Breakdown of the k-conservation rule in $Si_{1-x}Ge_x$ alloy nanocrystals: Resonant photoluminescence study

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Resonant photoluminescence from $Si_{1-x}Ge_x$ alloy nanocrystals as small as 4 nm in diameter embedded in SiO_2 thin film matrices was studied. In pure Si nanocrystals, phonon structures were clearly observed, indicating that optical transitions are assisted by momentum-conserving phonons. These structures are quenched by adding a small amount of Ge atoms in Si nanocrystals, i.e., due to the formation of $Si_{1-x}Ge_x$ alloy. Furthermore, the lifetime of the radiative recombination became much faster in doped nanocrystals. These results suggest that $Si_{1-x}Ge_x$ alloy formation leads to a disorder in the translation invariance of the crystalline lattice, thus resulting in the breakdown of the k-conservation rule. © *2000 American Institute of Physics.* [S0021-8979(00)04223-7]

I. INTRODUCTION

Different systems containing nanometer-size Si crystals (nc-Si) have been intensively studied because they are believed to be promising materials for novel optical devices and offer a good model system to study zero-dimensional quantum size effects in indirect-gap semiconductors. A continuous shift of the photoluminescence (PL) peak from the band gap of bulk Si to the visible range has been observed with a decrease of the nc-Si size.[1] By applying a variety of optical methods such as resonant PL,[2,3] resonant two-photon excited PL,[4] PL hole burning[5] and magneto-optical spectroscopy,[6] the mechanism of the PL and the symmetry of absorbing (emitting) states have been studied in detail. These studies strongly suggest that the PL is due to recombination of excitons confined in zero-dimensional Si quantum dots.

The PL lifetime becomes shorter with an increase of the detection energy or decrease of the nc-Si size. This is caused by spatial confinement of an electron and a hole in a small volume. This confinement increases the uncertainty of their quasimomenta, thus allowing nonphonon (NP) optical transitions. The increase of the NP transition rate relative to the phonon-assisted one results in shortening of the lifetime. However, at room temperature, even for particles as small as a few nanometers in diameter, the PL lifetime is still in the range of tens of μs. This relatively long lifetime is a major disadvantage for optoelectronic applications of nc-Si. Therefore a new approach to shorten the radiative exciton lifetime further is highly desired.

Enhancement of the NP transition rate is observed for $Si_{1-x}Ge_x$ alloy crystals and quantum wells due to perturbations of the crystal periodicity from alloy fluctuations.[7] In a similar manner, the increase of the optical transition oscillator strength due to disorder-induced breakdown of the k-conservation rule has been predicted in Ref. 8 for $Si_{1-x}Ge_x$ alloy nanocrystals (nc-$Si_{1-x}Ge_x$). The PL lifetime of porous-$Si_{1-x}Ge_x$ is reported to be faster than that of porous Si.[9,10] Therefore, $Si_{1-x}Ge_x$ alloy formation is one of the promising methods for further improvement of the emission properties of nc-Si.

The PL properties of nc-$Si_{1-x}Ge_x$ are expected to be dependent on both the size and the Ge concentration. In the previous studies of porous $Si_{1-x}Ge_x$, the size of particles has not been evaluated.[9,10] Therefore, the band structure and the carrier recombination dynamics of nc-$Si_{1-x}Ge_x$ are still not fully understood. In Refs. 11 and 12, the possibility of preparing nc-$Si_{1-x}Ge_x$ by a cosputtering method has been shown. The size of particles has been measured by high-resolution transmission electron microscopy. With increasing Ge concentration a shift of the PL peak energy from the widened band gap of nc-Si to that of nc-Ge has been observed. This shift is accompanied by shortening of the PL lifetime. PL spectra under nonresonant excitation are very broad and featureless. This inhomogeneous broadening of the PL band is mainly caused by the nanocrystal size and shape variation. In this work, in order to lift the inhomogeneous broadening, PL spectra are measured under resonant excitation conditions: only the particles having excitation threshold at the near-infrared laser energy are selectively excited. In pure nc-Si, resonant PL spectroscopy is widely used to study the nearly homogeneous spectral shape and to determine the ratio of the NP to phonon-assisted transition as a function of confinement energy.[3] In this work the enhancement of the NP optical transition rate due to alloying is discussed. The conclusions are based on the results of resonant

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J. Appl. Phys., Vol. 88, No. 10, 15 November 2000

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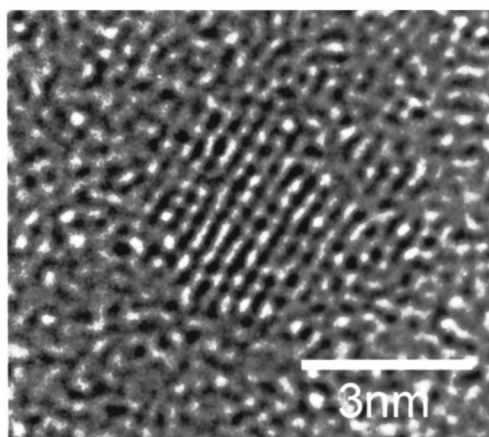
FIG. 1. Typical TEM image of nc-$Si_{0.73}Ge_{0.27}$.

FIG. 2. PL spectra of nc-$Si_{1-x}Ge_x$ at room temperature.

PL studies of pure nc-Si and nc-$Si_{1-x}Ge_x$ combined with the dependence of the PL lifetime on the Ge concentration.

## II. EXPERIMENT

$Si_{1-x}Ge_x$ nanocrystals were prepared by a cosputtering method. Details of the preparation procedure can be found elsewhere.[11,12] Si, Ge, and SiO_2 sputtering targets were simultaneously sputtered in Ar gas at 0.3 Pa using a multitarget sputtering apparatus. After deposition, the films were annealed in N_2 gas ambient at 1100 °C to grow nc-$Si_{1-x}Ge_x$ in SiO_2 matrices. To determine the size and the shape of particles, a cross-sectional image of samples was monitored with a transmission electron microscope (TEM). The samples for TEM observations were prepared by a standard procedure including mechanical and Ar ion thinning techniques. The TEM observations were made using a JEM-2010(JEOL) electron microscope operated at 200 kV.

Nonresonant PL was excited by the 488 nm line of an Ar ion laser and detected with a single monochromator equipped with a Ge *pin* diode. For resonant PL measurements, a Ti:sapphire laser was used for excitation. The spectral shape of the PL was detected using a monochromator combined with a Si charge coupled device (CCD) array. To suppress stray laser light, the asynchronous mechanical chopping technique was applied.[3] The resonant PL measurements were done at 4.2 K. All spectra were corrected to the sensitivity of the detection system. Time resolved PL measurements were performed with a fast (4 ns rise–fall time) photomultiplier and a digital oscilloscope. The samples were mounted in a cryostat operated in the temperature range from 1.5 to 300 K and the PL was excited by the 488 nm line of an Ar ion laser.

III. RESULTS

Figure 1 shows a typical cross-sectional transmission electron micrograph of a particle (about 3 nm in diameter) embedded in amorphous SiO_2 matrix. The spacing of the lattice fringes is 0.321 nm, which is between those of the {111} planes of Si (0.314 nm) and Ge (0.327 nm) bulk crystals. This is evidence that nc-$Si_{1-x}Ge_x$ is formed.
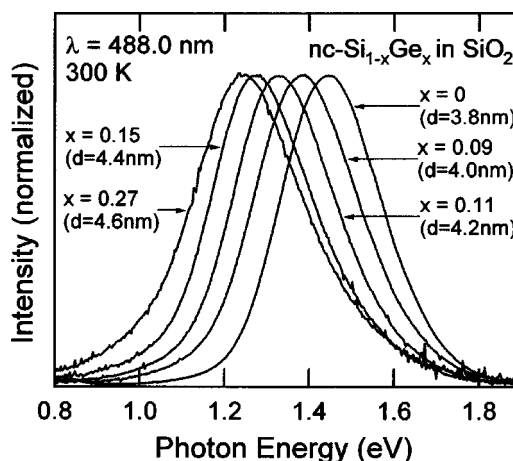
The nonresonant PL spectra of nc-$Si_{1-x}Ge_x$ with various Ge contents are shown in Fig. 2. Pure nc-Si (3.8 nm in diameter) has a PL peak at 1.45 eV. As the Ge content increases, the PL peak shifts to lower energies and reaches 1.24 eV for the sample with $x=0.27$. Although the size of nc-$Si_{1-x}Ge_x$ slightly increases with the Ge content (from 3.8 to 4.6 nm), the observed shift seems to be governed by $Si_{1-x}Ge_x$ alloy formation. For pure nc-Si a size variation from 3.8 to 4.6 nm results in the shift of the PL peak on the order of 50 meV.[13,14] This value is much smaller than the experimentally observed one (~ 200 meV). The spectral shape is almost identical for all samples, although the PL bandwidth increases for those having larger values of x.

Under nonresonant excitation no distinct PL features are observed and the full width at half maximum (FWHM) of the PL bands is about 250 meV (see Fig. 2). The large FWHM is due to inhomogeneous broadening. The standard method to lift this broadening is the resonant excitation mentioned before. Figure 3(a) shows the normalized resonant PL spectra of pure nc-Si at different excitation energies. The energy positions of the exciting light are shown by arrows. When the excitation is moved into the nonresonant PL band, distinct features appear in the spectra. This PL structure becomes more pronounced when the excitation energy is at the low-energy tail of the nonresonant PL band. For clarity the first derivative of the spectrum excited at 1.46 eV is shown in Fig. 3(b). From the energy separation of these PL features they can be assigned to optical transitions involving 1TA, 1TO, TO+TA and 2TO momentum-conserving phonons in absorption/emission cycle.

Figure 4 shows the resonant PL spectra of nc-$Si_{0.89}Ge_{0.11}$. As the excitation energy moves into the nonresonant PL band and approaches its maximum an ill-defined structure is observed. Even in the first derivative of the PL spectrum excited at 1.4 eV [Fig. 4(b)] only one peak is clearly distinguishable. This peak corresponds to the energy of the transverse optical (TO) momentum-conserving phonon of Si. In pure nc-Si, the phonon structure becomes more pronounced if the excitation energy is below the maximum of the nonresonant PL. On the contrary, for nc-$Si_{1-x}Ge_x$, the phonon structure is completely smeared
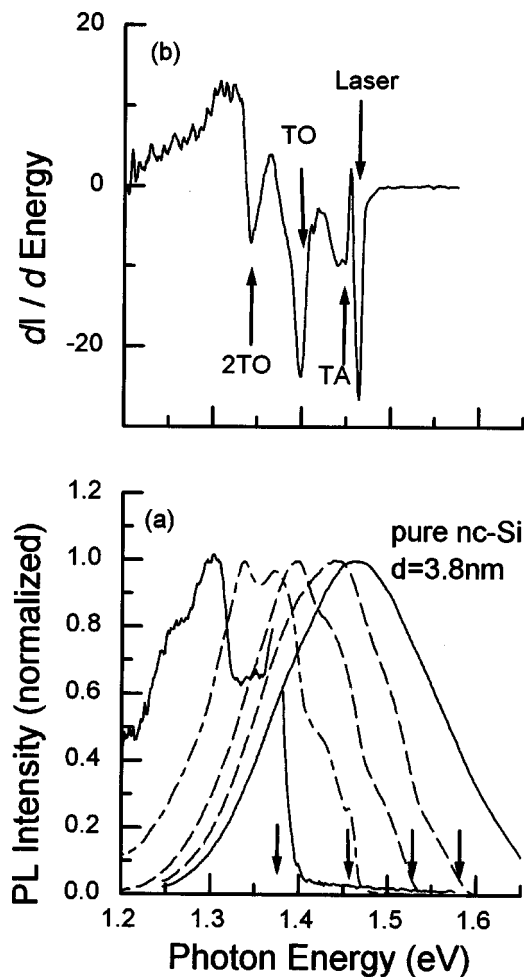
FIG. 3. (a) Normalized resonant PL spectra of pure nc-Si. Excitation energies are indicated by arrows. $T = 4.2$ K. (b) The first derivative of the spectrum excited at 1.46 eV. Phonon related structures are clearly seen.

FIG. 4. (a) Normalized resonant PL spectra of nc-Si$_{0.89}$Ge$_{0.11}$. Excitation energies are indicated by arrows. $T = 4.2$ K. (b) The first derivative of the spectrum excited at 1.40 eV.

out when the excitation energy is at the low-energy tail of the nonresonant PL. Very similar excitation energy dependence was observed for all samples with different Ge concentrations $(0.09 \leqslant x \leqslant 0.27)$.

Figure 5 shows the PL decay time at various detection energies for pure nc-Si and nc-Si$_{1-x}$Ge$_x$. In bulk crystals, the measured PL decay time (τ_{meas}) is defined by the relative strength of radiative (τ_r) and nonradiative (τ_{nr}) transitions: $\tau_{\text{meas}}^{-1} = \tau_r^{-1} + \tau_{nr}^{-1}$, where both times can be affected by the temperature. The quantum yield (η) is defined as $\eta = \tau_{nr}/(\tau_r + \tau_{nr})$. Under the assumption that the contribution of the nonradiative transition is negligible at low temperatures, the temperature dependences of τ_r and τ_{nr} are extracted from $\tau_{\text{meas}}(T)$ and $\eta(T)$.[15] From the observed temperature dependences of the PL lifetime and the intensity, it was found that, at temperatures below 150 K, $\tau_{\text{meas}} \approx \tau_r$, and above 150 K, the contribution of the nonradiative recombination is non-negligible. Therefore only lifetime values measured below 150 K have been taken into account since in this range the lifetime can be regarded as a radiative one.

The radiative lifetime becomes shorter as the Ge concentration increases (Fig. 5). As was mentioned before, the size of the particles increases slightly as the Ge concentration increases. This should lead to opposite lifetime behavior.
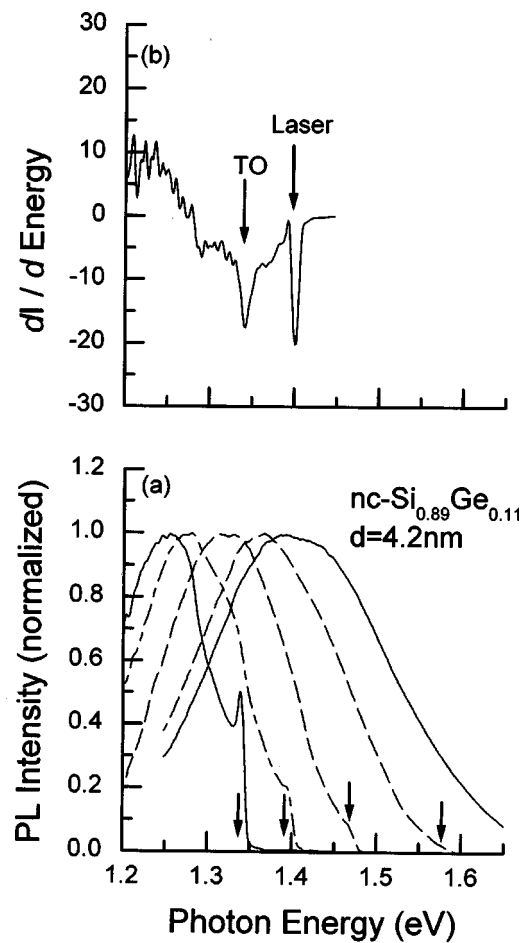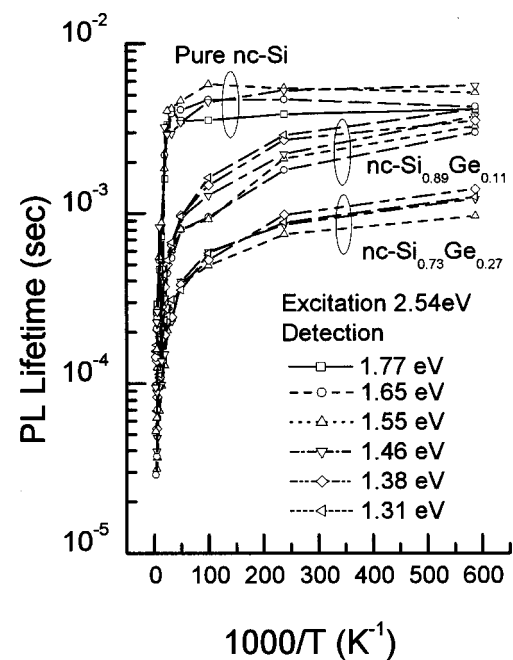

FIG. 5. Temperature dependence of the PL decay time detected at various energies for nc-Si, nc-Si$_{0.89}$Ge$_{0.11}$ and nc-Si$_{0.73}$Ge$_{0.27}$.

Therefore, the observed shortening of the lifetime is not a size effect but a result of Ge doping. The radiative lifetime of nc-$Si_{0.73}Ge_{0.27}$ is about five times shorter than that of pure nc-Si. Delerue *et al.*[8] calculated the band gap energy and recombination rate of a hydrogen-passivated $Si_{0.8}Ge_{0.2}$ particle. They demonstrated that the radiative efficiency of nc-$Si_{0.8}Ge_{0.2}$ increases by a factor of 5 compared to that of pure nc-Si. This value is in agreement with that observed in this work.

IV. DISCUSSION

The band gap energy of bulk $Si_{1-x}Ge_x$ alloys changes from that of Si to Ge depending on x. Si has conduction band minima in the vicinity of the X points of the Brillouin zone (Δ minima), while Ge has minima at the L points. The dependences of the band gap energy at Δ minima and at the L point on the Ge concentration are quite different. Thus, the band structure strongly depends on the Ge content. The band structure of $Si_{1-x}Ge_x$ is known to be Si like up to a Ge concentration of about 85%. The Δ minima have the lowest energy for bulk $Si_{1-x}Ge_x$ with low Ge concentration, and the crossover between Δ and L minima occurs at the aforementioned Ge concentration. In bulk $Si_{1-x}Ge_x$ alloy crystals and quantum wells with small x, PL peaks corresponding to the momentum-conserving TO phonons of Ge–Ge, Si–Ge and Si–Si vibrations at Δ minima were observed.[7,16] Similarly, since the highest Ge concentration in the samples used is about 0.3, the band structure is expected to be Si like. Thus phonons corresponding to Ge–Ge, Si–Ge and Si–Si vibrations at Δ minima are expected to be involved in the optical transitions.

However, as shown in Fig. 4, only an ill-defined structure is present under excitation near to the maximum of the nonresonant PL band. This structure can be assigned to TO phonons of Si. Furthermore, with a further decrease of the excitation energy, the structure is smeared out. No phonon structures corresponding to a $Si_{1-x}Ge_x$ alloy have been observed.

The smearing of the phonon structures which is possibly due to the breakdown of the k-conservation rule (caused by Ge doping) is also consistent with shortening of the radiative lifetime (Fig. 5). In Ref. 3 the ratio of NP to phonon-assisted transitions for porous-Si and oxidized nc-Si has been estimated. It was found that NP transitions become dominant as the nc-Si size decreases. Furthermore, for the same confinement energy, NP transitions are about three times stronger in nc-Si with a SiO_2 shell. In the samples studied, Ge doping is considered to further break the momentum-conservation rule due to perturbation in the lattice periodicity by Ge atoms. The enhancement of NP processes leads to smearing of the phonon-related features and shortening of the lifetime. By applying the method used in Ref. 3, the ratio of the NP to phonon-assisted transitions can be estimated from the resonant PL spectra if the phonon structures are clearly observed. However, the phonon structure observed for nc-$Si_{1-x}Ge_x$ is ill defined, and quantitative discussion of the ratio is not possible.

Another possible mechanism which can make the observation of the phonon structure difficult is the distribution of the Ge concentration. Besides the size and the shape distribution of nc-Si, particles are expected to have a varying Ge content as well. Therefore, at a certain excitation energy, particles with smaller size and higher Ge concentration are simultaneously excited with those having larger size and lower Ge concentration. Since the relative strength of Ge–Ge, Si–Ge and Si–Si vibrations as well as the vibration energies depend on the Ge concentration, its distribution results in smearing of the phonon structures.

The presence of the Si TO-phonon replicas under excitation at relatively high energy [1.4 eV, Fig. 4(b)] supports the existence of a Ge concentration distribution. Particles with low Ge concentration (or pure nc-Si) are expected to have, on average, larger band gaps and can be excited resonantly at a certain excitation energy. Since the number of such particles is small, as confirmed by Raman spectroscopy and electron diffraction studies,[12] the PL structure is ill defined.

The Ge concentration distribution also affects the temperature dependence of the PL lifetime (Fig. 5). In pure nc-Si, the temperature dependence of the PL lifetime can be fitted well within the framework of the model proposed by Calcott *et al.*[2] This model considers the ground exciton state as the spin singlet and the spin triplet states with the triplet one being the amount of Δ lower in energy.[2] At low temperatures, the PL originates from the triplet exciton, while at high temperatures the PL is dominated by recombination of the thermally occupied singlet exciton state. From the fitting procedure, the lifetimes of the triplet (τ_T) and the singlet (τ_S) states and Δ are estimated to be 4.7 ms, 71 μs and 5.8 meV, respectively, at the detection energy of 1.46 eV. The value of Δ obtained is slightly larger than that measured for porous Si at the same detection energy. The difference between these two systems of Si nanoparticles in surface termination may result in a small difference in the value of Δ.[3]

In pure nc-Si, the transition from slow to fast lifetime takes place at 10–20 K and is abrupt. On the contrary, in nc-$Si_{1-x}Ge_x$, the transition starts at lower temperatures and is gradual. In general, this would indicate a smaller value of Δ. However, no combination of all three parameters can reproduce the observed temperature dependence as well as for nc-Si. The gradual transition thus does not imply a smaller value of Δ. To our mind the gradual transition may be explained by a Ge concentration distribution. Due to the distribution, particles with different sizes can contribute to the PL at the same detection energy. The size distribution is accompanied by the distribution of Δ, thus making the slow-to-fast lifetime transition gradual.

V. CONCLUSION

Addition of a small amount of Ge to Si nanocrystals is found to smear the phonon structures in their resonant PL spectra. This result and shortening of the radiative lifetime of the PL suggest that the lattice periodicity of nc-Si is lifted due to alloying. This results in the breakdown of the k-conservation rule and enhancement of the optical transition oscillator strength.

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