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Resonant Raman scattering of discrete hole states in self-assembled Si/Ge quantum dots

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Abstract

We report the first resonant electronic Raman spectroscopy study of discrete electronic transitions within small p-doped self-assembled Si/Ge quantum dots (QDs). A heavy hole (hh) to light hole (lh) Raman transition with a dispersionless energy of 105 meV and a resonance energy of the hh states to virtually localised electrons at the direct band gap of 2.5 eV are observed. The hh–lh transition energy shifts to lower values with increasing annealing temperature due to significant intermixing of Si and Ge in the QDs. Structural parameters of the small Si/Ge dots have been determined and introduced into 6-band k · p valence band structure calculations. Both the value of the electronic Raman transition of localised holes as well as the resonance energy at the E_0 gap are in excellent agreement with the calculations.

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1. Introduction

Self-assembled Si/Ge quantum dot (QD) structures have been intensively studied in the last years for potential applications in Si based integrated optoelectronics. In particular, efforts have been done to study the valence band structure of Si/Ge QDs, because the application of intraband transitions within the valence band in QDs seems very promising for light detection in the mid-infrared range [1–4]. As the fundamental band gap of the Si/Ge system is indirect in space and momentum, optical single QD spectroscopy was not successful so far and the studies on inhomogeneous QD ensembles revealed only little information on the quantised level scheme of localised hole states.

Intraband transitions between localised hole states have been observed in absorption measurements [5–7] on Si/Ge islands. Further work on Si/Ge QDs was focused on photocurrent measurements and transitions to states near to the valence band edge or to wetting layer (WL) states [3,4,8]. Admittance measurements showed convincingly that the valence band of Si/Ge QDs is composed of discrete levels with a separation of quantum-confined heavy hole levels of about 40 meV [9,10]. Valence band calculations for small pure Si/Ge QDs predicted localised heavy hole (hh) states, an indirect band gap slightly below that observed in photoluminescence, and a hh to light hole (lh) band edge separation of about 100 meV [11].

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Resonant electronic Raman experiments on QDs have been performed on the III–V materials system and led to results resembling an atomic fine structure [12], but so far, for Si/Ge QD structures Raman studies have concentrated on phonon modes [13–15].

In this contribution, we present the first electronic Raman scattering spectra on p-doped self-assembled Si/Ge QDs. We observe a Raman transition of localised holes at 105 meV and a resonance to virtually localised electrons at the direct band gap $E_0 = 2.5$ eV for the QDs. A 6-band k · p valence band structure simulation based on experimentally obtained structural parameters and including elastic strain relaxation shows excellent agreement with the measured value of E_0 and asserts the attribution of the Raman signal at 105 meV to a transition between hh and lh ground states.

2. Experimental

The investigated samples were grown by solid-source molecular beam epitaxy on n^--(1 0 0) Si substrates. Si/Ge QDs form in the Stranski–Krastanow growth mode by self-assembly during deposition of 8 monolayers (ML) Ge at a substrate temperature of 510°C. Each sample contains 80 Si/Ge QD layers separated by 25 nm Si with a boron modulation doping in the centre and is capped with 100 nm Si. Several samples have been annealed at temperatures from 600°C to 800°C for 1 h. A reference sample with a buried and an uncapped layer of Si/Ge QDs was grown under the same conditions in order to investigate the structural and optical properties of the dots by AFM and photoluminescence (PL) measurements.

Micro-Raman measurements were performed at 6 K in backscattering geometry with a spectral resolution of 3.8 cm^{-1} using a triple Raman spectrometer equipped with a liquid nitrogen cooled Si charge coupled device camera system. The samples have been studied at Raman excitation energies ranging from 1.83 eV (677 nm) to 3 eV (413 nm) using Argon ion and Krypton laser lines. The laser was focused to a spot of about 1 μm with a laser power of 0.3 mW on the sample.

3. Results

The inset of Fig. 1 shows an AFM image of the uncapped reference sample. The Si/Ge QDs are elongated hut clusters. The lateral size is about 15 × 25 nm^2, the height about 2 nm and the sheet density 1.5×10^{11} cm^{-2}. TEM measurements show that the QDs are free of dislocations after overgrowth with Si. PL spectra are peaked at 730 meV with a full-width at half-maximum (FWHM) of 40 meV. A detailed and quantitative phonon Raman scattering characterisation of these structures has been performed earlier [15]. It revealed structural parameters affecting the QD band structure, such as Ge content and strain.

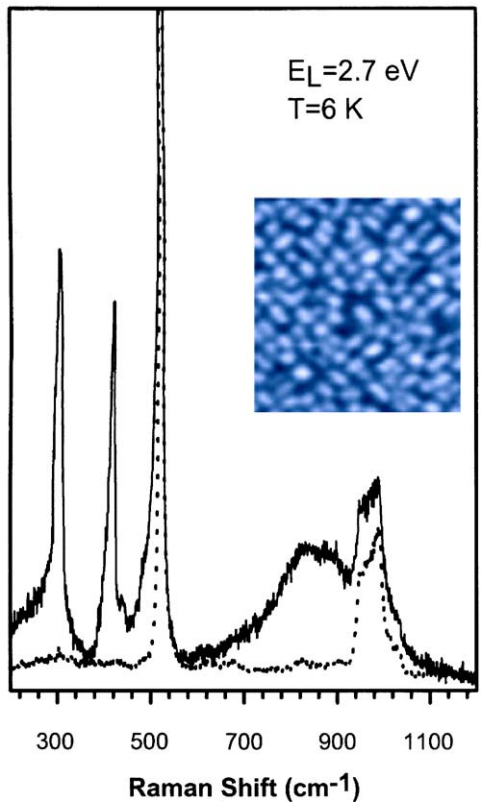

Fig. 1. Raman spectra of a Si/Ge QD sample (solid line) and a Si substrate (dotted line). At 850 cm^{-1} an electronic Raman line can be clearly distinguished from the second-order Si band. The inset shows an AFM image (200 × 200 nm^2) of an uncapped Si/Ge QD sample.

At 6 K, under an excitation photon energy of 2.7 eV the p-doped Si/Ge QD structures reveal an unpolarised Raman signal at 850 cm^{-1} (105 meV) with a FWHM of 25 meV. This signal can be clearly distinguished from the second-order Si phonon mode around 960 cm^{-1} as shown in the comparison with

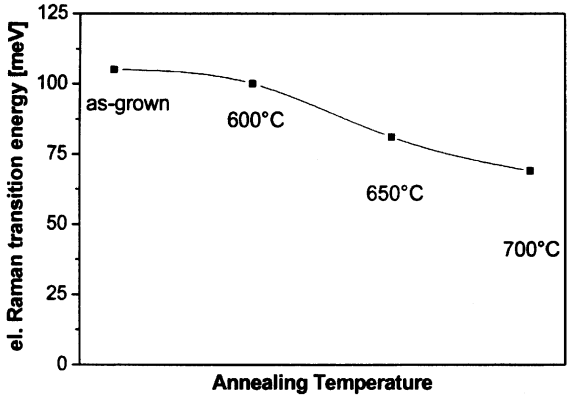

Fig. 2. Electronic Raman transition energy for the as-grown and annealed Si/Ge QD structures.

the Raman spectrum obtained from a Si substrate in Fig. 1. The Raman transition at 105 meV shows no dispersion with variation of the laser excitation energy. Thus, this broadened Raman line is attributed to a dispersionless intraband transition of localised holes in the Si/Ge QDs. Comparing this energy of about 100 meV and values of hole quantisation energies from model calculations and admittance measurements we assign it to an electronic transition from the hh QD ground state to (mixed hh–lh) states that correspond to a lh ground state. Annealing the samples for 1 h at temperatures from 600°C to 800°C results in a significant shift of the Raman signal towards lower energies with increasing temperatures, as shown in Fig. 2. For the structure annealed at 800°C the Raman line cannot be separated from alloy phonon modes with energies below 520 cm^{-1}. The intermixing of Si and Ge increases with the annealing temperature. Ge content is also reduced, but keeps amazingly constant within the island core, which is explained by a large Si diffusion constant within Ge-rich islands and has been shown by phonon Raman scattering [15]. In the as-grown structures the Ge content is approximately 80% whereas it drops to 40% after annealing at 700°C and to 28% at 800°C. With increasing intermixing, Ge-content, strain and the strain-induced splitting between hh and lh states diminishes. The quantum confinement along the growth direction should also be reduced. These qualitative explanations strongly support the assignment of the Raman line red-shifting with annealing to the hh–lh hole transition. The lateral confinement energies, in contrast, are expected to be much smaller and to be rather insensitive to interdiffusion of the flat island structures.

Samples with different p-doping levels ranging from 0 to 9 holes per QD in average showed no systematic dependence of hh–lh Raman intensity. Even the undoped Si/Ge QD sample was of comparable efficiency. This absence of a clear influence of the doping level is attributed to a high average number of photogenerated holes within the dots. Electron–hole pairs are generated by the excitation laser light within the silicon matrix. Holes relax into the QDs and have long estimated lifetimes in the range of μs or even longer due to the indirect nature of fundamental band gap in Si/Ge QDs. Thus, a high number of photogenerated holes is obtained within the QDs, even at low laser power densities reached with a macroscopic laser spot size.

The phonon Raman mode intensities as well as the hh–lh transition intensity at 105 meV have also been studied under variation of the Raman excitation energy from 1.83 to 3 eV. Fig. 3 shows the integrated intensities of the Ge–Ge mode and of the Raman line of the hh–lh transition as a function of the excitation energy after subtraction of the Si contributions. Both lines are due to contributions from the QDs as Ge WL contributions to the remnant Raman spectrum can be neglected [15]. The Ge–Ge phonon mode shows two resonances at about 2.3 and 2.5 eV. The resonance at 2.3 eV is close to the E_1 and $E_1 + \Delta_1$ gap in bulk Ge. This resonance at momentum vectors along the $\{1\ 1\ 1\}$-directions of the Brillouin zone is not observed for the hole transition. The second clear resonance at 2.5 eV is observed for the Ge–Ge phonon as well as the electronic hh–lh Raman transition. A resonance for Raman transitions of localised holes is expected to be strong for direct transitions to localised electronic states corresponding to the Γ-point, but not to transitions related to momentum vectors anywhere within the Brillouin zone. We thus assign this resonance energy to the direct band gap E_0 of localised hh and virtually bound Γ-electron ground states within the small Si/Ge QDs. This energy is much larger than the indirect fundamental band gap of SiGe heterostructures and thus the localized Γ-electron states are degenerate with continuum electron states within the Si matrix.

The detailed structural parameters obtained by AFM, phonon Raman scattering and X-ray diffraction

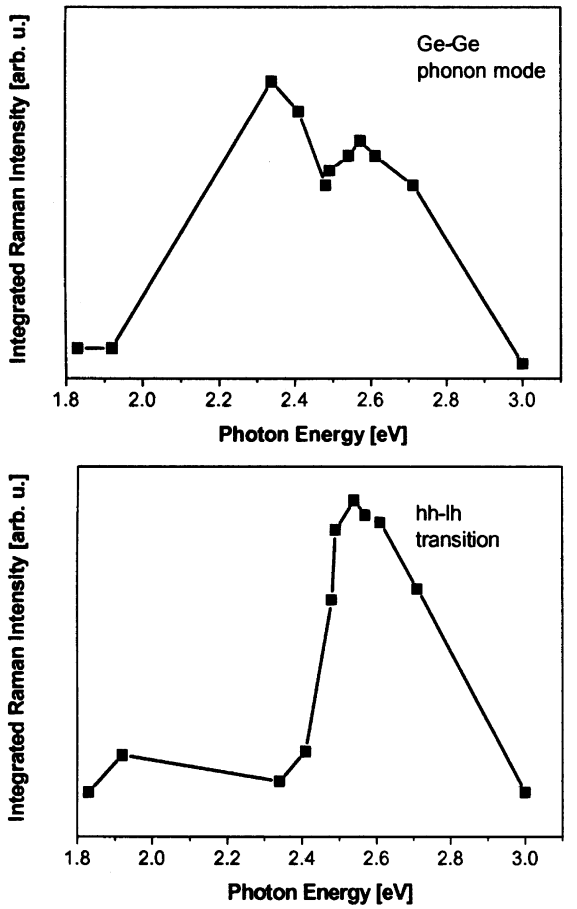

Fig. 3. Resonance behaviour of the integrated Raman intensities as a function of the excitation photon energy for (a) the Ge–Ge phonon mode and (b) the hh–lh Raman transition. Contributions of Si have been subtracted.

(XRD) [15] served as an input for valence band structure model calculations with the 6-band k · p simulator next**nano**[3]. The phonon Raman study showed that the interface region between Ge-rich regions within small as-grown Si/Ge QDs and their Si environment is very sharp. We thus considered lens-shaped 1.8 nm high Si/Ge QDs with a uniform Ge content of 80%, an underlying WL of 0.5 nm thickness also containing 80% Ge and lateral elastic strain of −3.4% in the QDs. The calculations yield an energy of 750 meV for the type-II PL recombination of the hh QD ground state with Δ-electrons in Si which is in excellent agreement with the PL measurements peaked at 730 meV. The predicted lateral confinement energy for holes of 42 meV also matches well with previous admittance studies performed on similar Si/Ge QD structures [10]. Within this simulation, the direct band gap between the hh ground state and the localised Γ-electron state is 2.3 eV and thus very close to the observed resonance Raman energy of 2.5 eV for the Ge–Ge mode and the electronic transition in Fig. 3. Finally, the first hole state of dominantly lh character is predicted to lie 114 meV above the ground state. This state shows a much higher transition matrix element than the surrounding hh states. The 6-band k · p valence band structure calculations are in very good agreement with the observed electronic Raman line at 850 cm^{-1} and thus also asserts its simplified assignment to a transition of localised holes between the hh and lh ground states.

4. Conclusions

We have presented the first resonant electronic Raman spectroscopy study of discrete electronic transitions in small p-doped Si/Ge QDs. An intraband transition of localised holes with an energy of 105 meV is observed as a broadened Raman line. It is attributed to a hh–lh-transition within the QDs. Due to significant intermixing of Si and Ge, i.e. reduced strain-induced hh–lh splitting and quantum confinement, this transition energy shifts to lower values with increasing annealing temperature. The hh–lh transition Raman efficiency shows a clear resonance at an excitation energy of 2.5 eV. This resonance energy is attributed to the direct band gap E_0 between localised states in the Si/Ge QDs.

Detailed structural parameters obtained from AFM, XRD and Raman phonon scattering have been used for 6-band k · p valence band structure models. The simulations are in very good agreement with previous PL and admittance measurements as well as the resonance energy of the direct E_0 gap. The calculations of several hole state eigenvalues and their overlap matrix elements with the hh ground state asserts the attribution of the 850 cm^{-1} Raman line (as-grown sample) to a transition between the hh and lh ground states.

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References

[1] A.I. Yakimov, A.V. Dvurechenskii, Y.Y. Proskuryakov, A.I. Nikiforov, O.P. Pchelyakov, S.A. Teys, A.K. Gutakovskii, Appl. Phys. Lett. 75 (1999) 1413.
[2] L.P. Rokhinson, D.C. Tsui, J.L. Benton, Y.-H. Xie, Appl. Phys. Lett. 75 (1999) 2413.
[3] C. Miesner, O. Röthig, K. Brunner, G. Abstreiter, Appl. Phys. Lett. 76 (2000) 2704.
[4] D. Bougeard, K. Brunner, G. Abstreiter, Physica E 16 (2003) 609.
[5] P. Boucaud, V. Le Thanh, S. Sauvage, D. Débarre, D. Bouchier, Appl. Phys. Lett. 74 (1999) 401.
[6] J.L. Liu, W.G. Wu, A. Balandin, G. Jin, Y.H. Luo, S.G. Thomas, Y. Lu, K.L. Wang, Appl. Phys. Lett. 75 (1999) 1745.
[7] T. Fromherz, W. Mac, A. Hesse, G. Bauer, C. Miesner, K. Brunner, G. Abstreiter, Appl. Phys. Lett. 80 (2002) 2093.
[8] N. Rappaport, E. Finkman, T. Brunhes, P. Boucaud, S. Sauvage, V. Yan, V. Le Thanh, D. Bouchier, Appl. Phys. Lett. 77 (2000) 3224.
[9] S.K. Zhang, H.J. Zhu, F. Lu, Z.M. Jiang, X. Wang, Phys. Rev. Lett. 80 (1998) 3340.
[10] T. Asperger, C. Miesner, K. Brunner, G. Abstreiter, Phys. Stat. Sol. (b) 224 (2001) 237.
[11] J.H. Seok, J.Y. Kim, Appl. Phys. Lett. 78 (2001) 3124.
[12] C. Schüller, Adv. Solid State Phys. 38 (1999) 167, and references therein.
[13] J. Groenen, R. Carles, S. Christiansen, M. Albrecht, W. Dorsh, H.P. Strunk, H. Wawra, G. Wagner, Appl. Phys. Lett. 71 (1997) 3856.
[14] A. Milekhin, N.P. Stepina, A.I. Yakimov, A.I. Nikiforov, S. Schulze, D.R.T. Zahn, Eur. Phys. J. B 16 (2000) 355.
[15] P.H. Tan, K. Brunner, D. Bougeard, G. Abstreiter, Phys. Rev. B 68 (2003) 125302.