Strong second-harmonic generation in silicon nitride films
Tingyin Ning, Henna Pietarinen, Outi Hyvärinen, Janne Simonen, Goëry Genty, and Martti Kauranen

Citation: Applied Physics Letters 100, 161902 (2012); doi: 10.1063/1.4704159
View online: http://dx.doi.org/10.1063/1.4704159
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/100/16?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Generation of second harmonic radiation from sub-stoichiometric silicon nitride thin films
Appl. Phys. Lett. 102, 141114 (2013); 10.1063/1.4801873

Observation of second-harmonic generation in an oriented glassy nematic phase of a closo-decaborane derivative
J. Appl. Phys. 102, 033108 (2007); 10.1063/1.2767868

Photoinduced second-harmonic generation in the indium tin oxide crystalline films
J. Vac. Sci. Technol. A 21, 201 (2003); 10.1116/1.1531251

Second-harmonic generation in amorphous silicon nitride microcavities
Appl. Phys. Lett. 81, 4706 (2002); 10.1063/1.1526171

Second-harmonic generation in silicon carbide polytypes
Appl. Phys. Lett. 75, 618 (1999); 10.1063/1.124459
Strong second-harmonic generation in silicon nitride films

Tingyin Ning, Henna Pietarinen, Outi Hyvärinen, Janne Simonen, Goéry Genty, and Martti Kauranen

Department of Physics, Tampere University of Technology, P. O. Box 692, FI-33101 Tampere, Finland
Optoelectronics Research Centre, Tampere University of Technology, P. O. Box 692, FI-33101 Tampere, Finland

(Rceived 17 January 2012; accepted 1 April 2012; published online 17 April 2012)

We observe strong second-harmonic generation from silicon nitride films prepared on fused silica substrates by plasma enhanced chemical vapor deposition. The components of the second-order nonlinear optical susceptibility tensor of the films are calibrated against quartz crystal. The dominant component has the magnitude of 2.5 pm/V, almost two orders of magnitude larger than reported for Si$_3$N$_4$, and about three times larger than for the traditional nonlinear crystal of potassium dihydrogen phosphate. The results indicate that silicon nitride has great potential for second-order nonlinear optical devices, especially in on-chip nanophotonics.

Silicon nitride (SiN) is a widely used material in the silicon-on-insulator (SOI) platform. In particular, the flexibility in the material composition and refractive index, the low loss at the visible and near infrared wavelengths, and compatibility with complementary metal-oxide-semiconductor (CMOS) processes make it a promising material for the fabrication of waveguides and resonators. CMOS-compatible materials with large second-order nonlinearity could greatly extend the functions of on-chip optical devices for applications such as electro-optic modulation and frequency conversion. However, SiN is generally thought to be amorphous and a centrosymmetric material with no second-order bulk nonlinear response.

Recently, relatively strong second-harmonic generation (SHG) has been observed from a Si$_3$N$_4$ ring resonator. The effect was ascribed to a surface nonlinearity, giving rise to an effective second-order susceptibility of $\chi^{(2)}_{zzzz} = 4 \times 10^{-14}$ m/V (Ref. 6), which is still about two orders of magnitude lower than that of traditional nonlinear crystals. Silicon nitride has also been used to strain silicon waveguides and enhance the nonlinear response up to $\sim 40$ pm/V but the nonlinearity in this case was mostly due to silicon itself.

In this letter, we demonstrate strong SHG from SiN films grown on fused silica substrates using plasma enhanced chemical vapor deposition (PECVD). We find that the response is up to three orders of magnitude larger than that of typical dielectric surfaces and scales with film thickness as expected from a bulk-type response. The nonlinear response of the film is calibrated against quartz crystal, and its dominant tensor component is found to be $\chi^{zzzz} \sim 2.5$ pm/V (where $z$ is the film normal). This value is about 60 times higher than the effective susceptibility observed in Ref. 6 for Si$_3$N$_4$ microresonators and comparable to that of traditional second-order crystals such as potassium dihydrogen phosphate (KDP)

The SiN films were deposited using PEVCD and a gas mixture of (2\% SiH$_4$/N$_2$):NH$_3$ = 100:3. The process temperature and pressure were $300^\circ$C and 1000 mTorr, respectively. Several films with different thicknesses in the range from 100 nm to 1.5 $\mu$m were fabricated. The refractive indices of the films were measured by ellipsometry as 1.94 and 1.99 at 1064 nm and 532 nm, respectively.

The SHG characterization was performed using a mode-locked Nd:YAG laser operating at 1064 nm and producing 70 ps pulses as illustrated in Fig. 1. The laser beam was collimated to a diameter of 1-2 mm at the SiN samples. The polarization state of the beam was controlled by the combination of a calcite Glan polarizer and a continuously rotating zero-order quarter-wave plate (QWP) or half-wave plate (HWP), allowing for polarization-dependent measurements. In order to perform SHG measurements for various angles of incidence, the sample was fixed on a high precision rotation stage with $0.001^\circ$ angular resolution. A visible-blocking filter was used to remove any SHG light generated before the samples. The SHG signal transmitted through the sample was detected with a photomultiplier tube (PMT) after blocking the fundamental beam using an infrared-blocking filter and interference filter (central wavelength 532 nm).

We first verified that the SHG signal intensity depends quadratically on the fundamental intensity. For this purpose, both the fundamental and SHG beams were $p$-polarized and the angle of incidence was set to $60^\circ$. The measurements...

FIG. 1. Optical setup used for the SHG measurement. M, mirror; GP, Glan prism; WP, wave-plate; VIS, visible-blocking filter; IR, infrared-block filter; IF, interference filter; RS, rotation stage, and PMT, photomultiplier tube. The coordinate systems ($xyz$) associated with the sample and the orientations of the crystallographic axes ($XYZ$) for quartz are shown.

---

\textsuperscript{a}Electronic mail: tingyin.ning@tut.fi.
\textsuperscript{b}T. Ning, H. Pietarinen, and O. Hyvärinen contributed equally to this work.
were repeated for several SiN film thicknesses, and in each case, excellent quadratic dependence was observed (see Fig. 2(a)). Significantly, the SHG signal levels from SiN were much larger than those measured from the surface of a typical centrosymmetric dielectric material. The response from the thickest (1.5 μm) SiN film was estimated to be as much as 8000 times larger than the maximum of the Maker fringes from a 1-mm thick fused silica plate. In fact, the green light generated from the SiN film was even observable to naked eyes when we placed a piece of paper as screen behind the IR filter. A picture of the green light from the 1.5 μm SiN film (fundamental laser power, 70 mW, beam size on film, about 0.1 mm², and angle of incidence, 60°) on the screen was taken by a digital camera (see the inset of Fig. 2(b)). The results suggest that the response of SiN is likely to be of bulk origin. This assumption is confirmed when fitting in the thickness dependence of the SHG intensity with a bulk-type model of the form $I \propto D^2 \sin^2(\Delta k D/2)$, where $D$ is a constant, $D$ the film thickness, and $\Delta k$ the phase mismatch between the fundamental and SH beams.

In order to obtain a better understanding of the nonlinear properties of the SiN films, we conducted polarization-dependent SHG measurements on the 800 nm thick film, which allows us to address the tensorial properties of the nonlinearity. The results are shown in Fig. 3. We first used the HWP to modulate the state of polarization of the fundamental beam. The fact that the $s$-polarized SHG signal vanishes for $p$- and $s$-polarized fundamental beams (see Fig. 3(a)) implies that the sample possesses in-plane isotropy (symmetry group $C_{\infty v}$). The nonvanishing tensor components of the second order susceptibility tensor are then

$$
\chi_{xxz} = \chi_{zzx} = \chi_{yyz} = \chi_{zxz},
$$

where $z$ is the film normal and $x$ and $y$ are two orthogonal in-plane directions. For isotropic achiral thin films, the $p$- and $s$-polarized components of the second-harmonic field can be expressed as $E_p = f e_p^2 + g e_s^2$ and $E_s = h e_p e_s$, respectively, where $e_p$ and $e_s$ refer to the $p$- and $s$-polarized components of the fundamental beam. In general, the expansion coefficients $f$, $g$, and $h$ are complex quantities that depend linearly on the susceptibility tensor components, the angle of incidence, and the linear optical properties of the material.

By using the simplified version of the Green’s function formalism of nonlinear optics where we neglect multiple reflections within the thin film, the expansion coefficients take the form,

$$
f = \frac{4\pi\omega\epsilon_0^2}{N_3 c} \frac{e^{i\Delta k} - 1}{\Delta k} T_{p13}^2 T_{p21} T_{p32} \times \left[ \sin 2\theta_3 \chi_{xxz} + \cos^2 \theta_3 \tan \Theta_3 \chi_{zzx} + \sin^2 \theta_3 \tan \Theta_3 \chi_{zzz} \right],
$$

$$
g = \frac{4\pi\omega\epsilon_0^2}{N_3 c} \frac{e^{i\Delta k} - 1}{\Delta k} T_{p13}^2 T_{p21} T_{p32} \tan \Theta_3 \chi_{xxz},
$$

$$
h = \frac{4\pi\omega\epsilon_0^2}{N_3 c \cos \Theta_3} \frac{e^{i\Delta k} - 1}{\Delta k} 2T_{s13} T_{p13} T_{s21} \sin \theta_3 \chi_{xxz},
$$

where the subscripts 1, 2, and 3 refer to air, substrate, and film materials, respectively, $\epsilon$ represents the speed of light, and $\omega$ is the angular frequency of fundamental light. The phase mismatch between the fundamental and SH beams is $\Delta k$. Quantities at the fundamental (SHG) frequency are denoted by lower- (upper-) case letters. The refractive
indices and propagation angle at the fundamental (SH) frequency are thus \( n(N) \) and \( \theta(\Theta) \), respectively. Finally, \( t \) and \( T \) are the Fresnel transmission coefficients corresponding to a particular polarization and for a specific interface, e.g., \( T_{p13} \) is the coefficient for \( p \)-polarized light through the air-SiN interface. Note that all expansion coefficients have the same overall phase, which depends on the phase mismatch and film thickness. For transparent materials, all other parameters are expected to be real such that there is no phase difference between the expansion coefficients.

The relative values of the expansion coefficients \( f, g, \) and \( h \) can be uniquely determined by modulating the polarization of the fundamental beam with the QWP and by detecting the different polarization components of the SH signal.\(^{14,15}\) The results for an incidence angle of 60° are plotted in Fig. 3(b). In order to get better accuracy, the results corresponding to different combinations of fundamental/SHG polarizations were simultaneously fitted resulting in values for the expansion coefficients of \( f = 1, g = 0.19, \) and \( h = 0.46. \) We emphasize that the quality of the fit cannot be improved by allowing the coefficients to be complex-valued, in agreement with the fact that the experiment was performed under non-resonant conditions for the samples.

The experimentally measured values of the expansion coefficients \( f, g, \) and \( h \) were subsequently plugged in Eqs. (1)–(3) to determine the relative values of the independent tensor components. We repeated the measurements for angles of incidence of 30°, 40°, and 50°, which allows us to determine the relative values of the tensor components with c.a. 10% uncertainty. The results are summarized in Table I, where \( \chi_{zxx} \) has been normalized to unity.

In order to obtain the absolute values of the tensor components of SiN, we have performed a calibration against the dominant tensor component \( \chi_{zxx} = 0.80 \text{ pm/V} \) (Ref. 8) of a Y-cut quartz crystal wedge with wedge angle of 0.5°, and whose relative expansion coefficient \( f_y^{\text{quartz}} \) is given by

\[
f_y^{\text{quartz}} = \frac{4\pi i N \cos \Theta_3}{N_S^2 C_0^2} \left( \frac{e^{i\Delta k} - 1}{\Delta k} \right) T_{p13} \cos(2\theta_3 + \Theta_3) \chi_{zxx}.
\]

(4)

The calibration is performed in two steps. We first translate the crystal wedge and measure the corresponding Maker fringes of the SH signal at normal incidence (see Fig. 1), which allows us to obtain the reference value of the quartz expansion coefficient. The calibrated expansion coefficient \( f \) for the SiN film can thus be obtained from the ratio of the SHG intensities measured from the film to that measured for the quartz reference.\(^{16}\) The calibrated tensor components are then calculated from their relative values and Eq. (1). As for the relative values of the independent tensor components, the calibration procedure was repeated at the four angles of incidence. The resulting absolute values for the independent tensor components are shown in Table I. Due to the neglected multireflection effects and laser power fluctuations, the uncertainty in the calibration procedure was estimated to be around 10%. We therefore believe that the total uncertainty of the calibrated tensor components of SiN should not exceed 20%.

The nonlinear response of the SiN films is remarkably high and the dominant component of the second-order susceptibility tensor is as much as 60 times larger than the effective susceptibility measured for a Si3N4 resonator \( (\chi_{eff}^{(2)} = 4 \times 10^{-14} \text{ m/V})\).\(^{8}\) Perhaps even more importantly, the value we report here is approximately three times larger than the dominant component of KDP and comparable to that for beta barium borate (BBO),\(^8\) both well-known nonlinear crystals.

The large second-order response reported here may seem surprising as SiN is usually believed to be an amorphous material. We emphasize, however, that the samples could be produced reproducibly. Although at present, the origin of the response is not yet fully clear, several explanations are possible. For example, theoretical and experimental results have suggested that the presence of small nanocrystals of silicon with dimension less than 2 nm may possess anharmonic Si-Si dimers due to ionic vibrations and/or excitonic self-trapping.\(^{17–19}\) This anharmonicity then breaks the centro-symmetry and can give rise to a very strong nonlinear polarization at the second-harmonic frequency. In our case, Si clusters could form during the CVD process,\(^{20–22}\) which would thus explain the large bulk response of our films. Yet, it is important to note that for the macroscopic response measured here, it would imply that the clusters have a net orientation along the normal of the thin film samples, which may be unexpected. Other factors that could influence the second-order response are the surface dangling and hydrogenated Si bonds or the interface strain.\(^{23–25}\) However, these mechanisms are most likely weak as we did observe a strong dependence of the response on film thickness. Further experiments, such as high-resolution transmission electron microscopy, Raman scattering, and Fourier transform infrared spectroscopy, will be performed in the near future so as to obtain more insight into the precise structure of the SiN film. It will also be important to compare the responses for samples with varying Si/N compositions as well as those fabricated by different methods.

In conclusion, we have observed strong SHG from SiN films prepared on fused silica substrates by PECVD. The polarization properties of the response show that the symmetry of the samples is broken along the film normal, but the samples exhibit full rotational symmetry about the normal. The dominant tensor component of the second-order susceptibility was measured to be \( \sim 2.5 \text{ pm/V} \), which is about three times larger than that of KDP. Our results suggest that SiN is a promising nonlinear optical material for photonic applications and in particular for on-chip photonic devices.

We would like to acknowledge Tommi Kaplas at the University of Eastern Finland for the ellipsometric measurement and kind help from Ravi Kumar and Saurav Kumar. This work is supported by the Academy of Finland (Grant No. 134980).

### Table I. The relative and calibrated values of tensor components \( \chi_{zxx}, \chi_{zxy}, \) and \( \chi_{zxy} \) in the SiN film.

<table>
<thead>
<tr>
<th>Relative values</th>
<th>Calibrated values (pm/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \chi_{zxx} )</td>
<td>1</td>
</tr>
<tr>
<td>( \chi_{zxy} )</td>
<td>0.2</td>
</tr>
<tr>
<td>( \chi_{zyy} )</td>
<td>0.19</td>
</tr>
</tbody>
</table>