Excitation Energies and Radiative Lifetimes of $Ge_{1-x}Si_x$ Nanocrystals: Alloying Versus Confinement Effects

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The composition dependence of the optical and structural properties of $Ge_{1-x}Si_x$ nanocrystals is investigated by means of *ab initio* total-energy and electronic-structure calculations. A trimodal distribution of the Ge-Ge, Ge-Si, and Si-Si bond lengths is found. The pair-excitation energies and the Stokes shift are calculated taking into account many-body and alloying effects. They show a distinct nonlinear behavior with changing composition. The radiative lifetime decreases exponentially with increasing Ge molar fraction. The theoretical results explain recent photoluminescence measurements. They show that composition and confinement effects can be discussed nearly separately.

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Since the observation of efficient visible photoluminescence (PL) from porous Si [1], Si and Ge nanostructures have been studied extensively because of their potential for Si-based optoelectronics. Quantum-confinement effects allow one to overcome the limitations of the indirect-gap semiconductors for photoelectric applications. Even optical gain has been demonstrated [2]. PL due to quantum-confined excitons remains one of the highly interesting aspects [3,4]. A high-energy shift of the PL peak and an increase in the PL intensity with decreasing size of Si crystallites have commonly been observed in the near-infrared (NIR) to red region [5–7]. For Ge crystallites, a clear size dependence of PL in the NIR has been observed only recently [8].

The optical properties of alloy nanocrystals depend on the composition x as well as on the particle size. This has been demonstrated by studies of nanometer-sized $Ge_{1-x}Si_x$ quantum dots in mesoporous silica [9] or in an amorphous SiO_2 matrix [10]. One observes a redshift of the PL peak with increasing Ge content. At the same time, the radiative lifetime decreases dramatically. The peak shift may be related to the nearly linear composition variation of the interband transitions in bulk $Ge_{1-x}Si_x$ crystals [11]. However, the substantial shortening of the exciton lifetime needs a deeper understanding. In general, both properties are influenced by the unknown interplay of confinement and alloying effects.

The goal of the present Letter is to explain the composition dependence of the PL for nanometer-sized $Ge_{1-x}Si_x$ dots. To this end, electron-hole pair-excitation energies and radiative lifetimes are studied for nanocrystals with relaxed geometries. The parameter-free calculations are based on density-functional theory (DFT) within the local-density approximation (LDA) [12], using non-norm-conserving pseudopotentials [13]. The electron-electron interaction is described within the parametrization of Perdew and Zunger [14]. Simple-cubic supercells corresponding to 216 atoms of bulk material are used with a plane-wave expansion of the eigenfunctions. Bulk calculations yield lattice constants of $a = 5.647$ Å (Ge) and $a = 5.404$ Å (Si). All-electron wave functions and matrix elements of the optical transition operator are calculated within the projector-augmented wave (PAW) method [15,16].

Spherical $Ge_{1-x}Si_x$ nanocrystals are constructed by starting from one atom and adding its nearest neighbors, thereby assuming tetrahedral coordination. Continuing in this manner, one obtains nearly spherical crystallites. Hydrogen atoms saturate the outer bonds. Alloying is introduced by randomly replacing Ge atoms by Si. Ionic relaxation is carried out both for the ground state and the excited state. The majority of the calculations have been performed for crystallites with 83 group-IV atoms and a diameter of about 1.5 nm. These are large enough to exhibit the characteristic features of a nanocrystal [16] but are still feasible for *ab initio* ionic relaxation.

We have studied nanocrystals with 16 Si and 67 Ge atoms for about ten different atomic configurations. Those with nearly uniformly distributed atoms possess the lowest total energies and nearly equal excitation energies. Nanocrystals with deliberately clustered Si atoms and, hence, rather different excitation energies give rise to total energies deviating by up to 10 eV from the average. According to the quasichemical approximation [17], their probability of occurrence is small. Consequently, the configurational average has been replaced by the study of one nanocrystal with nearly uniformly distributed Si and Ge atoms for each composition x.

Ten test calculations have been performed for smaller crystallites of 41 atoms, for each of the two compositions $x = 0.29$ and $x = 0.73$. The variations of the pair-excitation energies are small; we find ratios of $\Delta\varepsilon_{ex}/\bar{\varepsilon}_{ex} = 0.0065$ and 0.02 for the two compositions, $\Delta\varepsilon_{ex}$ being the standard deviation from the mean value $\bar{\varepsilon}_{ex}$. The variations for excited nanocrystals are somewhat larger. The radiative lifetimes are much more sensitive to changes in the atomic configuration. We find variations of $\Delta\tau/\bar{\tau} = 0.55$ and 0.70 for the ground state. For larger crystallites they will be smaller. The variations are largest near the pure ends of the composition spectrum, for the situation there is better characterized as a few impurities inside a Ge or Si crystallite than as an alloy.

The average lengths of the Ge-Ge, Ge-Si, and Si-Si bonds are shown in Fig. 1 and compared with the averages of all bonds. The trimodal distribution of the average lengths of the chemically different bonds is similar to that observed for bulk crystalline and amorphized $Ge_{1-x}Si_x$ alloys [18]. Besides the ground state, also an excited state with one electron-hole pair is studied. Optical excitation does not change the symmetry significantly within our static relaxation approach. The Ge(Si)-dominated bonds are slightly increased (decreased) with respect to the ground-state values. The opposite direction of the effect is apparently a consequence of the different symmetry of the wave functions of the electrons in the excited pairs, as it is known for bulk Ge and Si. The Ge-Ge, Ge-Si, and Si-Si bond lengths are nearly independent of the composition, corresponding to roughly the sum of the respective covalent radii. As in the bulk case, the alloy nanocrystals are closer to the Bragg-Pauling limit than to the Vegard limit [18]. However, the average bond lengths are smaller than the corresponding lengths in the bulk systems. Similar effects have been found experimentally [19,20]. The average over the three types of bonds roughly follows Vegard's rule with respect to the reduced Ge-Ge and Si-Si bond lengths.

For systems with spatial confinement, i.e., with free-exciton radii larger than or of the order of their spatial extent, the lowest pair-excitation energies ε_{ex} can be rigorously expressed in terms of DFT-LDA total energies [21]. Usually one uses $\varepsilon_{ex} = E(N+1) + E(N-1) - 2E(N)$ with the ground-state energies of the $N+1$, $N-1$, and N electron system. However, in this energy the effect of the attractive screened Coulomb interaction of the excited electron and hole is missing. In order to account for the excitonic effect, we use $\varepsilon_{ex} = E(N, e\text{-}h) - E(N)$. The first total energy is calculated with the constraint that the highest occupied single-particle state of the ground-state system contains a hole, placing the corresponding electron automatically into the lowest unoccupied single-particle state of the ground-state system. When the geometry of the alloy nanocrystal is fixed at that of the ground state, pair-excitation energies ε_{ex}^A arise that should define the optical absorption edges. We also relax the nanocrystal with an excited electron-hole pair present. At the resulting geometry, the lowest emission energy ε_{ex}^E is calculated. It has to be identified with the peak position of a PL experiment under low-excitation conditions. The difference of the two energies $(\varepsilon_{ex}^A - \varepsilon_{ex}^E)$ defines the Stokes shift which is due to the lattice relaxation after excitation.

Results for the two types of pair energies are plotted in Fig. 2. As expected, the variations are rather large near the pure ends of the composition spectrum. The composition dependence of the energy ε_{ex}^A of the ground-state geometry shows an S-shaped behavior resembling the familiar gap variation of bulk $Ge_{1-x}Si_x$ [17]. We interpret this fact as an indication that the confinement does not interfere strongly with the alloying effects. Comparison with the known bulk behavior shows that, despite the confinement and, hence, uncertain **k** vectors, the character of the indirect ΓX gap on the Si-rich side and the mixed character of the indirect ΓL and ΓΓ gap for small Si molar fractions persist, as well as a gap crossing near $x = 0.3$ [11]. The difference between the pair-excitation energies of Ge and Si is smaller than

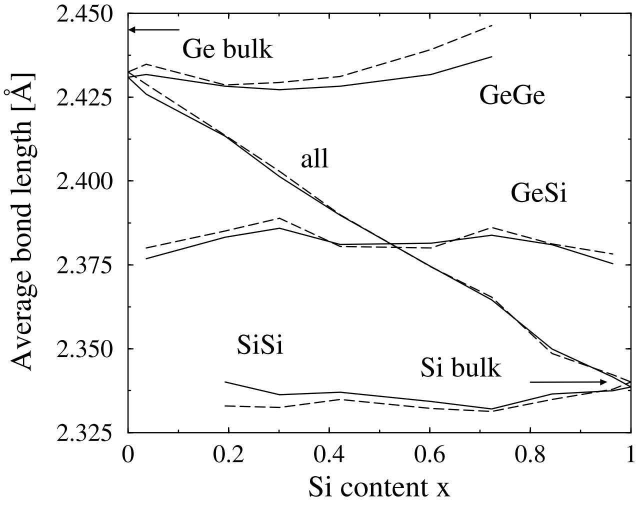

FIG. 1. Average bond lengths in relaxed $Ge_{1-x}Si_x$ crystallites. Solid lines: ground state; dashed lines: excited nanocrystal with one electron-hole pair. The arrows indicate the bond lengths in bulk Ge and Si.

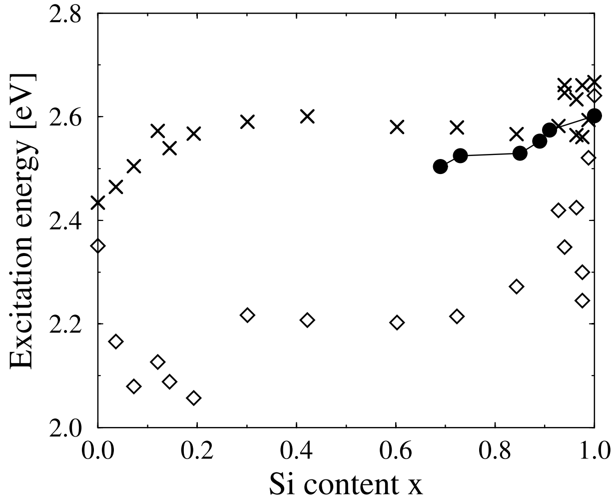

FIG. 2. Lowest electron-hole pair excitation energies calculated for the ground-state geometry (crosses) and the geometry of the excited state (squares) as well as the rescaled experimental PL peak energies [10] (filled circles).

the difference of the bulk gaps, which is related to the bond-lengths reduction. Unlike for ε_{ex}^{A}, the composition dependence of ε_{ex}^{E} for the excited-state geometries is nonmonotonous. The Stokes shift is very small for the Si and the Ge crystallites. However, it increases considerably to a nearly constant value of about 0.4 eV for nanocrystals with a composition $x = 0.3, \ldots, 0.8$. This is obviously a consequence of the much stronger pair-induced lattice relaxations possible in the alloy nanocrystals. Below $x = 0.3$, the excited-state excitation energies ε_{ex}^{E} are even lower than the nearly constant value between $x = 0.3, \ldots, 0.8$. Since in bulk $\mathrm{Ge}_{1-x}\mathrm{Si}_x$ the change from a Ge-like gap to a Si-like situation occurs at about $x = 0.3$, we conjecture that the reason for this behavior is a change in the gap character as well.

The calculated pair energies in Fig. 2 can be compared with values measured in absorption or emission spectroscopies. The value 2.65 eV for the Si nanocrystal with a 1.47 nm diameter is close to the value predicted for unoxidized crystallites but is larger than those measured in the presence of Si═O bonds [22]. The peak energy of about 2.3 eV calculated for the Ge nanocrystal seems to slightly overestimate the measured PL position [8]. Composition-dependent PL studies have been done only for $\mathrm{Ge}_{1-x}\mathrm{Si}_x$ nanocrystals with average diameters between 3.8 and 4.7 nm [10]. The presence of oxygen is not expected to alter the results in this size range [22,23]. In order to compare with experiment, the PL positions have been rescaled using the approximate $1/D$ variation of the excitation energies with the diameter D found for both Ge and Si [16]. The rescaled experimental values agree well with the ground-state excitation energies ε_{ex}^{A}, rather than with the excited-state-geometry excitation energies ε_{ex}^{E} because of the strong size dependence of the Stokes shift. While it is appreciable for our crystallites, it should already be negligible for the measured samples. Several arguments can be given to explain the remaining small discrepancies: the validity of the assumed $1/D$ scaling law, the definition of the PL excitation energy in an alloy, and the experimental determination of the nanocrystal diameter. The good agreement of the calculated energies and the rescaled measured PL positions, however, indicates that the effects of composition and size are nearly independent. The measured redshift of the PL energy with the Ge content indeed reflects the gap narrowing by alloying [10].

The PL is governed by the radiative recombination rate or its inverse, the radiative lifetime τ. We use an expression for τ which assumes completely thermalized distributions of the excited electron-hole pairs [24]. The results are plotted in Fig. 3 for various compositions and room temperature. The calculated values are compared with those measured for nanocrystallites with $x = 0.0, \ldots, 0.3$ and diameters between 3.8 and 4.7 nm [10]. In order to approximately separate the composition dependence from the size dependence, the values are normalized to that of the Si crystallite.

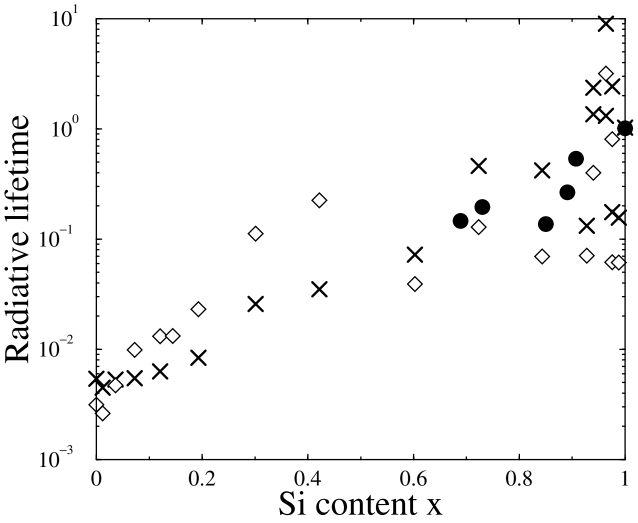

FIG. 3. Relative radiative lifetime vs composition for the ground (crosses) and the excited (diamonds) state. The values are normalized to those of the pure Si nanocrystals. The experimental values (filled circles) have been measured for larger nanocrystals. [10]

As mentioned above, the variations are rather large. Nonetheless, a roughly exponential behavior can be observed. The lifetime is longest for pure Si crystallites, reflecting the main contribution of bulk indirect-gap states to the optical transitions near the absorption edge. Consequently, with increasing Ge molar fraction the radiative lifetimes decrease strongly. The main reason is of intrinsic nature. Strong optical transitions corresponding to the allowed direct E_0 transitions in Ge crystals mix in and, hence, open strong radiative decay channels. The agreement with the experimental results is good despite the larger radii of the measured samples. As the radiative lifetime is strongly size dependent, this is another indication that the size effect and the effect of the alloying act independently, at least in the range of Si molar fractions between $x = 0.0$ and 0.3. Takeoka *et al.* [10] conjecture that the decrease in the PL lifetime is caused by either an increasing density of defects or by the Ge-Si alloying. The agreement with our results indicates that the alloying is the dominating effect. Nonetheless, additional effects have to be discussed. The ratio of the lifetimes of Ge and Si is strongly size dependent for diameters between 5 and 25 Å. The end points of the lifetime curve are expected to be further apart for bigger crystallites, making the curve steeper. On the other hand, a constant background of defect recombinations would render it less steep. Besides, an x-dependent defect density would lead to unpredictable results.

The spectrally resolved effect of the alloying is demonstrated in Fig. 4, where the oscillator strengths are plotted against the DFT-LDA transition energies. The

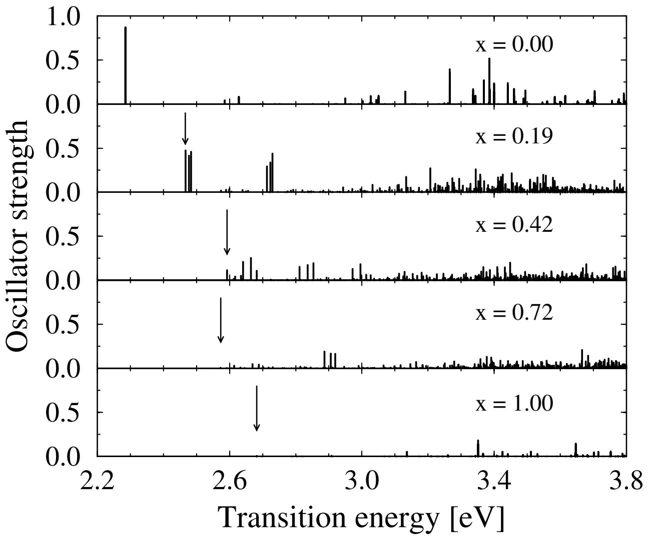

FIG. 4. Oscillator strength vs transition energy nanocrystals with different compositions. The arrows indicate the HOMO-LUMO gap (highest occupied molecular orbital-lowest unoccupied molecular orbital).

very strong lowest optical transitions of the pure Ge nanocrystal become weaker when Si is inserted. Moreover, the threefold degeneracy of the lowest transition is lifted. The strong reduction of the oscillator strengths at the emission edge explains the reduction of the lifetimes.

In conclusion, apart from the structural investigations of the bond lengths, we have determined the composition dependences of the excitation energies and the radiative lifetimes of $Ge_{1-x}Si_x$ nanocrystals. The average bond lengths show a trimodal distribution similar to the bulk case. However, they are shortened. The pair-excitation energies have been calculated taking into account both self-energy and excitonic effects. The scaling of the excitation energy with the diameter and the comparison of radiative lifetimes have been used to demonstrate that the size effect and the alloying act nearly independently. The dramatic decrease of the lifetime with increasing Ge content has been shown to be mainly of intrinsic nature. The increasing number of defects in the alloys, mentioned in Ref. [10], should be of minor influence.

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