Second-harmonic spectroscopy of nano-interfaces

L. Sun[*1], **P. Figliozzi**[1], **Y. Jiang**[**1], **M. C. Downer**[1], **W. L. Mochán**[2], and **B. S. Mendoza**[3]

[1] Physics Department,University of Texas at Austin, Austin, TX 78712-0264, USA
[2] Centro de Ciencias Físicas, Universidad Nacional Autónoma de México, 62251 Cuernavaca Morelos, México
[3] Centro de Investigaciones en Optica, León, Guanajuato, México

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Optical second-harmonic is shown to be a noninvasive, interface-sensitive probe of silicon nanocrystals. The TEM_{01} spatial mode of SHG radiation from a silicon nanocrystal composite indicates there is nonlocal dipolar (quadrupolar) polarization source which is proportional to the gradient of the incoming electric field. With two orthogonally polarized laser beams, we enhanced the SHG from nanocrystals by creating wavelength-scale, forward-radiating gradient in the second-harmonic polarization. The quantitative features of two-beam SHG were also studied with a fused silica slide. We demonstrate several techniques for isolating the nano-interface signal from the (bulk-quadrupolar) substrate signal in our samples.

1 Introduction

Embedded silicon nanocrystals (NCs) underlie flash memory[1] and light-emitting[2, 3] devices. Their unique charge-trapping and light-emitting properties originate from the sharply curved interfaces between the silicon NCs and their host (e.g. glass). However, the electronic structure of these nano-interfaces remains poorly understood, partly because of a lack of suitable experimental probes. Optical second-harmonic generation (SHG), which is widely used in probing planar interfaces, can also effectively probe these nano-interfaces, despite their overall centrosymmetry. We present results using a traditional single-beam, and a novel two-beam, configuration[4]. Similar techniques may be applicable to biological nano-interfaces[5].

2 Experiment

Our Si NC samples were prepared by sequential implantation of Si ions with six different energies (35 keV to 500 keV) into fused silica substrates. This produces uniform Si concentration profiles with Si densities of 2, 1, or $.5 \times 10^{22} cm^{-3}$ throughout the 1μm implantation depth. Then samples were annealed in Ar gas or Ar + 4% H_2 gas to form Si NCs. The presence of H_2 dramatically alters the Si NC interface chemistry. Transmission electron micrographs show that NCs form with average diameter $< d >_{NC}$=8, 5 and 3 nm, respectively (with 50% size fluctuation), and corresponding NC densities $n_{NC} = 7, 3$ and $1.5 \times 10^{18} cm^{-3}$. No NCs were implanted in an outer 1 mm wide margin of each substrate, which therefore served as a control sample to monitor SHG from the unimplanted glass.

* Corresponding author: e-mail: sunlf@physics.utexas.edu, Phone: +1 512 471 9411, Fax: +1 512 471 9637
** Current address: School of Physics, Peking University, Beijing 100871, China

2.1 Single-beam SHG results and discussion

A regeneratively amplified Ti:Sapphire laser beam (800nm, 200fs, 250KHz, 300nJ/pulse) was focused at normal incidence to a spot radius $w_0 \sim 10\mu$m onto the sample with TEM_{00} mode structure, and scanned across the sample (Fig. 1a). As the laser beam scanned across the sample, no SHG was observed from the unimplanted glass margin. SHG increased to $\sim$100 counts/s as the laser beam scanned into the Si NCs, proving that NCs caused the SHG. Moreover, SHG from the NCs proved sensitive to interface modification. As shown in Fig. 1a, the SHG generated from Ar gas annealed sample is about $10\times$ stronger than from Ar + H_2[6]. Annealing in H_2 enhances photoluminescence, an effect attributed to H passivation of Si/SiO_2 interface trap states. The correlation with SHG suggests that such interface states are responsible for most of the SHG from the Ar-annealed NCs.

The SHG radiation pattern was measured by imaging the SHG source region onto a photon-counting charge-coupled device. The image (Fig. 1a inset: bottom) shows that the NCs emitted SH in a TEM_{01} mode[4] with no SHG radiation in the exact forward direction, signifying a macroscopically quadrupolar SHG source proportional to $(\mathbf{E}\cdot\nabla)\mathbf{E}$[7, 8]. Quadupolar SHG can originate from the bulk of centrosymmetric media, but here it originates from the average interface dipole response of nano-spheres[7, 8]. With a single-beam, the only contribution to $\nabla\mathbf{E}$ that radiates in the near forward direction is the transverse gradients of the incident TEM_{00} mode, which point radially outward from its center. Thus for incident linear polarization, $(\mathbf{E}\cdot\nabla)\mathbf{E}$ has the TEM_{01} spatial structure, as observed. For a focused Gaussian beam, $\nabla\mathbf{E}$ scales as $|\mathbf{E}|/w_0$, where w_0 is the beam waist. To increase the signal, we can increase the beam intensity ($|\mathbf{E}|$) and decrease w_0 by tight focusing. However, sample damage limits this beam intensity, keeping the SHG signal stubbornly low (in the photon counting regime).

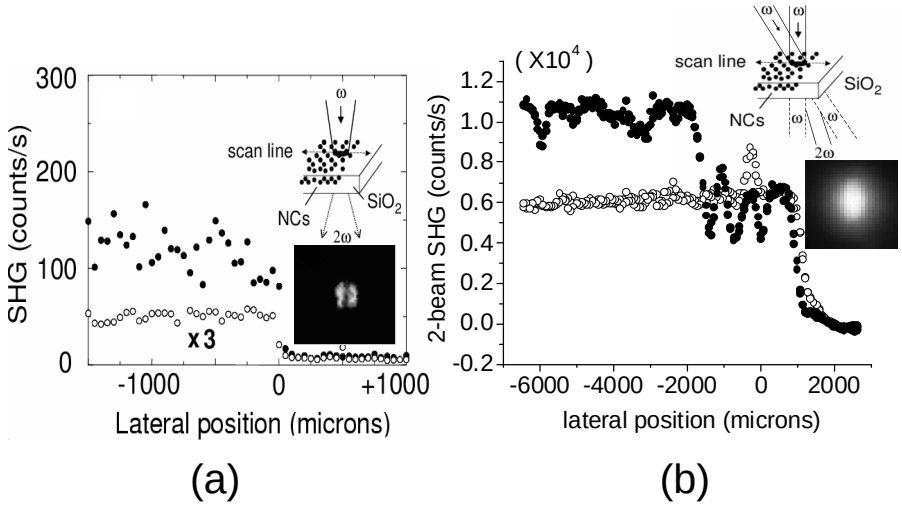

Fig. 1 Demonstrations of SHG sensitivity to H-termination of Si nano-interfaces. (a) Scan of single-beam SHG across the boundary between Si NC implant and unimplanted glass rim at edge of sample. $x < 0\mu$m – NCs implanted region; $x > 0\mu$m – pure fused silica margin. Solid dots (circles) correspond the sample annealed in Ar (Ar + 4% H_2). Inset: single beam configuration (top) and SH radiation pattern (bottom). (b) Same as (a) but for two-beam configuration. $x < 0\mu$m – NCs implanted region; $0 < x < 1000\mu$m – pure fused silica margin; $x > 1000\mu$m – air.

2.2 Two-beam SHG results and discussion

Since the quadrupolar SH polarization is proportional to the gradient of the incoming electric field ($\nabla\mathbf{E}$), the natural way to increase the gradient is to form an interference pattern with two laser beams. This is

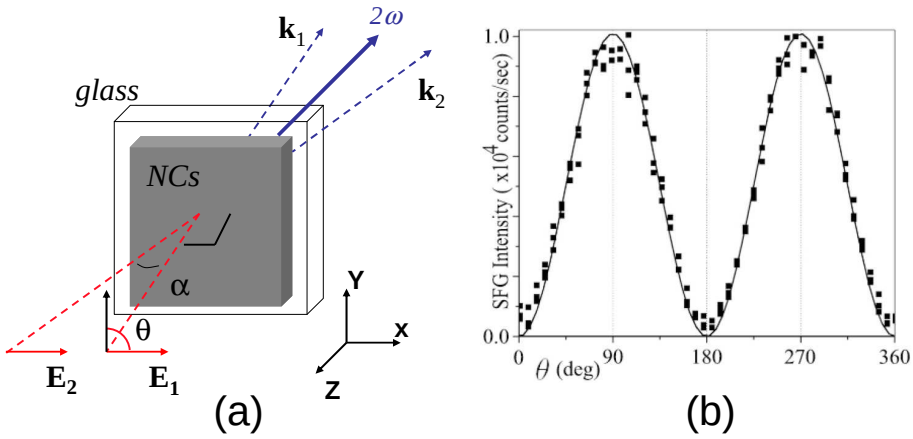

Fig. 2 (a) Two-beam SHG geometry. (b) dependence of two-beam SHG on the angle θ between $\mathbf{E}_1$ and $\mathbf{x}$ for the sample with $< d_{NC} >= 5$nm.

essentially the idea behind the gradient enhancement. However, we must orthogonally polarize the beams in order to avoid cancelation. When we use two laser beams (Fig. 2a), the electric field in the nonlinear polarization term $((\mathbf{E}\cdot\nabla)\mathbf{E})$ is the sum of the electric field of each laser beam ($\mathbf{E}_1$, $\mathbf{E}_2$). For two plane wave fields $\mathbf{E}_i = \mathbf{E}_i^0 e^{i\mathbf{k}_i\cdot\mathbf{r}}$ (where $i = 1, 2$), the quadrupolar SH polarization can be expanded to four terms[9],

$$\begin{aligned}\mathbf{p}_Q^{(2)} = \; & i(\delta-\beta-2\gamma)\{\mathbf{E}_1^0\cdot\mathbf{k}_1\mathbf{E}_1^0\exp(2i\mathbf{k}_1\cdot\mathbf{r}) + \mathbf{E}_1^0\cdot\mathbf{k}_2\mathbf{E}_2^0\exp[i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{r}] \\ & + \mathbf{E}_2^0\cdot\mathbf{k}_1\mathbf{E}_1^0\exp[i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{r}] + \mathbf{E}_2^0\cdot\mathbf{k}_2\mathbf{E}_2^0\exp(2i\mathbf{k}_2\cdot\mathbf{r})\},\end{aligned} \tag{1}$$

where δ, β and γ are independent material constants. The first and last terms in braces vanish, since the electric field is always perpendicular to the wave vector for each laser beam. If the two crossed beams are co-polarized, $\mathbf{P}_Q^{(2)}$ (sum of the second and the third terms in braces) points along the propagation direction ($\mathbf{k}_1+\mathbf{k}_2$), and therefore, does not radiate, though the interference pattern is formed in the two-beam overlap region. However, if $\mathbf{E}_1 \perp \mathbf{E}_2$ (*e.g.*, $\mathbf{E}_1\|\hat{x}$, $\mathbf{E}_2\|\hat{y}$), then $\mathbf{E}_2\cdot\mathbf{k}_1$ vanishes, but $\mathbf{E}_1\cdot\mathbf{k}_2$ does not, and $\mathbf{P}_Q^{(2)}\|\mathbf{E}_2$ (*i.e.* S-polarized). $\mathbf{P}_Q^{(2)}$ scales as $\mathbf{E}_1\cdot\mathbf{k}_2$, *i.e.* $(|\mathbf{E}_1|/\lambda_2)\sin\alpha'$, where α' is the angle between two beams inside the sample. Compared to single beam SHG, $|\mathbf{P}_Q^{(2)}|$ is enhanced by a factor $(w_0/\lambda_2)\sin\alpha'$, and SHG intensity by a factor $(w_0/\lambda_2)^2\sin^2\alpha'$ [4, 9], which is about 2×10^4 ($w_0 \sim 500\mu$m, $\lambda_2 = 810nm$, $\alpha' = 13.6^0$ in our experiments) as shown in Fig. 2b.

Two-beam SHG of Si NCs, like its single beam counterpart, is sensitive to interface chemistry. When samples annealed in Ar and Ar + 4% H_2 were scanned, 2-beam SHG was again much stronger than from the Ar-annealed sample (see Fig. 1b). In addition 2-beam SHG emerged in an S-polarized TEM_{00} mode (Fig. 1b, bottom inset), in agreement with the quadrupolar model (1).

We often observe strong fluctuations in both single- and two-beam SHG intensity when the laser beam(s) scans across the border between NC implanted and unimplanted glass, as shown in the $x \approx 0$ region in Fig. 1b. These fluctuations are believed to originate from local gradients ∇n_{NC} in NC density. In non-uniform nano-composites, such gradients also contribute to the SH polarization[4, 10, 11]: $\mathbf{P}_Q^{(2)} = n_{NC}\mathbf{p}_Q^{(2)} - \frac{1}{6}\nabla\cdot n_{NC}\tilde{Q}^{(2)}$. The first term is equivalent to Eq. (1), and describes the contribution of individual NCs of uniform density n_{NC}; the second term is proportional to the SH quadrupole moment, and interferes with SH fields from the first term in regions of local gradients in NC density, leading to fluctuations in SHG intensity.

2.3 Three strategies for discriminating nano-interface and glass host contributions to SHG

The two-beam enhancement mechanism applies to the bulk quadrupolar response of any centrosymmetric material, since that is proportional to $(\mathbf{E}\cdot\nabla)\mathbf{E}$. In particular, the SHG from our glass substrate was enhanced. Since this background signal is of the same order as the nano-interface SHG, we devised several methods of signal discrimination.

The NC layer is on one side of the glass, so we can take two measurements by inverting NC layer and glass order to discriminate the NC SHG (Fig. 3a). Two SHG scans in which an NC layer is either on the beam exit or entrance side of the substrate show that the glass and NC SHG interfere destructively. Since the NC layer absorbs about 2/3 of the SHG from glass, the stronger SHG was observed when the NC layer was on the exit side [4].

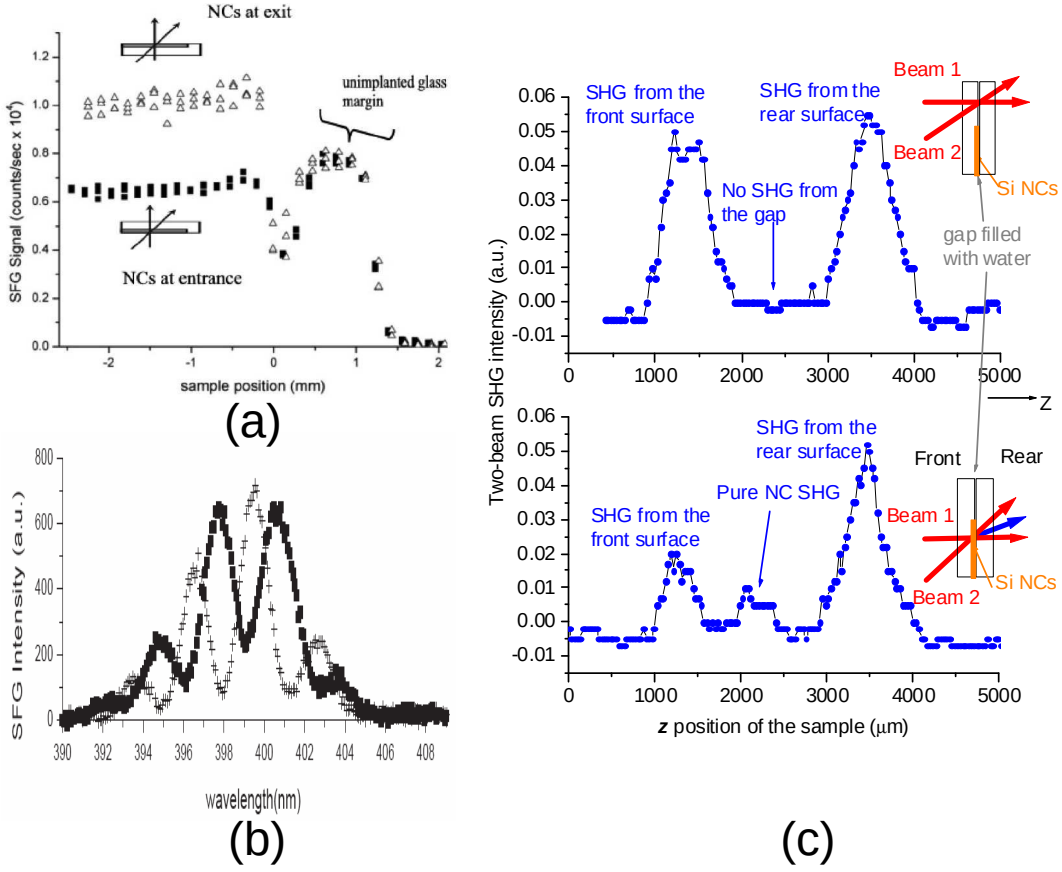

Fig. 3 Three methods of discriminating SHG from Si nano-interfaces vs. glass host. (a) Scan of two-beam SHG across the glass-NC boundary with an NC layer ($< d_{NC} >= 5$nm) at entrance (filled squares) or exit (triangles) side of sample, with orthogonally polarized incident fields. (b) Spectrally dispersed two-beam SHG from unimplanted glass (crosses) and NC implant (filled squares) of the same sample with NCs at exit, showing Maker fringes caused by frequency-dependent phase mismatch in glass substrate. (c) Two-beam SHG z-scan: a NC sample stacked with a same size fused silica slide with water filled in the gap. Top: z-scan in the pure fused silica margin; Bottom: z-scan in the NC implanted region.

Spectral dispersion of SHG was also used to discriminate the NC SHG. Since the SH coherence length is much larger than the thickness of the NC layer but much less than the thickness of the glass substrate, the spectrum of glass SHG exhibits ”Maker” fringes, but spectrum of NC SHG does not. As the laser beams

scanned across the sample from pure glass substrate into the NCs implanted region, the fringes shifted, as shown in Fig. 3b, representing the addition of the interfering Gaussian envelope of SiNC SHG to that of the glass. The glass SHG drops approximately to zero at 395, 398, 401, and 404 nm. At these four wavelengths, the nonzero SHG from signal from the NC implanted region can be regarded as pure NC signal [4].

Perhaps the best method of signal discrimination exploits the fact that the two-beam bulk-quadrupolar SHG vanishes as long as the beam overlap region is totally immersed inside the isotropic bulk substrate, which makes the quadrupolar SHG surface-like[9, 14, 15]. Moreover, if two isotropic materials have similar refractive indices and nonlinear susceptibilities, the two-beam SHG also vanishes on the interface between those two materials. We found that water and glass are such materials. By stacking a pure glass slide on top of a NC-implanted slide (with its 1 μm-thick implant facing the gap), then filling the gap with water, we observed no SHG when the 2-beams overlapped the gap outside the NC implant (Fig. 3c, top) and pure SHG from NCs when they overlapped the implant (see Fig. 3c, bottom).

With this method, we might be able to realize two-beam SHG microscopy, a potential complement to third-harmonic generation (THG) microscopy[12] for materials that absorb TH, but not SH, radiation.

3 Conclusions

We observed single-beam SHG from Si NCs embedded in fused silica, which emerges in a TEM_{01} mode and is sensitive to hydrogen termination of the nano-interfaces. The source of SH radiation is a quadrupolar SH polarization proportional to $(\mathbf{E}\cdot\nabla)\mathbf{E}$, which has contributions from the Si nano-interfaces and the glass host, and is enhanced dramatically when excited with two noncollinear, orthogonally polarized laser beams. The enhanced SHG can be useful for scanning, spectroscopy and real-time monitoring. Three methods were used to discriminate the NC SHG from glass SHG. One of them has potential application in SHG microscopy.

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