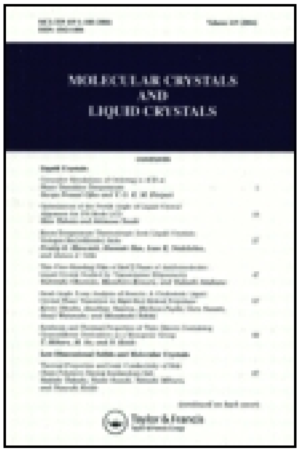

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Nonlinear Optical Studies of Polysilanes

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NONLINEAR OPTICAL STUDIES OF POLYSILANES

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Abstract We have measured third-order nonlinear susceptibilities $\chi^{(3)}$ for a variety of polysilanes with different side-groups, and for composites of polysilanes and metals. The value of $\chi^{(3)}$ varies substantially with changes in the side-groups, backbone conformation, film thickness, orientation, and volume fraction and size of metal particles. We have also prepared thin films of high optical quality, which have been used to study material properties and material response for waveguiding studies.

INTRODUCTION

Substituted silane high polymers [1] represent a new class of radiation-sensitive materials which are of technological interest as thermal precursors to silicon carbide, photoinitiators in vinyl polymerizations, in photoresist applications, and as non-linear optical materials, as the position of the absorption band may be varied by varying the substituent and/or molecular weight [2,3].

Organo-silane polymers consist of long (> 1000 atoms) σ -bonded silicon backbones with two organic substituent groups attached to each Si atom. In the planar zigzag backbone conformation, the σ -bonded electrons of the Si backbone are easily displaced along the chain, causing strong UV absorptions and large non-linearities. Butyl and pentyl sidegroups allow the backbone to form a helix, creating an amorphous film. Hexyl and higher sidegroups force the backbone into a planar zigzag conformation, allowing the formation of a crystalline phase at room temperature.

The polysilanes absorb strongly in the UV (300-400 nm), both in solution and in the solid state, despite the fully saturated backbone. This absorption has been described variously as a $\sigma\sigma^*$ or σ Si^{3d} transition [4], and is expected to be dependent on the backbone conformation. since there is considerable σ delocalization in the backbone. There is a close relationship between bond conformation and the electronic properties.

There have been considerable non-linear studies [5-7] dealing with one dimensional conjugated π electron systems, especially, the polydiacetylenes. These polymers are characterized by large values of $\chi^{(3)}$ enhanced in the vicinity of the multiphoton resonances in the near infrared.

Origin of strong optical nonlinearities in organic materials is due to great mobility of delocalized π and σ electron systems; electron donor and acceptor radicals; and intramolecular charge transfers. Advantages of polysilanes over π-bonded carbon chain polymers are: firstly, the $\sigma - \sigma^*$ absorption edge is typically 3.9 eV, so the material is transparent at all visible wavelengths. Secondly, this absorption band edge is related to the unperturbed length of the silicon backbone, and can be further shifted by adding various substituent groups making resonant enhancement of non-linear effects at visible wavelengths possible. Thirdly, these materials are soluble in hydrocarbon solvents such as toluene and xylene, making thin film waveguides with photoresist spinning technology possible.

The properties of organic or polymeric materials may be varied to optimize adjunct properties, e.g., mechanical & thermal stability, laser damage threshold, while preserving the electronic interactions responsible for nonlinear optical effect (materials can be tailored according to need).

The origin for nonlinear effects in conjugated organic systems is the polarization of the π or σ electron cloud, as opposed to displacement or rearrangement of nuclear coordinates found in inorganic materials. Thus, organic materials and polymers can be used for high frequency applications, as compared with the bandwidth limitations of the inorganic materials.

Conjugated organic systems exhibit extremely large nonlinear responses, in many cases much larger than their inorganic counterparts.

The polarization induced by an electric field in macroscopic or bulk media can be expressed as:

$P = \chi^{(1)}E + \chi^{(2)}EE + \chi^{(3)} \ldots EEE + \cdots$

Where the vector quantities P and E are related by the tensor quantities $\chi^{(1)}$, $\chi^{(2)}$, and $\chi^{(3)}$, which are often refered to as the linear susceptibility, second-order nonlinear susceptibility, and third-order nonlinear susceptibility, resp. The even order tensor $\chi^{(2)}$ is zero in centrosymmetric media, where as the odd order tensors do not have any symmetry restrictions. Since, the electric field vector is proportional to frequency, quite simply, if we can double the input frequency through the material, we can get $\chi^{(2)}$. Similarly, on frequency tripling, one can get $\chi^{(3)}$.

Applications for χ^2 include laser modulation and deflection, optical switches, light valves, etc., while applications for χ^3 include degenerate four-wave mixing, (involving real-time processing of optical fields), optical communications, integrated circuit fabrication, etc. Integrated circuits involving waveguides have important optical disk storage applications.

There has been some important recent work done on the nonlinear optical studies of polysilanes. Kajzar et. al. [8], reported third harmonic generation measurements on thin films of poly(methyl phenyl)silane. They determined both the modulus and phase of the susceptibility, and got an average value of $\chi^{(3)}$ equal to $1.5 \pm \times 10^{-12}$ esu at 1.064 μm. Their paper also presented a good theoretical model for comparison with the experimental data, to extract out the modulus and phase of the susceptibility. Baumert et. al. [9], recently reported the temperature dependence of the third-order nonlinear optical susceptibilities in polysilanes and polygermanes. They measured a $\chi^{(3)}$ value of 11.3×10^{-12} esu for poly(di-n-hexyl silane). They also found that $\chi^{(3)}$ varies substantially with changes in temperature and film thickness. There has been some recent theoretical work done by Haus et. al., and others [10,11] in which they predicted a dramatic increase for non-linear susceptibilities for composites of host medium and small metallic particles. They claimed enhancement of up to 10^7 to 10^8 times the magnitude of the susceptibilities, on presence of small metallic particles in the host medium, beyond a certain volume percent, for different shapes of metallic particles.

Polysilanes represent a new and distinct class of conjugated polymers for nonlinear optics. In this paper, we have measured third-order nonlinear susceptibilities $\chi^{(3)}$ for a variety of polysilanes with different side-groups, and for composites of polysilanes and metals. We have investigated variations in $\chi^{(3)}$ with changes in the side-groups, backbone conformation, film thickness, orientation, and volume fraction and size of metal particles. We have also investigated material properties to prepare high quality optical films, and material response of the polysilanes for waveguiding studies.

In this work, we enter a Nd:YAG laser beam at a wavelength of 1064 nm into a thin polysilane film, and through use of proper filters, monitor the third harmonic signal at 355 nm wavelength. The third harmonic signal, measured as a function of the incident angle, is then fitted to a theoretical expression, to extract out the modulus $\chi^{(3)}$ and phase of the susceptibility.

The technique used here allows us to determine both the modulus and phase of $\chi^{(3)}$ by comparing the harmonic field generated in the polymer film with that in the substrate itself [8,9]. Films of polysilane have been deposited on the fused silica substrate by a spinning technique, used in photoresist technology, which gives regular, smooth, and fairly reproducible films, of excellent optical quality.

EXPERIMENTAL SECTION

The polymers studied include poly(di-n-hexyl)silane, poly(hexyl-phenyl)silane, poly(methyl-phenyl)silane, poly(ethyl-phenyl)silane, poly(tertiary butyl-pheny)silane, poly(diisohexyl)silane, poly(pentyl-hexyl)silane, and polysilane-silver composites. The synthesis of this type of polymers has been described elsewhere [1,2]. Films of varying thickness from 0.075 microns to 1.0 micron have been used for these measurements. The substrate used is fused silica.

The third harmonic generation measurements have been performed using the Maker fringe technique at a fundamental wavelength of 1064 nm, which was produced by a Q-switched Nd:Yag laser (Quanta Ray DCR2A) operated at a repetition rate of 20 Hz and a pulse duration of 5 ns. The fundamental beam and beams of other undesired frequency were blocked in front of the photomultiplier detector (Hamamatsu R212) using high pass color glass filters (Corning 7-69, Schott KG5), and interference bandpass filters (Ealing). The thin polymer film on a fused silica substrate was mounted on a stage, driven by a computer controlled three-axis goniometer. This stage was aligned with respect to the laser beam and polarization direction. The sample was rotated along an axis parallel to the fundamental beam polarization direction and the third harmonic signal was recorded as a function of the angle of incidence. The experimental technique is the same as used by Baumert et. al. [9] The measurements have been performed in two steps. First we have measured the third harmonic signal form the polymer and substrate. After this, measurements were made at the same conditions on the substrate alone. Later discussions will reveal that this procedure allows us to determine both the modulus and the phase of the susceptibility [8].

Films of polysilane have been deposited on the fused silica substrate by a spinning technique, used in photoresist technology, which gives regular, smooth, and fairly reproducible films, of excellent optical quality. Spinning of thin films is an important function of the viscosity of the solution, which in turn depends on the molecular weight of the polymer, and the polymer concentration (which also determines the film thickness). The desired molecular weight of the polymer can be achieved by sonication. To get a smooth film of desired thickness, we had to optimize the polymer molecular weight, concentration, and the spin rate. If the molecular weight of the polymer was too high, the viscosity of the solution too was too high to make good films of desired thickness. The best films were obtained for a molecular weight around 300,000 to 500,000, and the concentration was varied from 2% to 5% to get films of desired thickness. Also, the substrate (fused silica) had to be thoroughly cleaned before spinning, and the cleaning involved a water rinse, detergent wash, acid wash, water wash, heating cycles, and finally baking at 130°C for 30 minutes to remove all water and other volatile material present. Also, the polymer solutions were filtered using a 0.5μm Fluoropore (Millipore Corp.) filter before spinning. The film thickness was then accurately determined using the Tencor Instruments Alpha Step 200. After spinning, the film was baked at a desired temperature, depending on the solvent used, for 10 minutes. For the $\chi^{(3)}$ measurements, toluene has been used as the solvent to make films. For the waveguiding studies, a few different solvents were tried, but the best films resulted from using xylene and toluene.

Composites of polysilanes and silver particles were made in two different ways. One method was to use Carey's technique [12,13] to get a silver colloidal solution, with particles of a desired size. The other method involved making the colloidal solutions using silver powder which was bought commercially. Two different particle sizes were used in the experiments: 10 microns, and 1 micron particle size, to study effect of particle sizes larger and smaller than the wavelength of the fundamental beam. It was desired to get particles even smaller than 1 micron, but the price was prohibitive. Different volume fractions solutions were made, ranging from 1% to 50%, and the thin films were spun as described previously.

THEORY AND FITTING PROCEDURE

The magnitude and phase of the third-order nonlinear susceptibility $\chi^{(3)}$ was obtained by fitting the experimental data obtained in terms of the third harmonic intensity versus incidence angle, to the following theoretical expression, the basis of which has been well described by Kajzar et. al.[8]

$$I_{3\omega}(\theta) = C\,|\,e^{i(\psi_{s,\omega}+\psi_{p,3\omega})}[T_1(1 - e^{-i\Delta\psi_s}) + \rho e^{i\phi}T_2(e^{i\Delta\psi_p} - 1)]\,|^2 (I_\omega)^3$$

where,

$I_{3\omega}$ is the third harmonic intensity

I_ω is the fundamental intensity

θ is the angle of incidence

C is a constant

i = s denotes substrate

i = p denotes polymer

phase is defined by $\psi_{ij} = \dfrac{6\pi l_1 N_{ij}}{\lambda_\omega}$,

where,

j = ω denotes fundamental

j = 3ω denotes third harmonic

λ_ω is the fundamental wavelength

$N_{ij} = n_{ij}\cos\theta_{ij}$.

n_{ij} are the complex refractive indices

The internal angle of propagation θ_{ij}

is given by complex Snell's law.

$\Delta\psi_i = \psi_{i\omega} - \psi_{i3\omega}$ represents the phase mismatch between the free and bound waves at 3ω and is responsible for the Maker fringe oscillations. T_1 and T_2 take into account the Fresnel transmission factors of the fundamental and harmonic beams as well as factors arising from boundary conditions at each interface [7](polymer-substrate, polymer-vaccum, vaccum-substrate).

The film thickness should be less than the coherence length, $l_c = \lambda_\omega/[6(N_{p,\omega} - N_{p,3\omega})]$, because for thin films, the free and bound waves propagating in the solid film add constructively, and the dispersion of the refractive index is not an important factor.

The relative phase of the polymer and substrate susceptibilities is given by ϕ and their relative magnitudes can be found from $|\chi_p^{(3)}/\chi_s^{(3)}| = \rho\,|(n^2_{p,\omega} - n^2_{p,3\omega})/n^2_{s,\omega} - n^2_{s,3\omega})|$. Since the film thickness is smaller than the coherence length, the third harmonic signal is only a slowly varying function of the angle of incidence, while the offset oscillations observed are due to the signal from the substrate. It is also important to take into account the complex nature of $n_{p,3\omega} = [n_{p,3\omega}]_{real} + i\kappa_{p,3\omega}$. The n_{ij} values used for the fits were obtained by waveguide techniques for the IR and visible wavelengths, and by Kramers-Kronig analysis of the absorption spectra for UV wavelengths.

Measurements were made first on the polysilane film and substrate, and then on the substrate alone. The experimental data from the substrate was fitted to the theoretical expression with $\rho = 0$, to extract out the amplitude and the substrate thickness. Then, knowing the film thickness, the experimental data from the film and substrate was fitted to obtain the amplitude, ρ (magnitude), and ϕ (phase). Knowing the value for silica, $\chi^{(3)} = 3.1x10^{-14} esu$, one can then calculate $\chi^{(3)}$ for the polysilane film using the equation:

$|\chi_p^{(3)}/\chi_s^{(3)}| = \rho\,|(n^2_{p,\omega} - n^2_{p,3\omega})/n^2_{s,\omega} - n^2_{s,3\omega})|$.

The exact position of normal incidence was determined by a least squares fit between left- and right-hand side positions of interference minima and/or maxima. The contribution to the third harmonic signal from the substrate can be made to vanish by adjusting the angle of incidence to correspond to a null of the first term of the theoretical equation. For our measurements, the angular positions of the nulls do not change much, and since the film thickness is much smaller than the coherence length, the third harmonic signal is always proportional to | $\chi^{(3)}$ | and changes can be easily detected.

For more information on theory and fitting procedures, please refer to the reported work of Kajzar et. al. [8], and Baumert et. al. [9]

RESULTS AND DISCUSSION

Figure 1 shows third harmonic data obtained from the substrate alone. The points are the experimental data, while the solid line represents the theoretical fit. Figure 2 shows third harmonic data obtained from the poly(hexyl phenyl)silane and substrate. The film thickness in this case is 120 nm. Figure 3 shows third harmonic experimental data for a thick film of 350 nm of the poly(hexyl phenyl)silane. As described earlier, for thin films, the contribution of the polymer to the third harmonic signal is only a slowly varying function of the angle of incidence, while the offset oscillations observed are entirely from the substrate signal. For thicker films, like the one shown in Figure 3, hardly any fringes were observed.

Table 1 lists the magnitude and phase (ϕ) of the third-order nonlinear susceptibilities $\chi^{(3)}$ for a variety of polysilanes. This table lists values of $\chi^{(3)}$ and ϕ for film thickness of 120 nm. Poly(di-n-hexyl silane), which has an all-trans planar backbone conformation at room temperature, resulting in easy displacement and delocalization of the σ -bonded electrons along the backbone, exhibits a fairly high value of $\chi^{(3)}$ of 5.7 x 10^{-12} esu. It has been observed that pentyl and butyl and lower sidegroups force the backbone to form a helix, creating an amorphous film. Hexyl and higher sidegroups force the backbone into a planar zigzag conformation, allowing the formation of a crystalline phase at room temperature. This is also evident in measurements of $\chi^{(3)}$, where polysilanes with side-groups below pentyl exhibit substantially lower values than those with side-groups higher than pentyl. Also, side-groups containing phenyl, particularly poly(hexyl phenyl)silane and poly(methyl phenyl)silane, exhibit quite high values of $\chi^{(3)}$. This may be due to some resonance effect of the contribution from the phenyl group coupled with that from the polymer backbone, probably because of the bathochromic shift. The high values in general of the polysilanes may be due to the large value of the dipolar transition matrix element product, due to the one dimensional character of the polymer backbone electronic states[6]. When the polymer backbone has a backbone-disordered conformation, the value of $\chi^{(3)}$ is substantially lower.

Figure 4 is a plot of the square root of the third harmonic intensity versus film thickness for the poly(hexyl phenyl)silane. It is seen that the measured third harmonic light intensity increases quadratically with the polymer film thickness up to 0.6μm. This indicates that the film thickness is much smaller than the coherence length up to about 0.6 μm. Thus, for films up to about 0.6 μm, the third harmonic light intensity does not depend on the dispersion of the refractive index.

Figure 5 is a plot of the third-order harmonic susceptibility $\chi^{(3)}$ versus film thickness for the poly(hexyl phenyl)silane. It is observed that the thinner films have higher $\chi^{(3)}$ values, probably because of increasing orientation of the polymer backbone as the film is made thinner, which results in greater anisotropy. Obviously then, the effort should be to make films as thin as possible, but problems arise in making regular and smooth very thin films, and also in fitting the theoretical expression to the experimental data because of the problems in doing in situ experiments, without any variations in the set-up. The highest value we could get for the poly(hexyl phenyl)silane was 8.3 x 10^{-12} esu, for a film thickness of 80 nm.

No second harmonic signal was observed for the polysilane films, indicating their structure to be centro-symmetric.

Optical microscopy experiments on the poly(hexyl phenyl)silane indicated existence of nematic liquid crystalline properties at high concentrations. Fairly regular films of the poly(hexyl phenyl)silane were made at high concentrations, and the film was oriented by shear rubbing with cloth. Third harmonic generation measurements were then made for scan directions parallel to and perpendicular to the preferred shear orientation. It was observed that when the scan direction was parallel to that of the oriented polymer, significantly higher values of $\chi^{(3)}$ were observed. For a film of 120 nm (for comparison with case where there is no induced orientation), we got $\chi^{(3)}$ to be about 9.2 x 10^{-12} esu, quite higher than the value of 6.8 x 10^{-12} esu for a film with no induced orientation. However, when the scan direction was perpendicular to the preferred polymer orientation, very low values of $\chi^{(3)}$ were observed, about 1.6 x 10^{-13} esu. Thus, orienting a liquid crystalline polymer can substantially enhance the $\chi^{(3)}$ values in the parallel orientation.

We made some very interesting and important observations with composites of polysilanes and silver particles. The results reported here are for the poly(di-n-hexyl silane). The preparation of films of these composite materials was described earlier. The first set of observations are for the case where the silver particle size is about 10 microns, much greater than the wavelength of the incident fundamental beam. Different volume fraction of the silver was considered, from 1% to 25%. However, no significant increase was observed for the $\chi^{(3)}$ values. The second set of observations were for the case where the silver particles were about 1 micron in size. Till about 10% volume fraction of silver particles, there is no significant increase in $\chi^{(3)}$. However, on increasing the volume fraction to 30%, we observe a drastic increase in $\chi^{(3)}$, with a value of 22.5 x 10^{-12} esu. On increasing the volume fraction to 50%, we observe $\chi^{(3)}$ to be 23.7 x 10^{-12} esu, indicating a plateau in the value of $\chi^{(3)}$ with increasing volume fraction of silver. For silver, $\chi^{(3)}$ is about 2.5 x 10^{-9} esu. The dramatic increase in $\chi^{(3)}$ on increasing the volume fraction of the silver particles, smaller than the wavelength of the fundamental beam, can be explained by suggesting that the magnitude of the local field is enhanced by the silver particles, and the surface plasmon resonance caused can result in enhancement of the Raman scattering cross section, causing a large increase in the non-linearity. The increase is still very little as compared with some theoretical predictions of increases of as high as 10^7 orders of magnitude in the nonlinear susceptibilities [10,11].

WAVEGUIDING STUDIES

The aim in waveguiding is to couple light rays in the slab of material through a grating or prism, at an incidence angle greater than that required for total internal reflection, so that light rays in the slab will be totally internally reflected and trapped in the slab. Waveguiding is important in optical storage of data, optical transmission of data, etc.

For our experiments, the polysilane film of poly(di-n-hexyl silane) has a refractive index n_g of 1.58, and poly(n-methyl phenyl) has n_g of 1.637, and is bounded on one side by a fused silica substrate with n_o of 1.3, and on the other side by air, with n_{air} of 1.0.

As was previously mentioned, we have also investigated material properties to prepare high quality optical films, and material response of the polysilanes for waveguiding studies. The optimizing of the material parameters like molecular weight, polymer concentration, viscosity, sonication, spin rate, solvent, etc. has been described earlier in the Experimental Section. We had also discussed the procedure to rigorously clean the substrate, and the filteration procedure for the polymer solutions before spinning. The fused silica substrates were 1 inch in diameter, and the film quality was better along with easier handling for substrates that were a quarter-inch thick.

For the waveguiding studies, we have concentrated our work on the poly(di-n-hexyl)silane, and poly(methyl phenyl)silane. The films have been made using xylene and toluene as solvents. The films made with xylene were of a better optical quality, and that may be because of lower vapor pressure effects in forming a better meniscus on the substrate before spinning.

The important parameters involved in thin film spinning are the thickness variation and surface roughness, and as discussed earlier, the factors affceting them are solution concentration, polymer molecular weight, etc. Properties of films desired for waveguiding would be that the fims are thick enough to support waveguiding (our experiments indicate film thickness to be at least 0.5 micron thick); are optically homogeneous, with uniform thickness and minimal scattering due to surface roughness. Poly(di-n-hexyl)silane films, for instance, at high molecular weights exhibit amorphous surface properties and crystalline spectral properties. Poly(n-hexyl methyl)silane films are amorphous in nature.

The technique for making waveguides is then to first prepare films with good optical quality. Next, use holography to make gratings on the film, of desired depth, period, and profile, by interference of two laser beams. For films of poly)n-methyl phenyl)silane, the films had to be heated at 100°C for about 5-10 seconds to observe the gratings. Next, point the visible laser (He-Ne) on the gratings of the film and observe waveguiding with little or no transmission of the laser light through the film. We can check the efficiency of the gratings by measuring the incident power input and the transmitted power output. To check for the efficiency of waveguiding , make another grating in the film, and measure power input into the waveguide through the first grating, and power output through the second grating.

To make the gratings on the polysilane films, a Helium-Cadmium laser of 325 nm wavelength, and in some instances an Argon-ion laser beam of 360 nm wavelength were used to make the gratings. The initial beam is split and the two subsequent beams, of desired same intensity, are made to interfere on the polysilane film, from the same angle, θ, which determines the period of the grating. The grating period is chosen such that when the visible laser hits the grating, the angle of incidence into the waveguide is greater than that required for total internal reflection.

The master grating equation is:

$\Lambda(\sin\alpha + \sin\beta) = n\lambda$,

where n is the order of diffraction,

Λ is the grating period,

λ is the wavelength of laser,

α is the angle of incidence of laser to the gratings.

β is the angle of reflection from grating into the waveguide.

The other important equation is:

$\sin\alpha = n_{eff} - \frac{\lambda}{\Lambda}$, which derives from conservation of k-vector, given by,

$k\sin\alpha = \beta_{sw} + \frac{2\pi n}{\Lambda}$

where, $\beta_{sw} = n_{eff}k$,

representing the surface wave.

The procedure is then to first calculate θ_c from

$\sin\theta_c = \frac{n_{quartz}}{n_{polysilane}}$.

Then, knowing that $\beta + \theta_c = \frac{\pi}{2}$, we get β. Next, to determine α , we use Snell's law,

$n_{air}\sin\alpha = n_{polysilane}\sin\beta$.

The value of α is then taken to find the period of the grating, Λ , which is then used to find the angle at which to interfere the beams, using the equation:

$\Lambda = \frac{\lambda}{2n_{eff}\sin\theta}$.

The depth of the grating is determined by the energy in the beam, and is thus a function of the exposure time.

Waveguiding in the films of poly(di-n-hexyl)silane and poly(n-methyl phenyl)silane were observed with the Helium-Neon (He-Ne) laser. But the efficiency of waveguiding was only about 10%. It was relatively easy to make gratings, and the film supported the first mode for thickness between 0.5 and 1.2 microns. To increase the efficiency to a higher level, there have to be several improvements made. First, we have to try to make better films, with minimal surface roughness and thickness variation, and very clean with no dust and impurities. Next, the gratings should have high frequency to minimize scattering losses, and enough depth to support high efficiency. Recent theoretical studies indicate that the coupling efficiency is highest for a 0.5 micron pitch grating if the depth of grating is about 50 nm. It is important to make regular, consistent gratings. Absorption and scattering losses have to be minimized.

For good coupling, it is important that the pitch (or period) of the grating be small, so that we do not lose light due to diffraction of several modes and scattering. The paradox here is that, measurements made by us, suggest that for high frequency (or smaller pitch) grating, the depth of grating reaches a plateau value very soon as we increase the energy of the beam (which is determined by the exposure time), and that we cannot increase the depth of the grating, even if we expose the material to longer times. More depth of grating can be achieved for the same energy (exposure time) for a grating with smaller frequency (greater pitch), but during waveguiding, there would be loss in the gratings due to diffraction of several modes. The Helium-Cadmium beam supported an energy of 0.1 milliwatts, while the Argon-Ion beam was 30 milliwatts strong. For the smaller frequency (120 line pairs/mm), or greater pitch gratings, we could reach a depth of 90 nm. Exposing the film too long caused it to bleach.

The Wyko Profile Meter was used to study surface roughness on the film, and on an average, the surface roughness was about 5 nm. The same instrument was also used to study the depth, profile, and period of the gratings. The gratings were sinusoidal in nature, and the pitch (or period) for different gratings varied from 1 micron to 6 microns (which could be adjusted by changing the angle at which the laser beams interfere on the sample).

Current work involves making better quality films, using polysilane with various side-groups to get optimum film properties, investigate the scattering and absorption losses for the guided mode, improve the efficiency of the waveguides, investigate the relative magnitude and response times of the fast electronic and slow thermal nonlinearities in the polysilanes, and investigate possible applications.

To be able to use polysilanes for optical mixing purposes, it is necessary to phase match the interacting waves. The advantage of using waveguiding structures for non-linear interactions is that phase matching can be achieved using waveguide dispersion, by controlling the phase velocity of the light wave by tailoring dimensions of the guided region and/or refractive index dispersion. The dimensions of the guiding region for optical wavelengths are of the order of micrometers and as a result it is possible to have large optical intensities, with modest optical powers. Problems encountered are that it is often difficult to maintain uniform guide dimensions to within a few percent over the waveguide length for phase matching. Other problems are scattering losses at the guide-substrate interface and the optical damage as a result of high optical intensities [14,15].

TABLE I The magnitude and phase of the third-order nonlinear susceptibilities $\chi^{(3)}$ for different polysilanes, of film thickness 120 nm.

polysilane (side-groups)	ϕ (rad)	$\chi^{(3)}$ (10^{-12} esu)
hexyl-hexyl	0.32	5.7
methyl-phenyl	0.43	6.8
hexyl-phenyl	0.40	6.2
hexyl-pentyl	0.37	2.3
ethyl-phenyl	0.28	5.3
ter-butyl-phenyl	0.33	4.9
diisohexyl	0.12	1.8

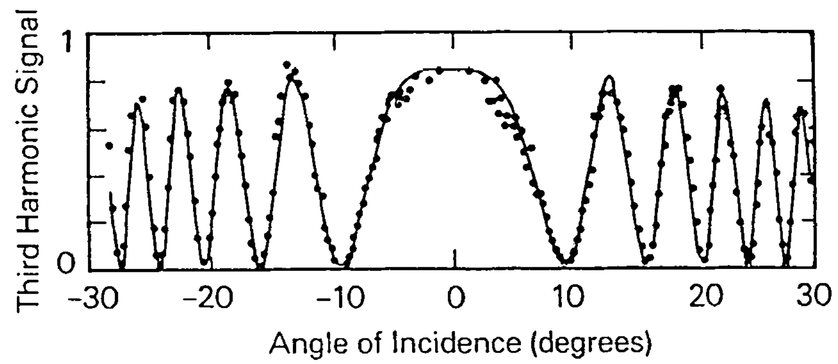

FIGURE 1 Third harmonic generation data from the fused silica substrate alone. Solid line represents the theoretical fit to the experimental data points.

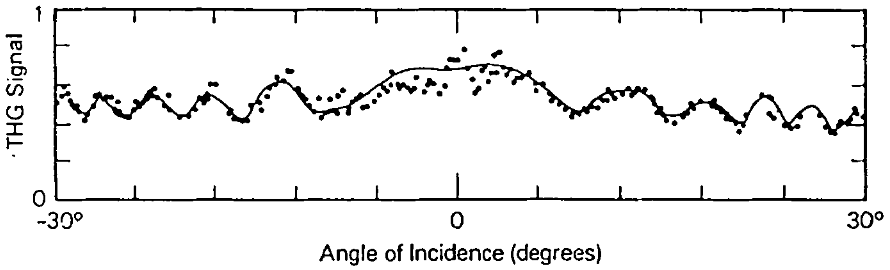

FIGURE 2 Third harmonic generation data from poly(n-hexyl phenyl)silane film (of film thickness 120 nm) and fused silica substrate.

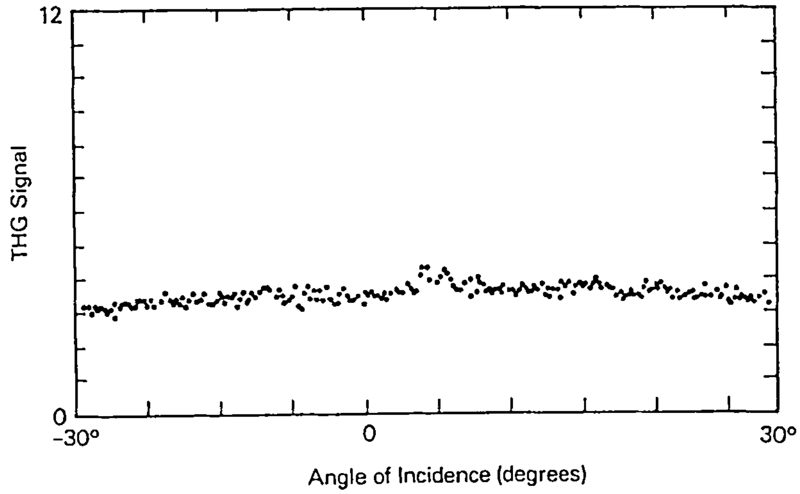

FIGURE 3 Third harmonic generation data from poly(n-hexyl phenyl)silane film (of film thickness 500 nm) and fused silica substrate.

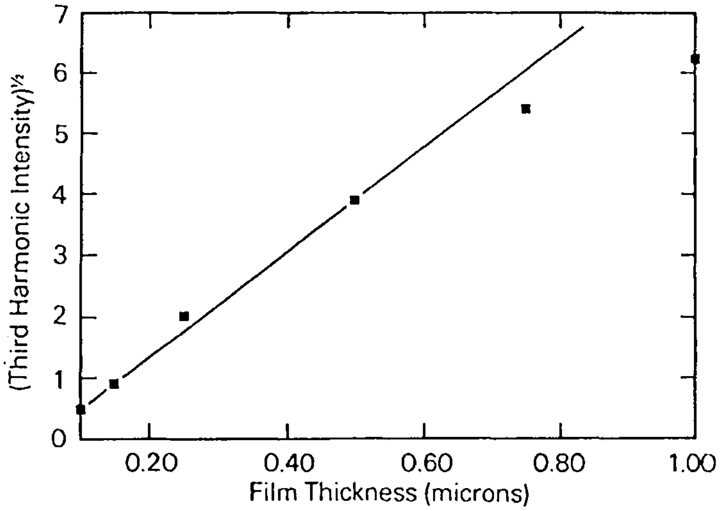

FIGURE 4 Plot of the square root of the third harmonic intensity as a function of film thickness for poly(n-hexyl phenyl)silane.

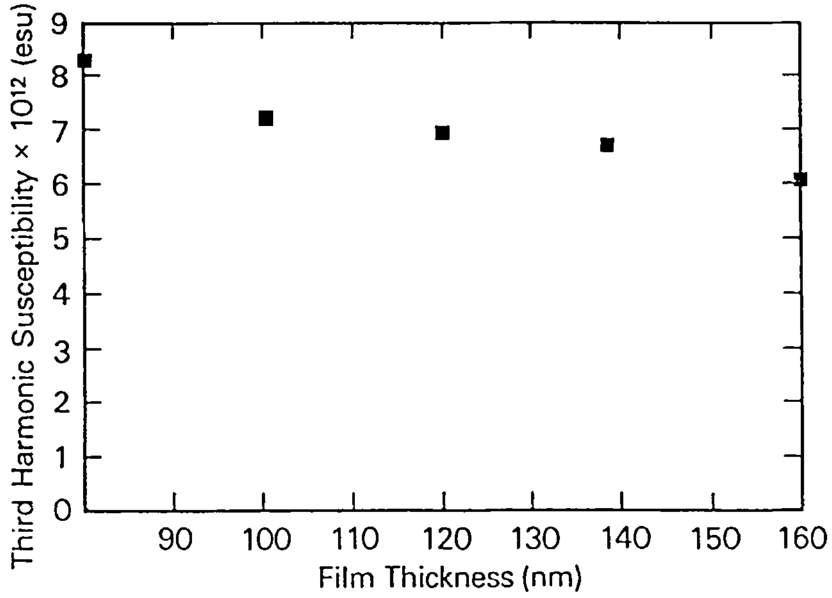

FIGURE 5 Plot of the third-order nonlinear susceptibility $\chi^{(3)}$ as a function of film thickness for the poly(n-hexyl phenyl)silane.

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