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Authors

Nayfeh, MH
Mitas, L
Gratton, E
et al.

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**Si₂₉ NANOPARTICLES AND RECONSTITUTED FILMS: A HIGHLY
FLUORESCENT NEW FORM OF SILICON**

Munir H. Nayfeh

**Department of Physics, University of Illinois at Urbana-Champaign
1110 W. Green Street, Urbana, Illinois 61801 USA**

Lubos Mitas

**Department of Physics, North Carolina State University
127 Stinson Rd. Raleigh, NC 27695-8202**

Enrico Gratton

**Department of Physics, University of Illinois at Urbana-Champaign
1110 W. Green Street, Urbana, Illinois 61801 USA**

Paul Braun

**Department of Material Science and Engineering and the Beckman Institute for
Science and Technology, University of Illinois at Urbana-Champaign
1110 W. Green Street, Urbana, Illinois 61801 USA**

ABSTRACT

We electrochemically dispersed bulk crystalline Si into ultrasmall Si nanoparticles (Si₂₉, ~ 1 nm diameter) that have novel optical, electronic and biological characteristics, and reconstituted them into micro-crystallites or uniform films. The particles are ultrabright blue luminescent, two-fold brighter than fluorescein, and efficient under UV or near-infrared two-photon excitation. The blue emission from single particles in colloids, frozen in gels or on quartz is readily detectable and highly photostable. In addition to being ultrabright, reconstituted films exhibit stimulated and directed blue emission with high gain, and second harmonic generation. I-V spectroscopy using STM and spectroscopic ellipsometry suggest a large drop in the dielectric constant, and a breakdown of the effective mass. Using density functional with exchange correlation, configuration interaction and Monte Carlo theory, we constructed a structural prototype for 29 atoms (magic number for the Td symmetry). The particle is a filled fullerene, at the edge of the sp³ diamond-like and the sp² graphite-like structures. Five atoms constitute a tetrahedral core. The remaining 24 atoms constitute a highly, puckered (wrinkled) cage with highly radiative quantum confinement-induced Si-Si reconstructed phase, found only in ultrasmall nanoparticles.

SYNTHESIS OF SILICON NANOPARTICLES

We pulverize a silicon wafer using chemistry and electricity in an electrochemical treatment that involves gradually immersing the wafer into a bath of HF and H_2O_2 while arranging for an electrical current to skim the top skin of the wafer[9]. H_2O_2 catalyzes the etching producing ultrasmall structures [10] and cleans impurities and produces a higher electronic and chemical quality with an ideal hydrogen termination and no oxygen[10]. This process erodes the surface layer, producing weakly interconnected nanostructures. The wafer is then immersed in an ultrasound bath[1-2], causing the fragile nanostructure network to crumble into particles. The slightly larger, heavier particles precipitate out and can be turned into a yellow luminescent colloid, while the ultrasmall particles remain in suspension, where they can also be recovered to form a blue luminescent colloid. The process is efficient and the wafer can be recycled. We determined the size of the blue luminescent particles by direct imaging using high resolution transmission electron microscopy (TEM). A thin graphite grid was coated with the colloid. Figure 1 shows the particles are 1 nm in diameter with roughly a 10 percent dispersion. Electron photospectroscopy shown in Figure 2 shows that the particles are composed of silicon with less than 10 percent oxygen.

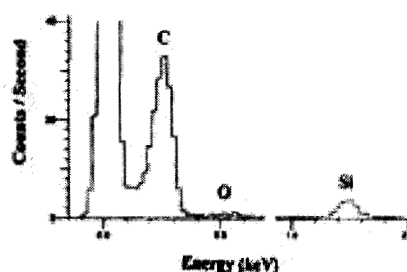


Figure 1 Transmission electron microscopy image of the Si nanoparticles coating a thin graphite grid

Figure 2 Material analysis profile of the coated grid using electron photo spectroscopy.

EMISSION / DETECTION OF SINGLE NANOPARTICLES

We prepare a colloid of the particles with a concentration of ~ 10 nM. The colloid is excited by 355 nm pulsed radiation. The blue emission is observable with the naked eye, in room light, as shown in Figure 3. Figure 4 gives the spectrum for excitation wavelength at 330, 350, 365, and 400 nm, showing a strong blue band that maximizes for 350 nm. Because UV is not friendly to biological molecules, we used near-infrared two photon excitation (700 to 900 nm). Figures 5-6 give (at 780 nm) the auto correlation function of the fluctuating time-series of the luminescence with progressive dilution to demonstrate the sensitivity of the detection: Si with 5.4 particles; a fluorescein standard with 1.5 molecule; Si with 2.75 particles; and Si a single particle (0.75) in the focal volume. The measurements yield a particle size of ~ 1 nm, consistent with direct imaging by TEM. They also yield a brightness fourfold larger than that of fluorescein. The photostability was tested by targeting stationery particle frozen in a gel. Figure 7a gives examples of luminescent images,

demonstrating the ability to observe / image single ones. "Parking" the excitation beam, focused to an average intensity as high as 10^6 W/cm², on stationary particles shows that the particles are photostable (See Figure 7b).

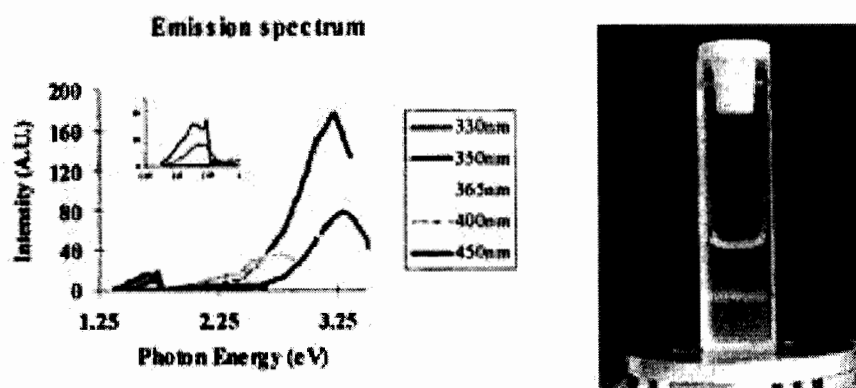


Figure 3 A photo of a Si colloid excited by 355 nm radiation.
Figure 4 Emission and excitation spectra (inset) of the particles

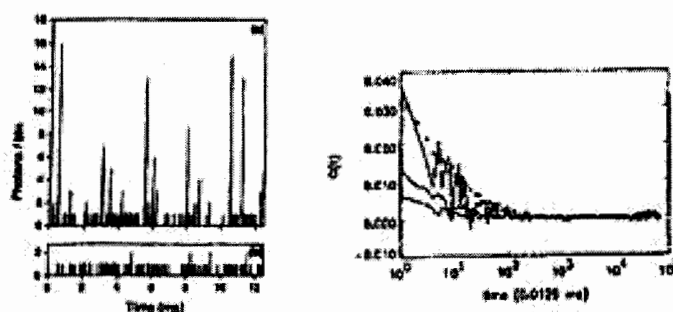


Figure 5a-b Raw traces of (a) a Si particles and (b) a fluorescein standard
Figure 6 Auto correlation of 5.4,2.75,0.75 Si particles, and 1.5 fluorescein molecules

OXIDE COATING

Detection of single particles paves the way for their use as labels in biosensing. For better biocompatibility, we readily capped the particles with an oxide at room temperature under ordinary conditions by immersion in H₂O₂[11]. Figure 8 gives the molecular vibrations of as-is particles and after capping with oxygen. In the as-is we see mainly hydrogen, but after capping we see hydrogen being replaced by oxygen. Upon oxygen termination, the spectrum suffers only minor changes, while the brightness drops only by a factor of two.

SUPERLATTICE MATERIAL ("NeoSILICON")

In addition to the novel properties that the individual particles provide, there is a potential to engineer additional properties by synthesizing two and three dimensional arrays of the particles. The ability to produce monosize particles gives us the opportunity to manipulate interspacing with atomic precision to tailor new

elemental silicon-based material with unique optical and electrical properties. The band gap of the new material is governed by the particle

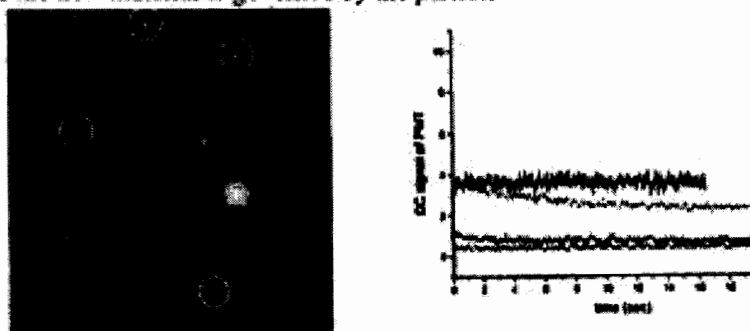


Figure 7 Frozen Si particles in a gel. (a) luminescent images, demonstrating the ability to observe / image single ones. (b) "Parking" the excitation beam on stationery particles shows that they are photostable.

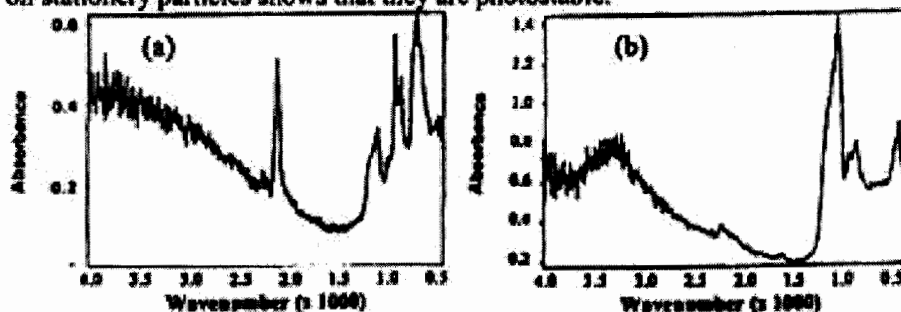


Figure 8 The molecular vibrations of (a) as-is and (b) after capping with oxygen.

size. The conductivity is controlled by the interspacing (tunneling spacing). The transport is governed by the size, termination, and dielectric properties (charging) of the particles. We used precipitation from a volatile solvent to reconstitute the particles into thin films. By gentle evaporation, microcrystallites is demonstrated on high quality Si or silicon oxide, or in free standing mode. The structures are optically clear. Optical imaging in initial experiments show colloidal crystals of 5 to 50 μm across (Fig. 9). We experimented with slower growth rates using slower evaporation rates at reduced temperatures to produce larger, flatter, clearer, and more uniform films. Careful regulation of the temperature allows precise adjustment of the destabilization.

STIMULATED EMISSION / GAIN COEFFICIENT

We first examined dispersed particles in a colloid. We performed power dependence studies of the emission under a single-particle condition. Figure 10 shows quadratic dependence as in two-photon processes. Next we examined the dependence from aggregates of particles. Aggregates are found on the solid precursor before sonification and dispersion into individual particles. The intensity of the emission from such aggregates has a sharp threshold, with highly nonlinear

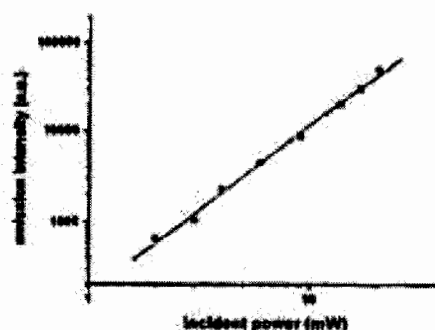


Figure 9 Optical image showing colloidal crystals of 5 to 20 μm across.
 Figure 10 Power dependence of emission of dispersed particles in acetone.

emission, rising by several orders. Figure 11 shows the emission intensity under femtosecond pulsed excitation as a function of the average power of the incident radiation. The inset is the log-log of the data. An average power of 15 mW corresponds to an average intensity of $5 \times 10^5 \text{ W/cm}^2$. At the threshold there is a dramatic increase in the slope of the power pumping curve from ~ 1.6 to $\sim 11-12$, similar to stimulated emission in inverted systems. The contrast is more dramatic in the case of CW excitation (not shown). The fluorescence is extremely weak, basically unmeasurable for low powers. However, at an average comparable to the threshold intensity in the pulsed case, the CW exhibits somewhat similar threshold behavior.

The region that exhibits the threshold behavior on the solid precursor [4] is abundant, but it is spotty, shallow, and uncontrollable. We created large, thick, uniform and under control layers of the ultrasmall material by reconstituting the dispersed particles as described above. Figure 12 gives the emission intensity from such films as a function of the average incident intensity. It is typical of the response from any part of the film. For low intensity, the emission is finite, but at an average intensity of $\sim 10^6 \text{ W/cm}^2$ ($\sim 20-25 \text{ mW}$), the emission exhibits a sharp threshold, rising by many orders of magnitude. Beyond the threshold, there sets in a low order power dependence that saturates at the highest intensities.

Figure 13 displays the interaction of the incident beam with the micro crystallites. It is normally incident (normal to the plane of the figure). The four examples in Figure 13a, show that directed blue beams emerge, propagating in the interior of the crystallite, in the plane of the sample, locally normal to the closest side. Due to re-absorption and scattering, it gets narrower as it fades away, propagating only 5-10 μm . Figure 13b shows two cases when the opposite faces of a crystallite are close. The beam, in this case, strikes the opposite face forming a weaker bright spot. The blue beams are characterized by a threshold. When the incident intensity is reduced, the beam fades away, and disappear, while the interaction spot remains bright (frames in Figure 14). Geometrically, the blue beam is favored when the incident beam strikes close to a face of a micro crystallites. If the beam requires feedback, then pumping

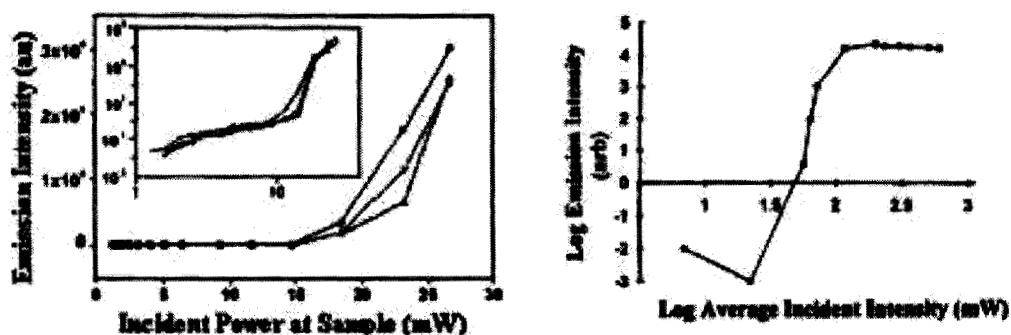


Figure 11 The emission intensity from solid precursor under femto-second pulsed excitation as a function of the average power of the incident radiation. Figure 12 Emission intensity as a function of the average incident intensity for a reconstituted thin film of Si nano particles close to one side, provides a reflector of 2π solid angle, i.e., high feedback.

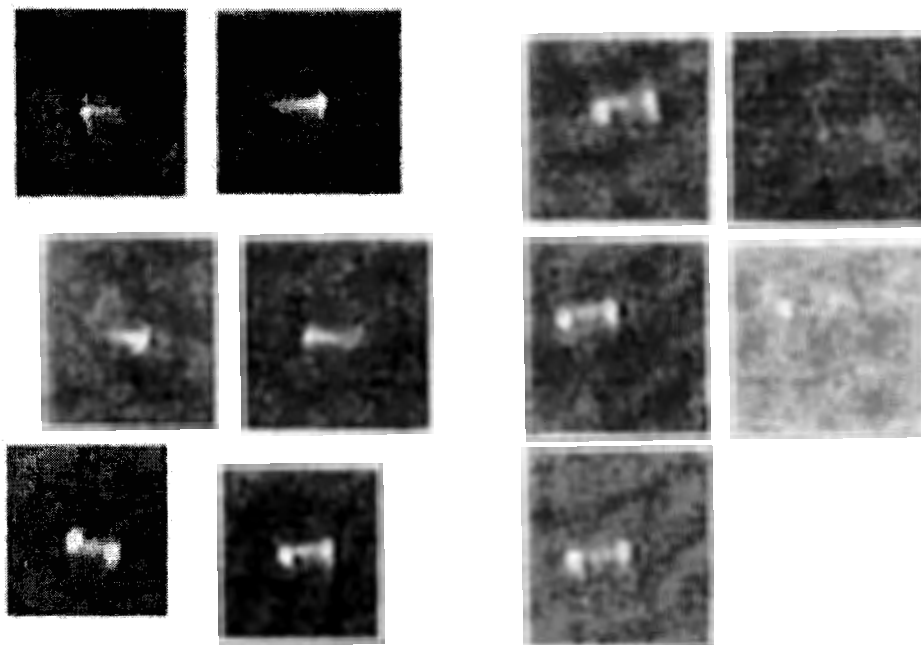


Figure 13 Photo luminescence images from the micro crystallite region. The interaction spot appears as "white" spot. (a) shows four examples of a blue beam. (b) shows two examples of a blue beam between opposite faces. Figure 14 Photo luminescence images from the micro crystallites showing five frames of the blue beam taken under decreasing incident intensity

SECOND HARMONIC GENERATION

Bulk Si is known to have negligible nonlinearity, being zero at the second order level (not allowed because of centrosymmetry), and very small at the third-order level. We recently reported the first observation of second harmonic generation

in films of ultrasmall silicon nanoparticles. Figure 15 gives the emission spectra for the three excitation wavelengths 780, 800, and 832 nm (not of the same intensity). Each shows a peak with a shoulder on the red wing. The shoulders are at 390, 400, 416 nm, half the wavelengths of the incident beam. The peaks in the spectra are at 380, 390, and 406 nm, i.e., blue shifted by 10 nm from the shoulder in each of the spectra. Those and other measurements show that the emitted wavelength tracks the incident wavelength. These results point to a mechanism in ultrasmall particles that break the centrosymmetry of bulk Si, the symmetry that inhibits second harmonic generation.

ABSORPTION MEASUREMENTS

The dispersion of the particles allowed the first direct absolute measurement of the absorption. Figure 16 gives the absorption coefficient spectrum of the colloid, along with that of bulk silicon. Bulk is immediately recognizable by the three sharp features near 3.4, 4.3 eV, the E_1 and E_2 peaks, and the 5.5 eV peak. The particle spectrum clearly shows crystalline resonance signature at 3.4, 4.5 and 5.5 eV, however with a significant redistribution of the intensity ratios. In isolated nanoparticles, one cannot define a conduction band, hence a continuum does not exist[12]. Moreover, theory has suggested that confinement tend to concentrate the oscillator strength in the lowest states at the edge of the direct band gaps[13-14].

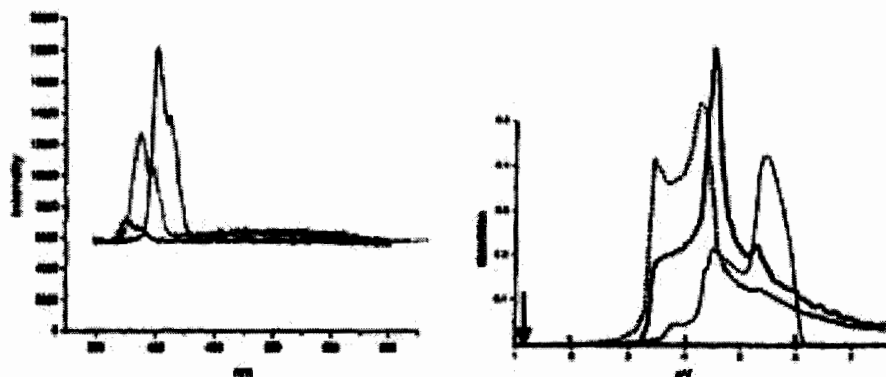


Figure 15 The second harmonic emission spectra for the three excitation wavelengths 780 (solid), 800 (dot), and 832 (dense dot) nm (at different incident intensities) respectively.

Figure 16 gives the absorption coefficient spectrum of the particle colloid, along with the experimental and theoretical of bulk silicon.

QUANTUM CONFINEMENT ELECTRONIC STATES

Particles are evaporated on p-type Si substrate. The tip of a scanning tunneling microscope (STM) is placed over the silicon particle film at a constant height. In this two-terminal arrangement, the tip acts as the source, while the substrate acts as the drain electrode. This may be represented by a double barrier model. The particle represents the quantum well, with a vacuum barrier due to a gap

between the particle and the tip, and a barrier due a gap between the particle and the substrate. Figure 17a gives the I-V spectra taken at room temperature under dark condition. Figure 17b, taken under light irradiation, shows a high visibility regular step structure, for negative tip biasing at ~ 1.0 eV period, the particle's quantum energy level spacing, however using the free mass.

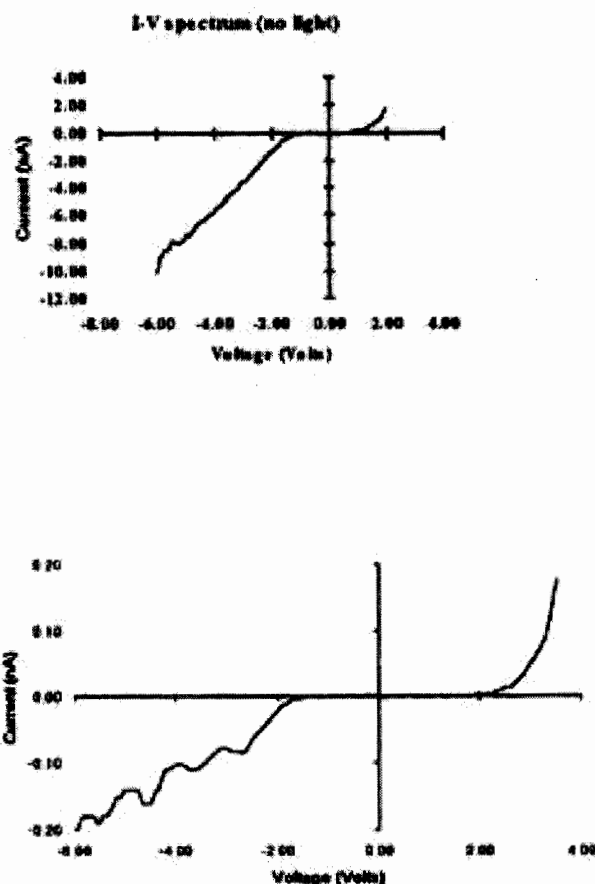


Figure 17 The I-V response for a film of nano particles on a device quality silicon substrate (grounded) taken (a) in the dark, and (b) under light illumination.

Under standard doping of $\sim 10^{15} / \text{cm}^3$, as in this sample, 1 nm particles contain less than one in a million holes, hence they behave as undoped, with the number of electrons in the conduction states extremely small. Laboratory temperatures are not sufficient to induce holes. Light irradiation, however, creates holes for the process to proceed. This development paves the way for operation of high-temperature Si-based single electron devices.

DERIVETIZATION OF THE PARTICLES

Because the particles are ultrasmall, ultrabright, photostable and do not blink, they show significant potential as the next generation of ultrabright nonorganic markers for ultrasensitive fluorescence analysis. We derivitized the nanoparticles by

termination with butylamine [15]. This reaction is sufficiently general for the assembly of a variety of functional organic molecules on the particles. We demonstrated that the exceptional brightness of the nanoparticles are maintained after derivatization. Present-day medical and biological fluorescent imaging is significantly constrained by the use of dye markers—the only markers currently available [16]. Dyes, especially the blue ones, are not photostable—they decompose under room light or higher temperatures. Efforts are being directed to produce different classes of markers, such as semiconductor particles. CdS (e) nanoparticles have recently been proposed as fluorescent markers [17-18]. Implementation of Si-based detection will require routes to couple biopolymers to the surface of the silicon nanoparticles via a covalent linkage. Here, we present a step toward this goal, the covalent linking of a model organic compound to the surface of the particles. We demonstrated the formation of an organic hydrophobic shell due to the attachment of butylamine while still maintaining the optical activity of the particle. The particles were chlorinated by reaction with Cl_2 gas, followed by the reaction with the functional amine group in butylamine to form a Si-N linkage. The linkage facilitates the attachment of organic functional groups capable of recognizing specific analytes such as proteins, DNA, or viruses. The exceptional optical properties, ultrasmall size (~ small molecules), uniformity of size, low cost and photostability provide the ultimate sensitivity and spatial resolution in imaging capabilities.

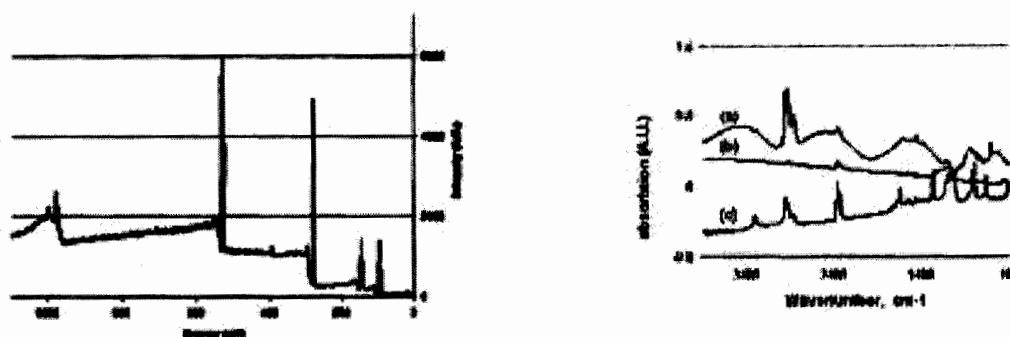


Figure 18 The XPS spectra of films reconstituted from the particles showing that the aminized particles have nitrogen and carbon peaks at ~ 400 and 300 eV respectively. A fit of the 400 eV peak in terms of two components is given in the inset.

Figure 19 The Fourier transform infrared (FTIR) spectra of (a) butylamine, (b) bare Si substrate, and (c) aminized particles cast on the substrate.

The chlorobenzene colloid of particles is saturated with Cl_2 gas at a temperature of -10°C . The dissolved chlorine gas chlorinates the particles, replacing the hydrogen with chlorine. Freshly distilled butylamine ($\text{C}_4\text{H}_9\text{NH}_2$) is then added to the dried sample and is heated to 90. The dried particles are dissolved in heptane. Several drops of the colloid are placed on a Si substrate. After drying in air or under nitrogen, a few micron thick particle film forms. Figure 18 presents the X-ray photo spectra (XPS) of a film of aminized particles. Both the N and C peaks at ~ 400 and 300 eV respectively are observed. The best fit of the 400 eV peak, shown in the inset,

gives two components at 397.120 and 398.436 eV with 1.762 and 1.875 FWHM and 43.9 and 56.1 percentage mass concentration respectively. These are associated with the N_{1s} of bulk Si nitride, and amine molecules, (typically at 399 eV) respectively. The low energy one is consistent with well-established surface chemistry in the absorption of NH_3 on Si surfaces and in the atomic layer growth of Si_3N_4 . These lend support for binding through a Si-N linkage. Further confirmation is derived from the Fourier transform infra-red (FTIR) spectra given in Figure 19. The aminized sample show strong N-H stretch at $\sim 3300\text{ cm}^{-1}$, and Si-N stretching mode at 860 cm^{-1} . The peaks at 2869, 2881, 2931, and 2966 cm^{-1} are characteristics of C-H stretch vibrations in butyl groups. The vibration at ~ 2300 and 1000-1100 pertain to CO_2 air and oxygen. The peaks at 1460 and 1260 are due to CH_2-CH_3 stretching and CH_2 wagging respectively. The 1450-1700 band is background seen also in control samples. XPS taken after air-exposure did not show significant change in the N_{1s} . The presence of the H-N bond is a strong indication of single Si-N formation as opposed to a bridge double bond linkage Si-N-Si. Aminization of Si flat or porous surfaces using a similar chemical treatment showed preference to the bridge formation. In these systems, XPS showed nitrogen bonds but FTIR showed the absence of the N-H vibration.

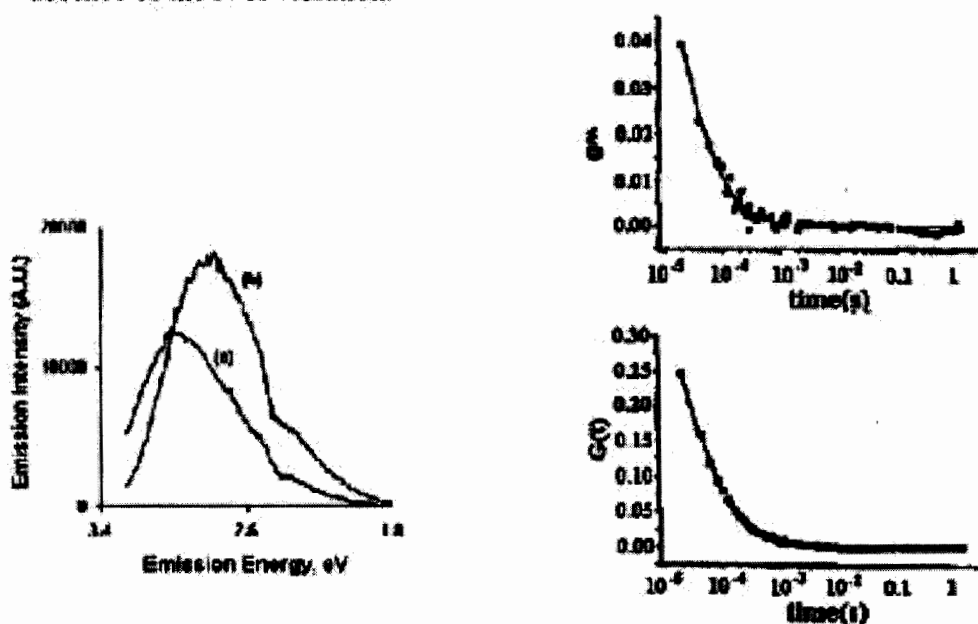


Figure 20 The unnormalized emission spectra of the dispersed particles at 365 nm, (a) before and (b) after the aminization. The peak of the blue band of the hydrogenated particle shifts from 410 nm to 450 nm upon aminization

Figure 21 The auto correlation function G as a function of time derived from the emission of (a) the particles in a colloid along with that of (b) a coumarine standard under two-photon excitation using mode locked near infrared. The functions belong to one particle and 0.2 molecules in the focal volume.

We used two-photon excitation (780 nm, 150 fs duration at 80 MHz) to determine the particle's brightness by autocorrelation fluctuation spectroscopy (FCS)

[1]. The raw traces of emission are recorded. Figure 21 gives the autocorrelation function of a very diluted particle sample along with a diluted coumarine dye. The results yield a volume of 0.997 pico cubic centimeters, and $N = 1$ particle. This corresponds to a density of $3.45\text{--}3.85 \times 10^{12} / \text{cm}^3$. A similar analysis yields 0.2 coumarine molecules in the focal volume. From the photon counting histograms (not shown), we find a brightness for the aminized particles two-fold smaller than that of coumarine.

STRUCTURAL PROTOTYPE OF THE PARTICLES

The search [19] for a realistic structural prototype started from a spherical piece of a crystalline Si which, for the experimentally observed size of ~ 1 nm, contains 29 atoms (magic number for the Td symmetry and spherical shape). All dangling bonds were terminated by hydrogen. However, the corresponding electronic energy gap was larger than 6 eV, suggesting that the observed clusters possess smaller number of terminating hydrogen/oxygen, with a part of the dangling bonds saturated by a nanocrystal surface reconstruction. By eliminating 12 H atoms we arrived at a structure of $\text{Si}_{29}\text{H}_{24}$ with 6 reconstructed surface Si-Si dimers similar to Si(001) surface 2×1 reconstruction. The resulting $\text{Si}_{29}\text{H}_{24}$ system was then relaxed using the Density Functional Theory (DFT) with the PW91 exchange-correlation functional, giving, after correcting for the well-known DFT gap underestimation, a band gap of 3.5 eV, close to the one observed. We next calculated of the optical absorption spectrum as shown in Figure 19. We employed the Configuration Interaction singles (CIS) method which constructs the wavefunctions with correct spatial and spin symmetries and which accommodates, to the first order, the excitonic effects. The correct overall shift of the spectrum due to the incomplete treatment of the electron correlation effects was estimated from a preliminary quantum Monte Carlo calculations of the first two transitions ($T1 \rightarrow T2$) which correspond to the edge of the absorption spectrum. The resulting spectrum with a Gaussian broadening of 0.14 eV, which qualitatively represent the temperature and size averaging, given in Figure 19, shows agreement with our measurement.

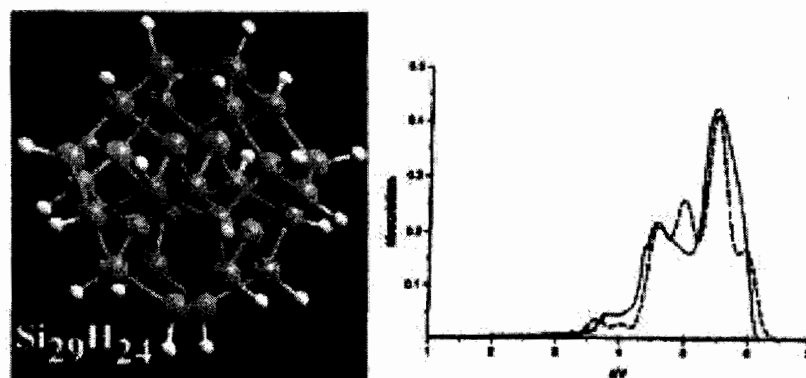


Figure 18 A configuration structure of a particle that contains 29 silicon atoms, with 5 core atoms and 24 on the surface. Hydrogen terminating atoms are in white.

Figure 19 The calculated (dot) and experimental (solid) absorption (normalized) of the 29 atom particle.

We evaluated the cluster polarizability, a uniquely defined property, using GGA/PW91 and 6-31G* basis set, giving ~ 793 (a.u.). A general definition of a dielectric constant in semiconductor nanoparticles is not possible since the energy levels are discrete. To arrive at an effective "dielectric constant" one has to define an appropriate "cluster interior volume". For an effective interior radius (~ 4.2 Å) we get a dielectric constant of ~ 5.7 . This value is close to estimations done before by Allan et al.[12] and by Zunger et al[20]. The Penn's model-based analysis [21] gives, for a diameter of 0.8 nm, a more reduced static dielectric constant of 2.

STRUCTURE OF SI-SI BONDS

Figure 20 gives a schematic of the interatomic potential of the Si-Si reconstructed bond[22] calculated by Allan et al using LDF in a 1.03 nm diameter particle, and the various pathways for absorption and emission calculated by Nayfeh et al[23]. The excited state is a double well with a potential barrier. The inner well (at 2.35 Å) is associated with the tetrahedral configuration and radiates on a long time scale of milli seconds. The outer well, a new state found only in ultrasmall nanoparticles (< 1.75 nm across), is a trap well (at 3.85 Å) that radiates with life times of 5 ns to 100 μ s. The calculations were performed with the silicon atoms terminated by hydrogen. Only minor changes such as a shift of the bottom of the outer well inward are expected for oxygen terminated dimers since they are less amenable to expansion. The state to which the outer well radiate vertically down is the ground electronic state. But, at extended bond lengths, the ground state is high lying and unpopulated, hence this system constitutes a stimulated emission channel, and possible gain. The blue emission proceeds at an interatomic distance at the top of the barrier (~ 3 Å), where the lifetime is in the nanosecond regime and mixing between the two states is most significant. Emission from the bottom of the outer well is of longer time characteristic and of longer wavelength (in the red or near infrared)

According to the Frank-Condon principle, absorption proceeds vertically up into the inner well at a bond of 2.35 Å, followed by transfer into the outer by bond expansion via tunneling (double well vibrations) or thermal activation (i.e., self trapping) as shown in Figure 21. Also, above-barrier absorption, followed by relaxation populates the trapping well. For sizes less than a critical size of ~ 1.4 nm, the trapping edge is lower than the absorption edge, allowing strong transfer to the outer well[23]. Evidence for a potential barrier was demonstrated by manipulation of the material by metal and oxide coatings[24].

We now examine the prospect of gain. The initial gain coefficient [25] is $\gamma = \Delta N \lambda^2 \Delta \nu / (8\pi n^2 \tau)$ where $\Delta N = N_2 - N_1$ is the population inversion, n is the refractive index, $\Delta \nu$ is the emission width, λ is the emission wavelength, and τ is spontaneous lifetime. Measurements in the precursor colloid show several emission channels with life times of 1 ns, 5 ns, 10 to 15 ns, and ~ 100 microseconds, with most of the blue emission being in the 10 to 15 ns time scale. With near saturated absorption, followed by strong transfer to the outer well, we expect the density of the excited emitters to be nearly 25 percent of the atomic solid density ($\sim 1.5 \times 10^{22}$ / cm^3). We use $\tau = .01$ to 1 μ s, $\lambda = 400$ nm, $n = 2$, and $\Delta \nu = 100$ nm ($\sim 10^{14}$ Hz). With these parameters, $\gamma \sim 1.5 \times 10^3$ to 1.5×10^5 cm^{-1} . This gain allows considerable growth over microscopic distances. The number of spontaneous emission modes is

given by $p = 8\pi\Delta n^3 V / \lambda^2 c$ where V is the active volume. Using an active cross section of $(2\ \mu\text{m})^2$ and an active sample thickness of $0.2\ \mu\text{m}$, we get $p \sim 10^3$, sizable even for microscopic volume.

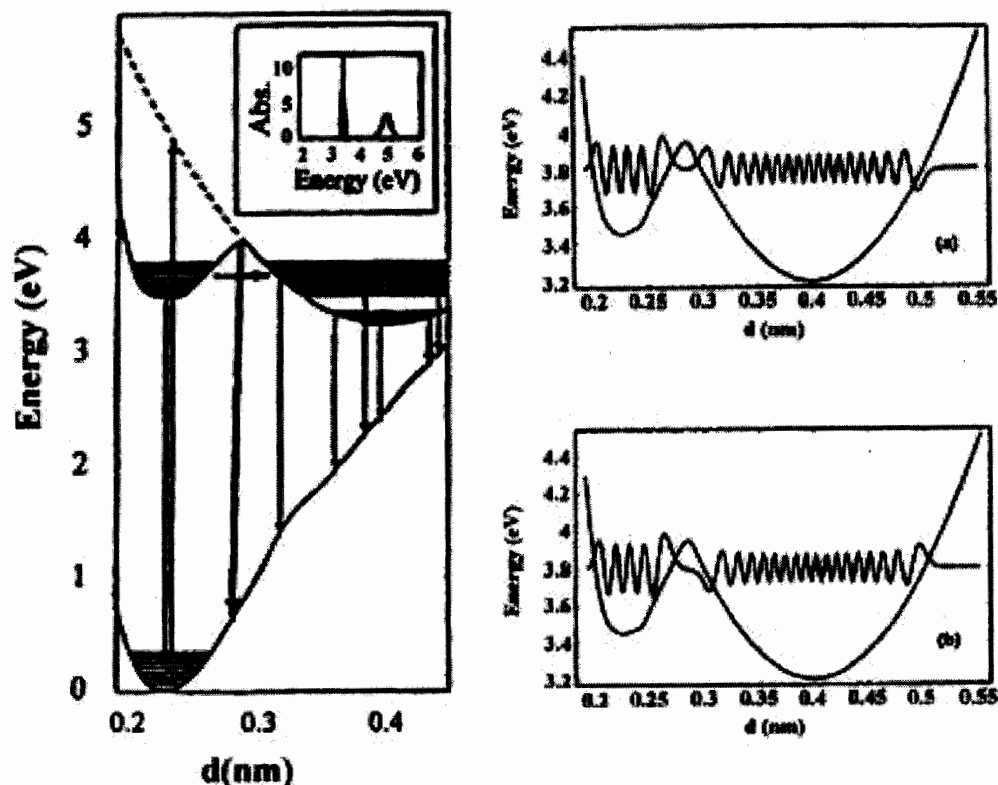


Figure 20. Interatomic potential of the dimers in 1.03 nm crystallites showing the ground and the first excited electronic states, along with the pathways for excitation and emission. The inset is the transition probability in absorption.

Figure 21. Double well vibrational wave function (8,33) in a 1.03 nm crystallite. (a) bonding and (b) antibonding.

The restructured Si-Si bonds provide anharmonicity and optical nonlinearity. To make an estimate, we expand the interatomic potential as a function of the bond length (Figure 20) about its minimum: $V(r) = ar^2 + D r^3$ where r is from the potential minimum. The fit gives $mD \sim 5.1 \times 10^{13}\ \text{V/m}^3$, where m is the mass of the electron. From D we can determine the frequency independent nonlinear optical coefficient $\delta = mD / 2e^3 N^2$ where N is the density of electrons that contribute to the polarization[25]. The polarization at the second harmonic is proportional to δ and to the susceptibilities at ω and 2ω : $P(2\omega) = 1/2 d^{(2\omega)} E_0^2 \cos 2\omega$, where $d^{(2\omega)} = \delta (\chi^{(\omega)})^2 \chi^{(2\omega)}$, and $\chi^{(\omega)}$ is the linear susceptibility at frequency ω . This gives $\delta \sim 7 \times 10^{13}$ for $N = 6 \times 10^{28} / \text{m}^3$. Note that the mean value of the parameter δ for 25 noncentrosymmetric crystals known for second harmonic generation is 2×10^9 . The blue peak (shifted by 10 nm from the second harmonic) suggests a higher order nonlinear coherent process such as stimulated anti-Stokes scattering[26]. We previously calculated 42 meV for

the vibrational spacing using a numerical matrix method[23]. For incident wavelength of ~ 780 nm, this would produce an anti-Stokes line at 759.4 nm, with a shift of 20.6 nm. Harmonic generation of the Raman shifted radiation gives 380 nm, with a shift of 10.3 nm.

CONCLUSION

We developed a process for converting bulk silicon into ultrasmall nanoparticles. The particles - which are about one billionth of a meter in diameter and contain 29 silicon atoms - can be formed into colloids, crystals, films, and collimated beams for unique applications in the electronics, optoelectronics and biomedical industries. We have observed some most unexpected and totally surprising phenomena. Unlike bulk Si, an optically inactive indirect gap material, ultrasmall Si nanoparticles are extremely active optically, exceeding the level of fluorescein, produce stimulated emission with blue collimated beams, and exhibit harmonic generation. The phenomenon occurs when a crystallite dimensions are brought down to one nanometer or less. In these particles, the atoms, especially the surface ones, get subjected to unbalanced forces, strong enough to reshape or re-engineer the molecular structure. Under these conditions, a new configuration or phase of Si, which otherwise is non-existent, forms.

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