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Observation of linear solid-solid phase transformation in silicon nanoparticles

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In bulk single-crystal silicon, the semiconducting diamond-to-metallic ß-Sn phase transformation nucleates on defects, and is manifested by a sharp uptake in light absorption at a threshold of ∼11 Gpa, accompanied with the creation of nanosized (20–50 nm) fragmentation domains. We report on the observation of linear uptakes in the absorption and in the luminescence and with insignificant spectral change in ultrasmall 1-nm Si particles. We associate the gradual absorption uptake and luminescence yield with silicon-metal transformation on the surface. The insignificant change in the spectral content of the luminescence points to surface stability for particles, which are smaller than the bulk fragmentation domain. First-principles atomistic calculations yield absorption behavior that exhibits gradual uptake followed by sharp uptake at ∼9–11 Gpa. The results point to the conclusion that two-dimensional surface-like phase transformations are manifested by linear uptake in absorption and luminescence.

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I. INTRODUCTION

Bulk single-crystal silicon exhibits pressure-induced phase transformation from the semiconducting diamond phase to the metallic ß-Sn phase. The newly transformed metallic phase nucleates on defects and is manifested by a sharp uptake in absorption at a threshold of ∼11 Gpa. The transformation is accompanied with the creation of nanosized fragmentation domains in the range of 20–50 nm.[1–4] The transformation may also be accompanied with shape and surface changes.

Studying pressure-induced transformation in the nanosize regime is interesting. Because interior defects in nanoparticles are fewer due to the spatial confinement, surface effects may be isolated from bulk pressure effects, providing an opportunity to study the nature of two-dimensional phase transformation.[1–12] Moreover, when the sample size is smaller than the fragmentation nanodomains, there is the potential of reduction of the effect of fragmentation or hysteresis. Nanoparticles are luminescent, which may provide additional means to monitor the phase transformation as well as surface changes. Nanosystems, on the other hand, produce wide overlapping scattering x-ray lines, limiting the usefulness of x-ray diffraction in monitoring of structural and surface changes. Moreover, ultrasmall particles exhibit significant surface reconstruction, consequently introducing a significant level of defects.[13,14] Thus, it is not clear what the interplay among bulk contribution, surface contribution, interior defects, surface defects, or surface reconstructed networking in nanoparticle phase transformation is.

In this paper, we study pressure-induced phase transformation in monodisperse 1-nm silicon particles—highly luminescent particles at the limit of size. The particle has only a single tetrahedral bulk unit with a ratio of surface to bulk atoms of 5 : 1. In addition, the particle is much smaller than the bulk fragmentation domains, eliminating fragmentation effects. Because they are etched from device-quality single-crystal wafers, the particles contain much fewer interior defects. We measured the absorption and luminescence of the particle under high pressure in the range up to 6 Gpa just below the pressure where solid-solid phase transition takes place. Our results show that, unlike bulk, which shows no uptakes in this range (exhibits a sharp uptake at a pressure of 11–12 Gpa) due to semiconductor-metal transformation, we observe gradual uptake with the absorption and luminescence. We carried out first-principles atomistic calculations using time-dependent density functional theory (TDDFT) of the excited states of the particle. We find that the absorption oscillator strength to the lowest band exhibits gradual uptakes, in agreement with the experiment. The results point to the conclusion that two-dimensional surface-like phase transformations are manifested by linear uptake in absorption and luminescence.

II. EXPERIMENTAL

The particles are produced by dispersion of (100) oriented, 1–10-ohm-cm resistivity, p-type boron-doped Si, by lateral anodization in hydrogen peroxide and HF acid.[15–22] Subsequent immersion in an ultrasound acetone or water bath dislodges the ultrasmall particles. When it is excited by a pulsed nanosecond radiation at 355 nm, blue emission is observed with the naked eye in room light. A graphite grid was dipped in the colloid. Direct imaging of the nanoparticles on the graphite grid was performed using transmission electron microscopy, as given in Fig. 1. The particles are nearly spherical with 1-nm diameter, with insignificant size or shape dispersion.[23] The particles exhibit several novel properties, including strong direct-like optical activity,[18,19] which enables detection of single particles,[15] gain and stimulated emission,[16,17] and nonlinear optical behavior, such as harmonic generation.[20] Electronically, electron affinity values drop to those characteristic of atoms and molecules, and single electron charging exceeds the thermal energy.[21] Mechanically, the particle exhibits breakage of bulk centrosymmetry, washing out of bulk-like phonons and emergence of molecular-like vibrations.[22] In its structural prototype, 24 Si atoms form a

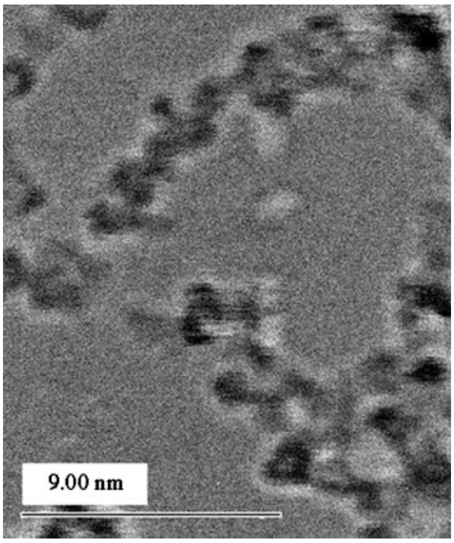

FIG. 1. High-resolution transmission electron microscopy (HTEM) image of the 1-nm silicon nanoparticles placed on a graphite grid.

network of reconstructed molecule-like Si-Si dimer species on the surface, with five atoms constituting a single unit of diamond-like tetrahedral bulk core ($Si_{29}H_{24}$).[24] The super molecule structure can also be considered as a 28-silicon atom fullerene cage with single-atom filler at the center of the cage.[25] The particles may be prepared with hydrogen, oxygen, or polymer termination.[23] The optical characteristics have been attributed to hydrogenated surface reconstructed molecule-like Si-Si network.[13,14]

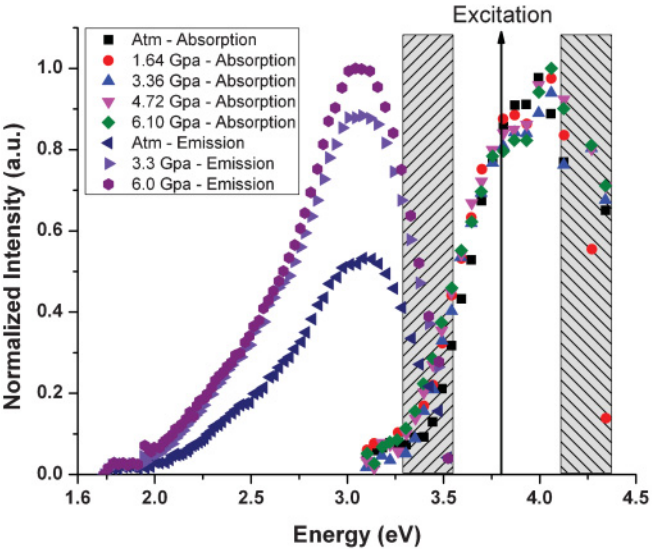

FIG. 2. (Color online) (Spectra on the right): The measured absorption as a function of the incident photon energy in the range 300–400 nm under several applied pressures: atmosphere, 1.64, 3.36, 4.72, and 6.10 Gpa (top five in the pressure list inset). (Spectra on the left): The figure gives the luminescence spectrum taken under incident excitation photon energy of wavelength of 325 nm (3.8 eV), at the three pressures: atmosphere, 3.3, and 6.0 Gpa (bottom three in the pressure list inset). The vertical arrow at 3.8 eV indicates the excitation photon energy used to generate the luminescence spectra on the left. The shaded energy region covering the range 3.29–3.55 indicates the range of the lowest excited band consisting of the three lowest calculated excited states (depicted in Fig. 5). The shaded energy region covering the range 4.1–4.39 eV indicates the range of the second excited band consisting of seven calculated excited states (depicted in Fig. 5).

High-pressure experiments were carried out on the nanoparticles using piston-cylinder-style diamond anvil cell.[26] The particles were dispersed in a PMMA matrix. Pressures were determined using standard ruby fluorescence techniques. The absorption measurements were performed with a xenon arc or tungsten-halogen light source, Kratos monochrometer, and a photomultiplier with photon counting. Fiber optics were used to direct the light from the monochrometer to the pressure cell

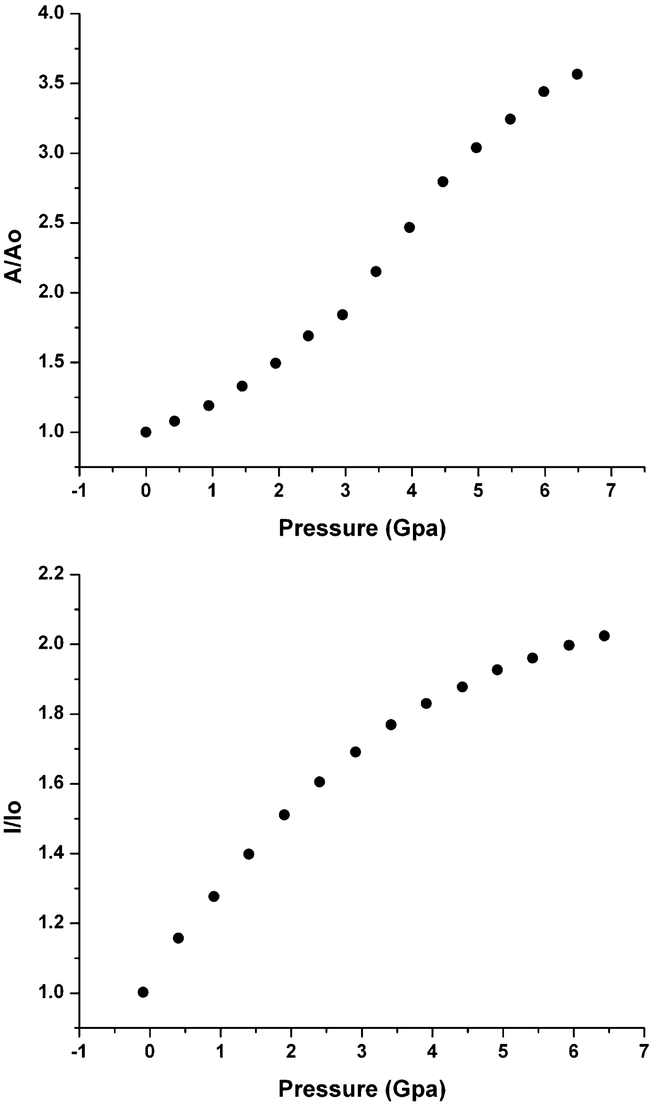

FIG. 3. (a) The measured absorption of the Si nanoparticles taken at a specific absorption photon energy at the low-energy wing of their absorption band (~3.35–3.37 eV) (red wing of the absorption band) as a function of pressure; (b) the peak of the luminescence intensity of the Si nanoparticles taken at the same photon energy of 3.8 eV as a function of pressure. The absorption and the luminescence results in (a) and (b) are normalized to their respective values at atmospheric pressure.

and from the cell to the detector. High-pressure emission data at 325 nm from a He-Cd laser were measured. Emission in the backward direction is directed to a monochrometer followed by single photon counting.

III. RESULTS

Figure 2 presents the absorption of the particles in PMMA as a function of the excitation photon energy in the range 370–286 nm or 3.35–4.34 eV under several values of pressure: atmosphere, 1.64, 3.36, 4.72, and 6.10 Gpa. The absorption band is seen to slightly blue shift and widen at higher pressure. Figure 2 also gives the luminescence spectrum under incident excitation of wavelength of 325 nm (3.8 eV), at the pressures: atmosphere, 3.36, and 6.10 Gpa. The luminescence is dominated by a strong blue/ultraviolet (UV) band. The spectrum has structureless weak red-orange tails. The broadening and the extended red tail in the emission are not homogeneous broadening resulting from a size distribution. Rather, it is inhomogeneous broadening due to the indirect nature of silicon.[19] The absorption at energy (3.35–3.37 eV) near the opening of the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gap is very useful for analysis since it involves the least number of excited states and impacts the luminescence in the visible more directly. Since the absorption approaches background levels in this region, we performed in this region more detailed measurements, which are shown in Fig. 3(a). It shows the absorption increasing gradually with pressure, increasing by a factor of ~3 over a pressure of 5 Gpa. The peak of the luminescence intensity with pressure shown in Fig. 3(b) rises linearly by more than twofold, saturating at 6 Gpa. As to the spectral distribution, we observe no significant change except for a slight blue shift of ~5 nm at the higher pressures. The observed gradual pressure dependence of the absorption and the luminescence is nonbulk-like. Bulk-like absorption stays unchanged until the applied pressure reaches the threshold where sharp uptake takes place.

IV. THEORETICAL

To elucidate the linear uptake, we carried out first-principles calculation to obtain the electronic structure, and hence the optical characteristics of the nanoparticles subjected to high pressure. The 1-nm particle is interesting in this regard because macroscopic amounts can be routinely produced in the laboratory. Second, the 1-nm $Si_{29}H_{24}$ is small enough to be amenable to calculations, and its prototype structure is known to allow *ab initio* calculation, which provides the opportunity for testing results against detailed theoretical predictions.[18,19,22,24] We employed time-dependent density functional theory (TDDFT) based atomistic simulations. We determined the Eigen energies, excitation energies, wave functions and excitation oscillator strength or cross section.

We used the position of atoms in normal vibration mode of the particle to model the pressure; the positions of atoms were obtained by starting from the equilibrium ground state and choosing a normal mode to follow. We calculate the vibration modes of the particle and determine the corresponding coordinates of atoms. We then calculate the pressure which would correspond to each position. Assuming elastic or harmonic contraction, the pressure exerted is just the rate of change of the total energy U with volume V, $P = -dU/dV$, or $P = -(U - U_0)/(V - V_0)$. Moreover, the bulk modulus (capital K) is related to the energy and volume by $K = -V(d^2U/dV^2)$, or simply by $K = -2(U - U_0)V/(V - V_0)^2$. We calculate five data points of compressions and fit the data to arrive at the same self-consistent K (for elastic or harmonic compressions). The lowest-energy normal vibration is a symmetric Td breathing mode, where the entire particle expands and contracts fairly uniformly as shown in Fig. 4. For each equilibrium position of atoms with the particle under compression, we calculate the electronic structure in the ground state using TDDFT. We also calculate, using TDDFT, parameters of the excited absorption state at the same atomic positions, meaning using vertical excitation with no subsequent relaxation. In other words, the excited states are calculated at the same configuration of the ground state, i.e. vertical excitation according to the

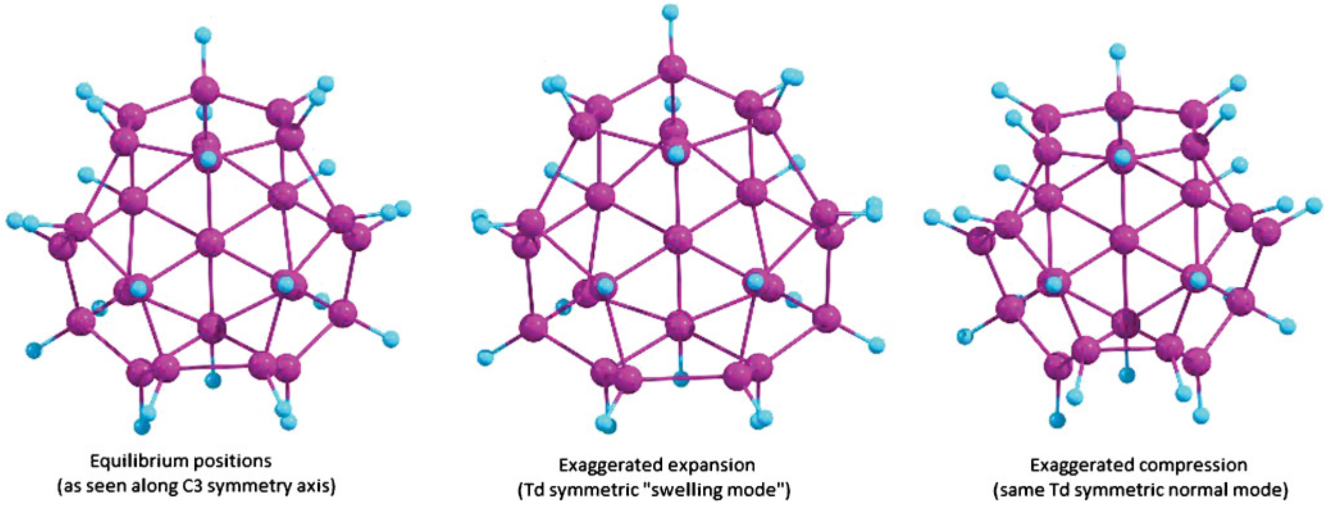

FIG. 4. (Color online) Prototype of hydrogenated 1-nm silicon nanoparticles ($Si_{29}H_{24}$) showing exaggerated stretched and compressed snapshots for the fully symmetric lowest energy tetrahedral vibration, silicon atoms (dark), hydrogen atoms (light).

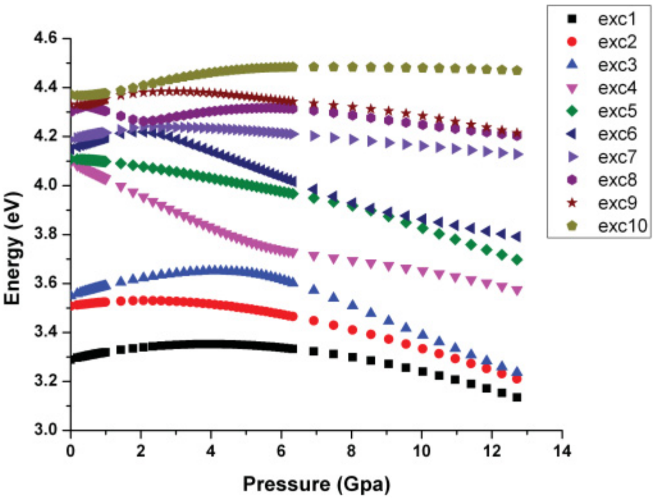

FIG. 5. (Color online) Calculated eigen energy of the lowest 10 excited states using a TDDFT formalism of 1-nm silicon nanoparticles in eV as a function of applied pressure in Gpa.

Born–Oppenheimer approximation, which freezes the nuclear coordinates.

Figure 5 presents the energy for the 10 lowest-lying discrete excited electronic states as a function of pressure. The lowest band of states consists of the three lowest allowed states; at atmospheric pressure they lie at ∼3.29, 3.5, and 3.55 eV above the ground state, which is taken at zero energy. The lowest state is associated with the LUMO. Over the pressure range accessible in the experiment, the LUMO state shifts to the blue side by 50–60 meV (or 5–6 nm). We marked (shaded) in Fig. 2 the range of the excitation energy associated with these states at atmospheric pressure. The next band of discrete excited states consists of seven allowed states, which lie in the range 4.1–4.39 eV at atmospheric pressure. The range of absorption into this band is marked (shaded) on Fig. 2, and they constitute the blue side of the absorption band. The overall extent of the 10 states slightly widens and blue shifts as the states fan out with pressure. The excitation at 325 nm (3.8 eV), which was used to excite the luminescence spectrum is marked on Fig. 2. At atmospheric pressure, it falls in the continuum region between the two sets of calculated discrete states.

Figure 6 presents the pressure dependence of the calculated oscillator strength of the transitions from the ground state to the lowest absorption band, consisting of the three low-lying excited states. The lowest two exhibit an uptake, but the highest state suffers quenching. Note for broadband excitation, the average oscillator strength in the band increases initially and saturates at ∼5–6 Gpa at a level nearly equal to twice the atmospheric pressure value, consistent with the measurements. The weak uptake at 9–11 is close to that of bulk uptake and may be associated with the inner tetrahedral unit in the core of the particle.

V. DISCUSSION

The linear pressure dependence is nonbulk-like. Bulk-like absorption exhibits a sharp uptake. Allen *et al.* and Nayfeh *et al.* suggested that absorption and emission take place on the surface by reconstructed Si-Si dimers.[13,14] These form because next nearest neighboring atoms move across a barrier at ∼ 3 Å from an interspacing of 5.4 to 2.3 Å to reconstruct. Absorption takes place on a dimer at 2.3 Å bond length followed by bond expansion, and emission takes place on the same dimer[13,14] at a range of an extended bond length of ∼3 Å, resulting in a down shift (Stokes shift), and broadband emission. Hence, absorption and emission are expected to display similar pressure dependence, as seen in the measurements. Since there is an insignificant change in the spectral content of the luminescence, we believe the electronic structure of the luminescent dimer network has not suffered significant change, pointing to no pressure-induced deformations, i.e. points to stability of the surface. This may be related to the fact that the particle is much smaller than bulk fragmentation domain. Previous measurements on 49-nm Si particles showed shape change which was reflected in a difference in domain size in the 001 (54.9 nm) and in the 100 (26.7 nm) direction.[5]

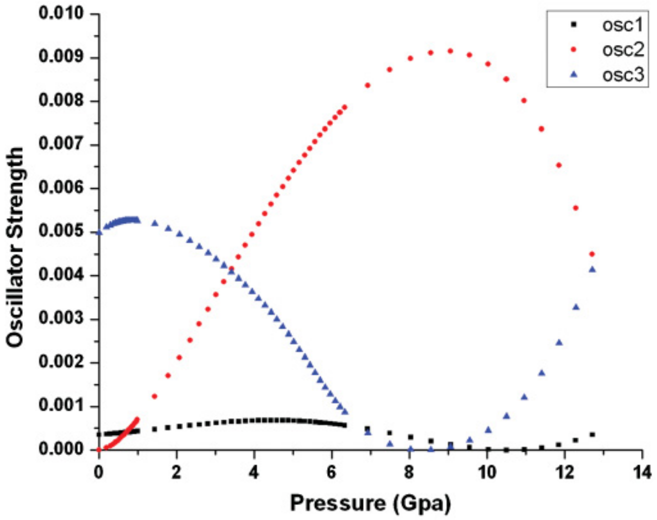

FIG. 6. (Color online) Calculated oscillator strengths using TDDFT formalism for absorption from the ground state to the three low-lying excited states shown in Fig. 5 as a function of applied pressure in Gpa. First excited state: square (black); second excited state: dot (red/dark gray); third excited state: triangle (blue/medium gray).

VI. CONCLUSION

In conclusion, high-pressure experiments in the range up to 6 Gpa were carried out on H-terminated Si nanoparticles of 1-nm diameter. We observed linear uptakes in absorption as well as in luminescence. This feature is unlike bulk, which exhibits no uptakes in this range and show sharp uptake at a pressure of 11-12 Gpa due to semiconductor-metal transformation. Atomistic calculations show that the absorption oscillator strength exhibits gradual uptake, consistent with the measurements. The calculated oscillator strength exhibit another regime of sharp uptake at ∼9–11 Gpa, which we associate with the bulk-like transformation in the core of the particle. We associate the gradual absorption uptake and luminescence at the lower pressure with silicon-metal transformation on the surface.

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[1] J. Jamieson, Science **139**, 762 (1993).

[2] J. Hu and I. Spain, Solid State Commun. **51**, 263 (1984).

[3] R. Wentorf and J. Kasper, Science **139**, 338 (1963).

[4] F. Bundy, J. Chem. Phys. **41**, 3809 (1964).

[5] S. H. Tolbert, A. B. Herhold, L. E. Brus, and A. P. Alivisatos, Phys. Rev. Lett. **76**, 4384 (1996).

[6] S. H. Tolbert and A. Alivisatos, J. Chem. Phys. **102**, 4642 (1995).

[7] R. Hanneman, M. Banus, and H. Gatos, J. Phys. Chem. Solids **25**, 293 (1964).

[8] U. D. Venkateswaran, L. J. Cui, B. A. Weinstein, and F. A. Chambers, Phys. Rev. B **45**, 9237 (1992).

[9] L. J. Cui, U. D. Venkateswaran, B. A. Weinstein, and F. A. Chambers, Phys. Rev. B **45**, 9248 (1992).

[10] S. Tolbert, Ph.D. thesis, University of California, Berkeley, 1995.

[11] K. Littau, P. Szajowski, A. Muller, A. Kortan, and L. Brus, J. Chem. Phys. **97**, 1224 (1993).

[12] W. Wilson, P. Szajowski, and L. Brus, Science **262**, 1242 (1993).

[13] G. Allan, C. Delerue, and M. Lannoo, Phys. Rev. Lett. **76**, 2961 (1996).

[14] M. H. Nayfeh, N. Rigakis, and Z. Yamani, Phys. Rev. B **56**, 2079 (1997).

[15] O. Akcakir, J. Therrien, G. Belomoin, N. Barry, E. Gratton, and M. Nayfeh, Appl. Phys. Lett. **76**, 1857 (2000).

[16] M. Nayfeh, O. Akcakir, J. Therrien, Z. Yamani, N. Barry, W. Yu, and E. Gratton, Appl. Phys. Lett. **75**, 4112 (1999).

[17] M. H. Nayfeh, N. Barry, J. Therrien, O. Akcakir, E. Gratton, and G. Belomoin, Appl. Phys. **78**, 1131 (2001).

[18] A. Smith, Z. H. Yamani, N. Roberts, J. Turner, S. R. Habbal, S. Granick, and M. H. Nayfeh, Phys. Rev. B **72**, 205307 (2005).

[19] S. Rao, J. Sutin, R. Clegg, E. Gratton, M. H. Nayfeh, S. Habbal, A. Tsolakidis, and R. M. Martin, Phys. Rev B **69**, 205319 (2004).

[20] M. H. Nayfeh, O. Akcakir, G. Belomoin, N. Barry, J. Therrien, and E. Gratton, Appl. Phys. Lett. **77**, 4086 (2000).

[21] O. Nayfeh, D. Antoniadis, K. Mantey, and M. H. Nayfeh, Appl. Phys. Lett. **90**, 153105 (2007).

[22] S. Rao, K. Mantey, J. Therrien, A. Smith, and M. Nayfeh, Phys. Rev B **76**, 155316 (2007).

[23] G. Belomoin, J. Therrien, and M. H. Nayfeh, Appl. Phys. Lett. **77**, 779 (2000); G. Belomoin, E. Rogozhina, J. Therrien, P. V. Braun, L. Abuhassan, M. H. Nayfeh, L. Wagner, and L. Mitas, Phys. Rev. B **65**, 193406 (2002).

[24] L. Mitas, J. Therrien, R. Twesten, G. Belomoin, and M. H. Nayfeh, Appl. Phys. Lett. **78**, 1918 (2001).

[25] E. W. Draeger, J. C. Grossman, A. J. Williamson, and G. Galli, Phys. Rev. Lett. **90**, 167402 (2003).

[26] G. Yang, Z. A. Dreger, Y. Li, and H. G. Drickamer, J. Phys. Chem. A **101**, 7948 (1997).