear and linear phenomena, a bridge that has promoted growth at such a rate as to find applications in nearly all areas of science and engineering.

Quite simply, nonlinear optics is the study of phenomena that result from a field-induced modification in the optical properties of a material system. Since such modifications require field strengths on the order of 10^3 to 10^4 V/cm, ordinary incoherent light sources are much too weak to produce nonlinear interactions in matter. In the years since the discovery of second-harmonic generation (SHG), nonlinear optics has grown to include such

A LEXICON OF NONLINEAR OPTICAL TERMS

Nonlinear optics. The branch of optics that explores the coherent coupling of two or more electromagnetic fields. In these processes, new field components are generated at frequencies that are either the sum or difference of the coupling fields.

Nonlinear susceptibility. The optical parameter that describes the coupling efficiency of two or more optical fields. For example, the second-order nonlinear susceptibility $\chi^{(2)}$ describes the coupling efficiency of two optical fields.

Optical waveguide. An optical component that is capable of confining optical radiation over propagation distances that are much longer than the wavelength of the light source. Typically, the cross-sectional dimensions of the structures must be on the order of the wavelength of the confined light source. As such, the thickness of most fiber or planar waveguides is on the micrometer scale.

Second-harmonic generation (SHG). The coupling process in which two optical fields of frequency ω are coherently mixed to generate a third field at frequency 2ω.

Sum-frequency generation (SFG). The coupling process in which two optical fields of frequency ω_1 and ω_2 are coherently mixed to generate a third field at frequency $\omega_1 + \omega_2$.

diverse fields as optical chaos and bistability,[3] optical rectification,[4] and stimulated Raman scattering.[5] The rapid growth in the nonlinear optical community has been driven, in part, by the technological need for new coherent light sources and optoelectronic devices in the telecommunications industry. In addition, the nonlinear response of matter has long been recognized as a powerful probe of the electronic and chemical nature of the illuminated material. In the years since Franken's SHG measurements, considerable work has proceeded in developing nonlinear approaches for analytical probes in the worlds of physics, chemistry, and biology.

A common question from researchers who are not familiar with the field of nonlinear optics is, "What does the expression 'nonlinear' mean?" The term *nonlinear* refers to the fact that the optically induced modification in the material depends on more than one optical (or direct current [DC]) field strength in the illuminated region. Typically, only the very high optical fields from laser light are sufficient to produce perturbations in the optical properties of a system. This behavior is quite different from a conventional or "linear" optical response, where processes such as reflection, transmission, and absorption scale linearly with the intensity of the applied optical source. In the experiment of Franken, for example, the SHG response was characterized by a quadratic dependence on the strength of the applied optical field.

Although many nonlinear effects have been observed in gases, liquids, and solids, the nonlinear interaction usually manifests itself as a small deviation relative to the linear response. Optical or DC energy that can be applied in materials investigations without the threat of breakdown or damage usually limit most nonlinear effects to phenomena that depend on two- or three-field mixing processes. Nonlinear interactions of this nature are referred to as either second- or third-order responses, respectively, in the material.

Obviously, a variety of optical or DC field combinations can be produced in most materials, which provides a host of nonlinear phenomena for applications in both basic and technological research. For example, second-order nonlinear effects such as sum-frequency generation (SFG) and SHG have become routine tools for both analytical investigations and new high-power optical laser sources. Similarly, stimulated Raman scattering and optical-field induced birefringence are examples of third-order processes that can be used for either materials investigations or optical switching applications. Table 1 gives a partial listing of second- and

Table 1. Second- and third-order nonlinear phenomena.

Second-order phenomena: $\chi^{(2)}$	Third-order phenomena: $\chi^{(3)}$
Sum-frequency generation	Stimulated Raman scattering
Difference frequency	Two-photon absorption
Second-harmonic generation	Optical-field induced birefringence
Parametric amplification	Self-focusing
Optical rectification	Phase conjugation
Optical field-induced magnetization	Third-harmonic generation
Electro-optic effect	Electric-field induced, second-harmonic generation
Magneto-optic effect	Degenerate four-wave mixing

third-order effects, which include electro- and magneto-optics, four-wave mixing, and optical parametric amplification.

A detailed discussion of the broad range of nonlinear optics is clearly beyond the scope of this article. For the interested reader, several excellent review books on nonlinear optics are available in the literature.[3–7] In this article, we discuss nonlinear phenomena currently used for research applications in the APL Research Center. The techniques presented are based on two second-order nonlinear processes: infrared– (IR–) visible SFG, and ultraviolet (UV) SHG. In keeping with the diversity of nonlinear optics, the discussion of SFG will demonstrate applications for analytical studies of surfaces and interfaces. The interfacial boundary between two dissimilar materials, such as a liquid and a solid, represents a far more nonlinear spatial region than the surrounding bulk media. The intrinsic surface nonlinearity of such interfaces provides a direct optical probe of technologically important processes such as interfacial corrosion and lubrication. An IR-SFG measurement of interfacial adsorption at a liquid/solid interface is presented here to illustrate the surface and molecular sensitivity of the nonlinear optical response. UV-SHG results are also presented from a recent nonlinear investigation of GaN, a wide-bandgap III-V semiconductor that has the potential for incorporation into optical waveguide structures. Applications of SHG in waveguides include the efficient generation of UV light for read/write processes in high-memory optical storage devices as well as optical modulators for far-IR optical sources.

GENERAL DESCRIPTION OF NONLINEAR OPTICS

Nonlinear optical phenomena are analogous to conventional linear processes in that their behavior and interaction with matter are governed by Maxwell's laws of electromagnetism:[8]

$$\nabla \times \mathbf{E}(r,\omega) = -\frac{1}{c}\frac{\partial \mathbf{B}(r,\omega)}{\partial t}, \qquad (1a)$$

$$\nabla \times \mathbf{B}(r,\omega) = \frac{1}{c}\frac{\partial\left[\mathbf{E}(r,\omega) + 4\pi\mathbf{P}(r,\omega)\right]}{\partial t}, \qquad (1b)$$

$$\nabla \cdot \left[\mathbf{E}(r,\omega) + 4\pi\mathbf{P}(r,\omega)\right] = 0, \qquad (1c)$$

$$\nabla \cdot \mathbf{B}(r,\omega) = 0, \qquad (1d)$$

where $\mathbf{E}(r, \omega)$, $\mathbf{B}(r, \omega)$, and $\mathbf{P}(r, \omega)$ are the electric and magnetic fields and electric polarization, respectively, at frequency ω. Also, x, c, and t represent displacement, speed of light in a vacuum, and time, respectively. The wave equation for the electric field can be obtained by substituting Eq. 1b into the curl of Eq. 1a. After some algebraic manipulation, we obtain the following wave equation for wave propagation in the material:

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

It is noteworthy that the form of the wave equation in Eq. 2 is identical for both linear and nonlinear optical propagation. The effects of the interaction of light with matter, whether linear or nonlinear, are contained in the electric polarization and as such do not affect the general behavior of wave propagation.

In the case of conventional optics, the electric polarization induced by an applied electric field is generally expressed in the following form:

$$\mathbf{P}(r,\omega) = \chi^{(1)}(\omega) \cdot \mathbf{E}(r,\omega), \qquad (3)$$

where $\chi^{(1)}$ is the linear susceptibility of the material that describes linear reflection, transmission, and absorption. The electric polarization is linearly dependent on the strength of the applied field and oscillates at the same frequency as the driving source. The extension of conventional optics into the nonlinear world is most often described by an expansion of the total electric polarization $\mathbf{P}^{\mathrm{T}}(r, \omega)$ in a power series of the field strength:

$$\mathbf{P}^{\mathrm{T}}(r,\omega) = \mathbf{P}^{\mathrm{l}}(r,\omega) + \mathbf{P}^{\mathrm{nl}}(r,\omega), \qquad (4)$$

where the linear polarization $\mathbf{P}^{\mathrm{l}}(r, \omega)$ is given by the expression in Eq. 3, and the nonlinear polarization $\mathbf{P}^{\mathrm{nl}}(r, \omega)$ is given by[7]

$$\mathbf{P}^{\mathrm{nl}}(r,\omega) = \chi^{(2)}(\omega) : \mathbf{E}(r,\omega_1)\mathbf{E}(r,\omega_2) + \cdots. \qquad (5)$$

In Eq. 5, terms higher than the second-order term in the expansion have been ignored. The quantity $\chi^{(2)}$ is referred to as the second-order nonlinear susceptibility of the material. In this nonlinear process, the frequency ω of the electric polarization is equal to the sum of the frequencies of the two mixing fields, $\omega_1 + \omega_2$. The validity of Eq. 5 is maintained only in the limit that the nonlinear terms represent perturbations to the linear response, that is, the nonlinear electric polarization is orders of magnitude smaller than the expression in Eq. 3. Since the nonlinear terms are necessarily weak, a "good" nonlinear material will possess a second-order susceptibility that is about five to six orders of magnitude weaker than the value of $\chi^{(1)}$ (Ref. 9). Despite the obvious weak nature of the nonlinear interaction, the ability to apply very high optical or DC electric fields in a sample can make nonlinear optical processes such as SHG highly efficient.

An important implication arises in the expression for the electric polarization in Eq. 5 as compared with the linear counterpart in Eq. 3. In the nonlinear response, the phase-velocity and wave vector of the electric polarization are determined from the optical dispersion of the media at frequencies ω_1 and ω_2, whereas the propagation characteristics of the SFG electric field are governed by the dispersion at frequency ω. In general, $\mathbf{P}^{\mathrm{nl}}(r, \omega)$ and the radiated SFG field $\mathbf{E}(r, \omega)$ propagate with different phase velocities in the bulk region of the material unless the refractive indices at the three optical frequencies are equal. Since wavelength dispersion usually negates this possibility, the phase mismatch leads to destructive interference between $\mathbf{P}^{\mathrm{nl}}(r, \omega)$ and $\mathbf{E}(r, \omega)$ when these two quantities are out of phase by 180°. In fact, efficient SHG and SFG in the visible and UV for most dielectric materials such as quartz are limited to a distance of only a few micrometers before destructive interference reduces efficiency in the crystal.[10] Obviously, this characteristic is not an issue in the linear response because the polarization and emitted electric field are characterized by the same phase velocity.

The effect of the phase-velocity difference is observed in the SFG intensity $I(\omega)$, which depends on the square of the nonlinear polarization source in Eq. 5:

$$I(\omega) = \left|\mathbf{P}^{\mathrm{nl}}\right|^2 \left[\frac{\sin(\Delta k z/2)}{\Delta k z/2}\right]^2 . \tag{6}$$

The term Δk represents the wave-vector (phase-velocity) mismatch between the electric polarization and emitted SFG field, and $\mathbf{P}^{\mathrm{nl}}$ is the component of the electric polarization that is perpendicular to the propagation direction z. Equation 6 shows that the SFG intensity will oscillate with propagation distance into a nonlinear material. For highest conversion efficiency, it is of utmost importance to work with materials or optical geometries that reduce the phase-velocity mismatch to approximately zero.

Another important characteristic of nonlinear optics is the symmetry rule, which forbids second-order processes such as SFG and SHG in bulk materials that are centrosymmetric or isotropic. The symmetry rule is discussed in the next section. Briefly, this criterion serves as the underlying principle for second-order nonlinear measurements at surfaces and interfaces. In addition to interfaces, the noncentrosymmetric crystal structure of most compound semiconductors allows very efficient SFG and SHG because of the large intrinsic value of $\chi^{(2)}$ in many II-VI and III-V materials.[11] As such, these inorganic materials should provide sufficient SHG up-conversion of the visible light into the UV range of the spectrum.

SURFACE NONLINEAR OPTICS: SUM-FREQUENCY GENERATION

Research on interfacial phenomena at metal, semiconductor, and dielectric surfaces is driven by the quest for control over processes such as corrosion, lubrication, adhesion, and reactivity. Nearly 25 years ago, the development of surface analytical probes, most notably electron beam spectroscopies, provided scientists with submonolayer sensitivity for the interfacial processes performed in a pristine, ultrahigh-vacuum environment. A severe limitation of all electron beam spectroscopies, however, was the inability to transmit the incident source through high-pressure media without beam attenuation prior to the sample. As such, in situ investigations of "buried" interfaces were limited to techniques that relied on non-surface-specific optical spectroscopies.[12] In particular, the lack of surface specificity in linear optical probes imposed severe constraints on most of the early liquid/solid interfacial investigations because discrimination between the response of the adsorbed molecule and the same species in the solution phase was very difficult.

With the discovery of second-order nonlinear optical phenomena in the early 1960s, it was soon recognized that effects such as SHG and SFG from isotropic or centrosymmetric media could be developed into powerful and versatile probes of surfaces and interfaces. Researchers understood the symmetry selection rule, which forbids second-order nonlinearities in spatial regions with inversion symmetry,[7] limiting the SHG and SFG response of an isotropic material to the atomic-scaled region at the boundary interface.

Why does symmetry forbid second-order processes in isotropic media? To understand the origins of this symmetry selection rule, we must examine the expression for the second-order electric polarization in Eq. 5 *after* an inversion symmetry operation. In centrosymmetric media, the application of the inversion operation to a polar vector such as the second-order electric polarization must generate the following equation:[13]

$$\mathbf{O}(r)\mathbf{P}^{\mathrm{nl}}(r, \omega) \rightarrow -\mathbf{P}^{\mathrm{nl}}(-r, \omega) . \tag{7}$$

The term $\mathbf{O}(r)$ represents the operation that inverts polar vectors such as $\mathbf{P}^{nl}(r, \omega)$ and $\mathbf{E}(r, \omega)$ into new vectors that are the negative of the original while leaving scalar quantities such as $\chi^{(2)}$ unaffected. If the inversion operation is performed on the right side of Eq. 5, the following expression for the second-order term is obtained:

$$\begin{aligned}\mathbf{O}(r)\mathbf{P}^{nl}(r,\omega) &\rightarrow \chi^{(2)}(\omega):\left[-\mathrm{E}(-r,\omega_1)\right]\left[-\mathrm{E}(-r,\omega_2)\right],\\ &= \chi^{(2)}(\omega):\mathrm{E}(r,\omega_1)\mathrm{E}(r,\omega_2)\,,\\ &= \mathbf{P}^{nl}(r,\omega)\,.\end{aligned} \tag{8}$$

Clearly, the application of the inversion operator to the nonlinear source term does not produce a new vector that is the negative of the original. To overcome this apparent violation of inversion symmetry, one must equate the value of $\chi^{(2)}$ in the bulk region of an isotropic material to zero. However, the interfacial region between two isotropic media does not possess inversion symmetry because this spatial plane separates two dissimilar materials. Therefore, SHG and SFG can, by symmetry, occur at the boundary layer between two isotropic materials. Note that the inversion symmetry argument does not negate the linear response from isotropic media because the inversion operation will change the sign of the linear electric polarization vector in Eq. 3.

The high sensitivity of second-order nonlinear processes to interfacial conditions was first noted by Brown and Matsuoka in 1969, when they observed that the SHG signal from a freshly evaporated silver film in vacuum became markedly weaker on exposure of the film to air.[14] The authors proposed that oxygen contamination of the silver film ambient environment reduced the free-electron concentration at the metal surface, resulting in a lower nonlinear polarizability. Although this experiment verified the surface sensitivity of SHG, few investigations of this sort were performed until the early 1980s. At this time, a resurgence in optical probes of surfaces was under way because of the discovery of electromagnetic enhancement mechanisms at metal surfaces, which provided techniques such as Raman scattering and IR absorption/reflection with submonolayer sensitivity to adsorption phenomena.[15] At the same time, Chen et al. observed that SHG could serve as a probe of surface reactions and adsorption/desorption phenomena with sensitivity that was on the level of submonolayer.[16] With the interest in buried interfacial examinations on the rise, the development of surface SHG and SFG as probes of interfacial phenomena grew at a tremendous rate, in part because of the lack of alternative in situ procedures.

In the late 1980s, Guyot-Sionnest et al. demonstrated the surface and molecular specificity of a new nonlinear optical technique termed IR–visible sum-frequency generation with a series of investigations at both liquid/solid[17] and air/solid[18] interfaces. As shown in Fig. 1, this nonlinear optical phenomenon involves the mixing of an IR beam and a visible laser beam in the interfacial region so as to generate a third field at the sum frequency of these two input fields. The powerful characteristic of IR–visible SFG lies in the fact that the molecular second-order polarizability of the adsorbate is resonantly enhanced when the incident IR field is tuned through a vibrational mode in the surface species, which is both IR and Raman active.[9] Under these resonant conditions, the second-order susceptibility of the adsorbate, $\chi^{(2)}$, has the following form:

$$\chi^{(2)} = N\sum_i \frac{A_i \cdot M_i}{(\omega_{IR} - \omega_i + i\Gamma_i)}\,, \tag{9}$$

where A_i and M_i are the IR and Raman transition matrices, respectively, for the ith vibrational mode with frequency ω_i and linewidth Γ_i, and N is the density of the adsorbate in the surface layer. Because the SFG signal is proportional to the square of the nonlinear susceptibility, the measured nonlinear response will scale quadratically with the surface coverage of the adsorbate. The vibrational sensitivity of this spectroscopy makes SFG very similar to IR absorption or Raman scattering in that the nonlinear resonances are associated with the vibrational modes in the surface species. The vibrational signature of the adsorbate allows the characterization of the physical and chemical environment at the surface layer as well as the average orientation of the adsorbate. Unlike Raman and IR techniques, which cannot discriminate between molecular

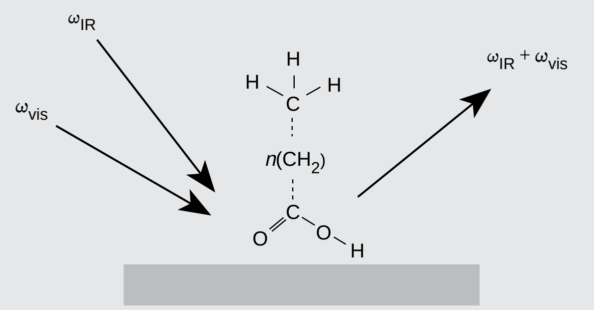

Figure 1. Schematic of IR–visible SFG from a molecule adsorbed on a surface. The IR beam (ω_{IR}) and visible beam (ω_{vis}) coherently mix because of the nonlinearity of the molecule. If the frequency of the IR source were tuned through a vibrational excitation in the molecule, the up-converted SFG signal would be resonantly enhanced.

species in solution and at the surface, the inversion-symmetry selection rule dictates that the SFG signal must disappear when the molecular species is removed from the surface. Thus, SFG possesses both molecular and surface specificity.

In most IR–visible SFG experiments, one of the incident fields is a fixed visible laser source, whereas the second beam is a high-power tunable IR laser. In the SFG investigations conducted at the Research Center, the IR source is produced using stimulated Raman scattering in a high-pressure volume of hydrogen, a third-order nonlinear phenomenon.[5] As is typical of most optical measurements, the experimental arrangement of surface SFG is fairly simple. Figure 2 shows that the SFG measurement is performed by directing an IR and visible laser source onto a sample, generating a coherent nonlinear response, and collecting the SFG output with a simple optical detection system. In these spectroscopic SFG investigations, the two laser sources have a pulse duration on the order of a few nanoseconds, which provides incident peak intensities on the order of 10 MW/cm^2. This source intensity is more than sufficient to generate a detectable SFG signal from the adsorbed layer. Since the SFG signal is at the sum frequency of these two laser sources, the light is typically in the visible to UV end of the spectrum, which allows easy optical filtering of the incident laser sources and convenient detection with high-gain photomultiplier tubes.

As a demonstration of the surface sensitivity of SFG measurements at an interface between isotropic media, Fig. 3 shows the nonlinear response obtained from a molecular layer on a metal oxide surface. Specifically, the experiment illustrates the effects of competitive adsorption between water and ethanol at a cubic zirconia surface. Both the solution phase and substrate are isotropic, which forbids the SFG in the bulk regions of these materials. In this experiment, the zirconia/solution interface was irradiated with the IR and visible laser sources after a solution containing a fixed concentration ratio of the two molecular species was placed in contact with the oxide surface. The peaks in the spectra are associated with the C–H vibrational stretches in the adsorbed ethanol molecule, which enhance the SFG response in accordance with Eq. 9. The spectra in the figure, which are plotted as a function of the IR frequency, show a decrease in the resonant intensity from the C–H vibrations with increasing water concentration, which indicates the displacement of ethanol from the surface. Since the square of the peak amplitude in the SFG spectra is proportional to the surface concentration of the ethanol species, the resonant response seen in Fig. 3 provides information regarding the relative surface versus bulk concentration of the ethanol species.

Figure 4 shows a plot of the square root of the SFG peak signal at an IR frequency of 2930 cm^{-1} versus ethanol and water solution concentrations. In this plot, the decrease in the signal intensity denotes the displacement of the alcohol from the oxide surface, a process that has a monotonic dependence on the water concentration in the solution. The behavior of the ethanol adsorption/desorption process on zirconia obeys a Langmuir isotherm model (represented by the curve through the data), which is an indication of the relatively weak hydrogen bond between the adsorbate and substrate.

The importance of the previous type of surface science experiments at buried interfaces should not be understated. The vibrational resonance from the ethanol molecule was clearly absent from the SFG spectra, which indicated that the molecule was no longer on the surface despite the presence of this species in the solution phase. When compared with conventional surface

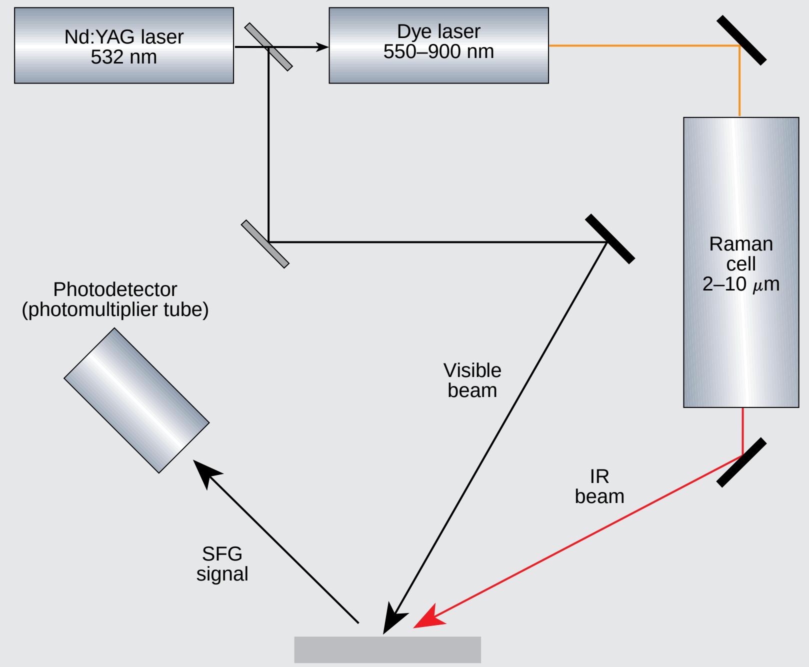

Figure 2. Schematic of the optical source and detection setup used for our SFG measurements. The visible laser source is the 532-nm output of a doubled Nd:YAG laser. The incident IR source is generated from stimulated Raman scattering of dye laser radiation in hydrogen so as to produce a tunable source in the 2- to 10-μm range. The generated SFG signal is usually detected with a high-gain photomultiplier tube.

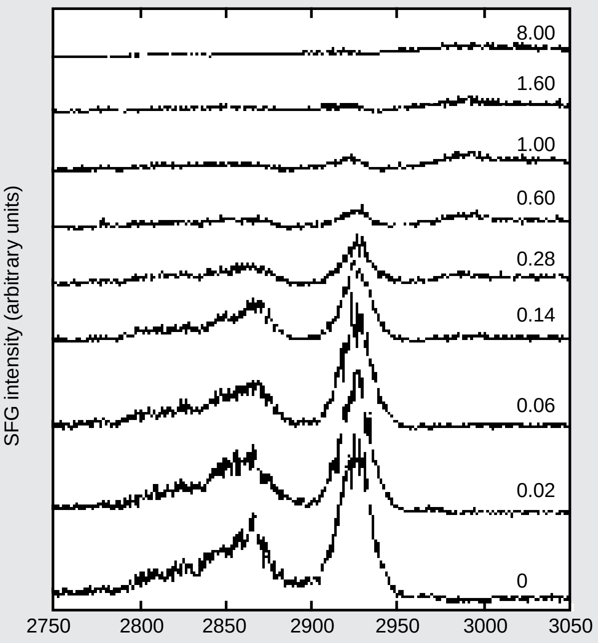

Figure 3. IR–visible SFG spectra from ethanol adsorbed on a zirconia surface. The results show the surface sensitivity of SFG measurements at an interface between isotropic media. The SFG response is plotted against the frequency of the IR laser source. Peaks occur when the IR beam is tuned through a C–H vibration in the ethanol molecule. The number to the right of each spectrum is the water:ethanol ratio in the solution that is in contact with the zirconia.

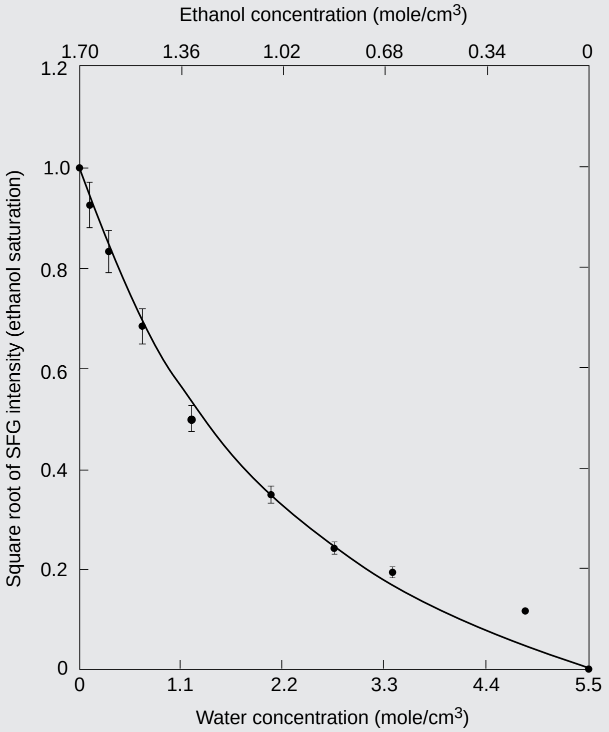

Figure 4. Square root of the SFG signal at an IR frequency of 2930 cm^{-1}. The data are plotted as a function of the ethanol and water concentrations in the solution phase in contact with the zirconia surface. The curve represents the behavior of a Langmuir isotherm for adsorption at the surface.

probes such as IR absorption/reflection or Raman scattering, which would be unable to discriminate between the bulk and surface response, the second-order processes are clearly superior for in situ spectroscopic investigations of buried interfaces. It is not surprising that SFG and SHG experiments pertaining to molecular arrangement, orientation, and reactivity at buried interfaces are routinely performed with little difficulty.

SHG IN SEMICONDUCTOR WAVEGUIDES

During the past decade, research on the growth and preparation of semiconducting films has resulted in the development of crystalline samples with electronic and optical properties that are suited for electro-optic devices in the IR to UV range of the spectrum. Many of these materials possess crystal symmetries that are either a zincblende or wurtzite phase, resulting in a structure that is noncentrosymmetric. As discussed previously, the symmetry of this structure will permit the generation of second-order nonlinear phenomena, such as SHG and SFG, from the bulk region of the crystal. In fact, most direct band-edge III-V semiconductors, such as GaAs and InAs, possess intrinsic $\chi^{(2)}$ values that are of sufficient magnitude for the efficient production of SHG, SFG, and parametric amplification[19] throughout the optical transmission window of the material.[11]

A particular focus of nonlinear optics of semiconductor films is in applications pertaining to one- or two-dimensional optical waveguide structures. Integrated optical devices using nonlinear materials offer the potential for advances in important engineering fields such as optical mixing and modulation, signal processing and computing, and optoelectronics. Success in this applied field depends on (1) a fundamental understanding of nonlinear phenomena in waveguides, (2) the development of novel materials that possess relatively large second-order nonlinear susceptibilities, and (3) convenient deposition as homogeneous films. Fortunately, most III-V and II-VI compound semiconductors of technological interest are intrinsically nonlinear, with large second-order susceptibilities that display little or no degradation on exposure to high-power laser radiation. With regard to growth, materials research on inorganic thin films has culminated in the development of nonconventional deposition techniques, such as metal–organic chemical vapor deposition, for the production of high-quality semiconducting films.[20]

Over the past few years, considerable research has been conducted in nonlinear characterization of the III-V metal nitride semiconductor GaN.[21–23] Investigations have concentrated on measurements of $\chi^{(2)}$ for SHG photon energies near the fundamental band edge of GaN as well as in the IR and visible regions. In most of these second-order studies, the dye laser system seen in Fig. 2 was used as the incident radiation source for generating a transmitted SHG response from the thin-film GaN. Since the measured intensity of the SHG signal is proportional to the square of $\chi^{(2)}$ (see Eq. 6), the magnitude of this nonlinearity can be evaluated from the second-order response.

Figure 5 shows the results of a typical SHG transmission measurement obtained from a GaN film on sapphire. The schematic in the figure shows the arrangement used to generate the nonlinear response. This arrangement is significantly simpler than that used in the IR–visible SFG studies discussed previously, for only one laser source is required in the generation process. In the SHG study, the GaN film was irradiated using a tunable visible laser source that generated a nonlinear response at the fundamental absorption edge of the semiconductor.[23] The profile of the response near this optical transition did not display the same sharp resonant behavior as the previously discussed SFG results. However, the bulk nature of the semiconductor response was orders of magnitude larger than the corresponding surface SFG signal seen in Fig. 3, with typical values for $\chi^{(2)}$ (denoted in Gaussian electrostatic units in Fig. 5) on the order of 10^{-7} e.s.u. These values for second-order susceptibility correspond to a nonlinearity that can up-convert about 10^{-8} of the incident visible radiation into the UV range of the spectrum when propagation distances in the GaN are on the order of the 1- to 2-μm film thickness. The relatively high conversion efficiency allows detection of the nonlinear signal with either a photodiode or high-gain photomultiplier tube.

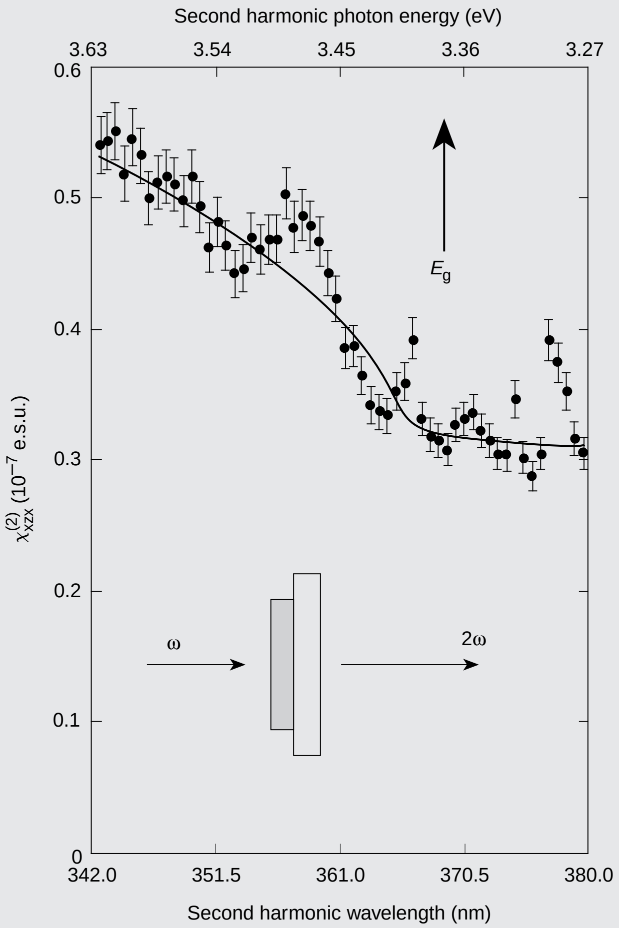

Figure 5. Magnitude of the nonlinear susceptibility, $\chi^{(2)}_{xzx}$, in GaN.[23] The arrow denotes the position of the fundamental band edge E_g. The schematic shows the incident (ω) and transmitted (2ω) directions with respect to the GaN sample. The shaded region represents the GaN film deposited on a sapphire surface. Susceptibility is measured in electrostatic units (e.s.u.).

Although the nonlinearity of GaN is larger than that of many conventional materials such as KDP or $LiNbO_3$,[9] the conversion efficiency is limited by the micrometer-scale propagation lengths in the thin-film structure. An obvious way to increase the SHG production in the GaN is to inject the incident light into the sample so as to propagate the incident beam along the surface length of the film. This optical waveguiding procedure has, in fact, received considerable attention over the past few years, in part because of interest in optical fiber communications. The structure of optical waveguides is actually ideal for nonlinear interactions because thin-film or channel structures provide strong beam confinement over propagation distances that can be on the order of centimeters.[24]

Figure 6 shows a schematic of thin-film slabs and channels, which are the two most important structures for integrated optical waveguides. These structures confine the guided optical wave in either two dimensions or one dimension, respectively, where the dimensions of the waveguide are generally on the order of the wavelength of the field. The channel guide is the preferred structure because guided waves can actually propagate without beam diffraction for distances that are limited only by the attenuation effects of scattering and absorption. The primary prerequisite for all wave-guide structures is that the guiding region have a higher refractive index than the surrounding media, a condition that is met for the GaN and sapphire system. Under most conditions of confinement, it is possible to confine more than 80% of the total optical power to the guiding region.

How does beam confinement enhance nonlinear generation? First, the ability to confine optical fields of moderate input powers can lead to surprisingly large intensities in either planar films or channel guides. For

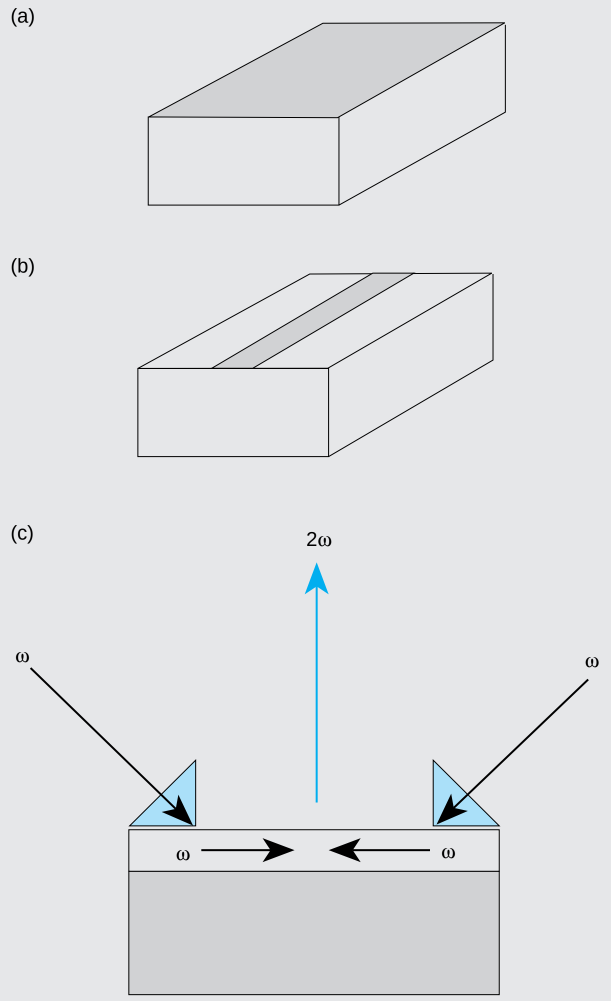

Figure 6. Schematic of (a) planar and (b) channel waveguide structures on a dielectric substrate. The shaded region is the confining thin-film deposit. (c) Counterpropagating geometry used to produce SHG in a direction normal to the surface of the waveguide. The triangular features are coupling prisms to the waveguide.

example, if 1 W of power were injected into the channel waveguides shown in Figs. 6a and 6b, an intensity of 100 MW/cm^2 would be produced in a 1-μm^2 channel. Intensities of this level are more than enough to generate detectable nonlinear effects in most compound semiconductors with remarkably high conversion efficiencies under certain conditions.

The second mechanism for SHG enhancement is a bit more subtle but no less important than a high-intensity characteristic. A limitation for SHG in GaN is that it suffers from the previously discussed phase-velocity mismatch problem, which causes destructive interference between the nonlinear electric polarization and the second-harmonic field. In bulk GaN, the effect of the phase-velocity difference is to limit high conversion efficiencies to a length scale on the order of 2 to 3 μm. Fortunately, the dispersive characteristics of a confined electromagnetic wave in a waveguide differ considerably from those associated with plane wave propagation in the same material. This difference is due to the dependence of the former on the geometric properties of the thin-film structure,[25] a characteristic that allows tailoring of the thin-film deposit so as to create "phase matching," or a zero phase-velocity difference in the waveguide.

GaN waveguide structures currently under development will produce efficient up-conversion of visible light into the UV region. Electromagnetic calculations predict that at the appropriate phase-matching conditions, which have been found to depend on the frequency of the incident and SHG fields as well as the thickness of the GaN film, conversion efficiencies in the waveguide can be enhanced by a factor of 10^5 to 10^6 relative to bulk measurements. This level of conversion should, in fact, permit the replacement of a pulsed laser source with focused continuous wave milliwatt systems for the production of SHG with milliwatt powers.

Figure 6c shows a proposed structure that uses two counterpropagating visible beams of the same frequency to produce a UV SHG signal in a thin-film GaN waveguide. The two prisms on either side of the structure are used to couple the incident light into the waveguide structure with efficiencies on the order of 50%. The nonlinear mixing of the two guided visible modes produces a nonlinear electric polarization in the spatial regions where they overlap. An interesting result of the counterpropagating geometry is the emission of a coherent signal of 2ω that radiates in a direction orthogonal to the waveguide surface. Because of the nature of SHG radiation, this type of structure is a potential useful device for surface-emitting sources in the UV.

SUMMARY

The use of the second-order nonlinear processes of IR–visible SFG provides a useful probe of the vibrational characteristics of adsorbed species at buried interfaces. The unique surface and molecular sensitivity of this technique is capable of following the interfacial process of water-induced displacement of an ethanol layer from zirconia even when both molecules are present in the solution phase above the surface. This type of nonlinear probe illustrates the potential of nonlinear optics for interfacial measurements pertaining to phenomena such as reactivity and corrosion.

We have also shown that the SHG nonlinear response from a GaN semiconductor film possesses a large intrinsic $\chi^{(2)}$ relative to other common nonlinear materials. Although the conversion efficiency for a single pass through the film is rather low, very large enhancement values are predicted for SHG, provided the incident beam can be confined in an optical waveguide structure.

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