Strain and composition of capped Ge/Si self-assembled quantum dots grown by chemical vapor deposition

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We have investigated the composition and the strain profile of Ge/Si self-assembled quantum dots. The quantum dots, grown by low-or high-pressure chemical vapor deposition, were covered by a silicon cap layer. The composition and the strain were measured by the selected area transmission electron diffraction of a *single* quantum dot. The self-assembled quantum dots exhibit a quadratic deformation. No lateral relaxation of the lattice is observed from the main part of the quantum dot. An average composition of Ge around 50% is deduced. The average composition is found dependent on the size of the islands. This composition is correlated to the photoluminescence energy. © *2000 American Institute of Physics*. [S0003-6951(00)01129-3]

A considerable amount of work has been devoted in the past few years to the study of semiconductor self-assembled quantum dots. Self-assembled quantum dots can be successfully grown with III–V[1] or IV–IV[2] materials using a Stranski–Krastanow growth mode between lattice-mismatched semiconductors. Ge/Si self-assembled quantum dots are attracting specific interest because of their compatibility with Si-based electronics. The growth of high-quality Ge/Si self-assembled quantum dots can be achieved either by molecular beam epitaxy[2,3] or chemical vapor deposition.[4–6] It is obvious that the electronic properties of the nanostructures depend on many parameters, including the size, shape, strain profile, and composition of the dots. The knowledge of these parameters is of crucial importance for future optoelectronic applications of the quantum dots.

Depending on growth conditions, Ge/Si quantum dots with square based pyramidal shapes,[7] hut clusters shapes,[2] or dome shapes[8,9] have been reported in the literature. The strain profile and the composition of the islands remains an issue which is more difficult to tackle. Strain and composition are evidently dependent on the capping of the islands with silicon, a step which is required to achieve three-dimensional confinement. This capping procedure is likely to modify the morphology and composition of the islands. Several processes like the segregation of germanium atoms, thermal intermixing, or the strain driven alloying[10] are expected to occur and can influence the final composition of the islands. In the case of Ge/Si quantum dots grown by molecular beam epitaxy, a strong intermixing in the islands between Ge and Si was reported.[3] For Ge/Si self-assembled quantum dots grown by chemical vapor deposition, photoluminescence spectroscopy also indicates that the composition of the islands is not likely to be 100% Ge rich. However, no quantitative study of the composition in capped islands has been published to our knowledge.

In this work, we have investigated the composition and strain profile of Ge/Si self-assembled quantum dots grown by chemical vapor deposition. The quantum dots were grown either under low-or high-pressure condition. After deposition of Ge, the quantum dots are capped with a silicon layer. The composition and the strain profile is inferred from the selected area transmission electron diffraction pattern of a *single* island. The strain profile is characterized by a quadratic deformation of the lattice. A strong intermixing between Ge and Si is measured for the capped quantum dots resulting in an average composition of around 50%. The composition is found to be dependent on the size of the islands. The measured composition is correlated to the photoluminescence of the islands. Significant intermixing explains the spectral position of the photoluminescence associated with the Ge islands.

The quantum dots were grown on Si(001) by chemical vapor deposition using silane and germane as gas precursors. Sample B was grown in an industrial ASM Epsilon 2000 high-pressure chemical vapor deposition reactor.[11] The epitaxial growth was performed at 650 °C under hydrogen carrier flow with a 20 Torr typical base pressure. Sample A was grown by ultrahigh-vacuum chemical vapor deposition.[6,12] The growth pressure was around 5×10^{-4} Torr. The growth temperature was 550 °C. The Ge time deposition was 240 s, corresponding to a deposited thickness of 4 monolayers. For both samples, a single Ge layer was deposited. This layer was subsequently covered by a silicon cap. Details of the growth procedure can be found in Refs. 6, 11, and 12. For transmission electron diffraction (TED) measurements, the samples were prepared for a cross section along the [110] direction. The composition of the dots is deduced from the

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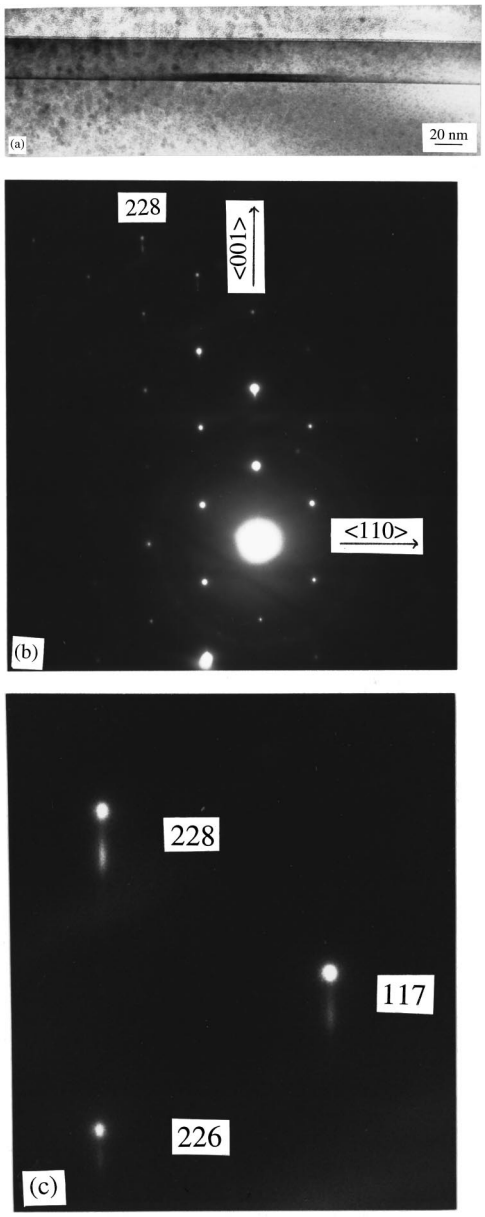

FIG. 1. (a) Cross-section electron microscopy image of sample A. Bright field image in three-beams symmetrical Bragg conditions between the (004) and the $(00\bar{4})$ directions. (b) Selected area electron diffraction pattern on the island shown in (a). The orientation of the sample is off the [110] zone axis to put in Bragg conditions some *hhl* spots with a high *l* index. (c) Magnification of the 228 region of (b).

diffraction of a single island. The use of this technique based on the selected area electron diffraction allows us to work on a relatively thick area of the sample (at least 100 nm). The major part of the signal is therefore not disturbed by the free surface introduced by the sample preparation.

Figure 1(a) shows a cross-section electron transmission microscopy image of a single island of sample A. The island appears in dark contrast. The base and top surfaces of the island are determined by a (001) plane. The height of the island is about 5 nm. The lateral limits of the island appear blurred and not well defined, probably because of its shape which is a square base with the edges along the [100] and [010] directions while the cross-section is along the [110] direction. The length of the diagonal of the island, as observed by microscopy, can be estimated to be around 180 nm. We emphasize that a constant homogeneous strain is likely to be observed in these flat dots with a very large base.

Figure 1(b) shows the selected area electron diffraction pattern associated with this island. The electron diffraction pattern of an individual island corresponds to a set of spots which differ from the diffraction pattern of the surrounding silicon. A splitting is observed between the *hhl* spots associated with the silicon matrix and the spots of the island if the *l* index is different from the 0. On the other hand, the *hh0* spots are completely superimposed. It indicates that no visible lateral relaxation occurred. Note that, similarly, no lateral relaxation could be measured on the *hk0* spots in plan view. Similar observations have been made for each observed island in both samples. The buried islands of sample A exhibit, therefore, a pseudomorphic deformation with a tetragonal distortion in the [001] direction similar to that of a two-dimensional strained layer. We cannot rule out a deviation from this quadratic deformation at the edge of the island. However, this represents only a small volume fraction of the island.

From the splitting of the diffraction spots, it is possible to determine the mismatch between the islands and the silicon matrix (Δa_0), and consequently to estimate, individually, the composition of the islands. Assuming a pseudomorphic quadratic deformation, the natural lattice parameter a_0 of the island can be simply and precisely calculated according to

$$\frac{\Delta d}{d} = \frac{1+\nu}{1-\nu}\frac{\Delta a_0}{a_0}. \tag{1}$$

Δd is the splitting measured on the electron diffraction pattern between the two *hhl* spots. The assumption of pure pseudomorphic deformation is justified by the absence of any visible lateral relaxation. The measurement is performed for diffraction spots with a high *l* index value in order to increase the accuracy of the measurement. ν is the Poisson ratio. Note that the Poisson ratio of germanium is very close to that of silicon: $\nu_{Ge}=0.2732$ and $\nu_{Si}=0.2782$.[13] To estimate the composition, the Poisson ratio is linearly extrapolated between ν_{Ge} and ν_{Si}. The influence of the sample preparation on the strain state can be neglected at first order because of the thickness of the preparation (100–200 nm). We have checked that the measurements on islands located at a different position lead to the same composition. The influence of an uniaxial deformation of the islands can also be discarded since it would only concern the edge of the sample and would represent at maximum 10% of the island volume. Note that in Bragg conditions, the splitting of the diffraction spots does not depend on the sample orientation.

A remarkable feature shown in Fig. 1(b) is that the measured splittings between the diffraction spots are approximately half of the expected value for pure Ge. This feature indicates a strong intermixing in the capped islands. A mean Ge composition of 50% is estimated for the island in Fig. 1(a). In the case of the smaller islands (3–4 nm height) of sample A, the germanium concentration in the islands is even smaller and can be estimated around 30%.

We emphasize that the diffraction spots associated with the islands are not exactly dotty and that their shapes are lengthened along the [001] direction. This indicates that the

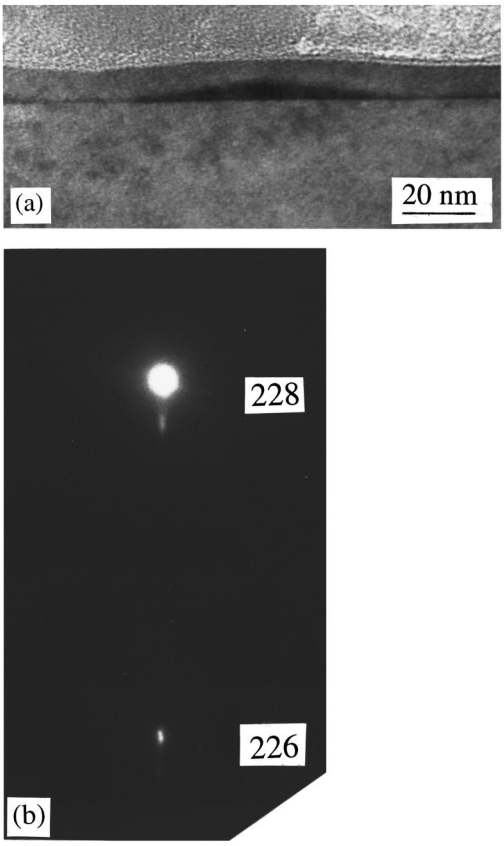

FIG. 2. (a) Cross-section electron microscopy image of sample B with the same imaging conditions as in Fig. 1(a). (b) Magnification of the 228 region of the selected area diffraction pattern of the island shown in (a).

composition of the islands is not perfectly homogeneous. The center of the spot corresponds to the mean composition of the island. The elongation of the diffraction spot along the [001] direction is even more obvious in Fig. 1(c) which shows a magnification of the 228 region of the TED pattern. A gradient of composition in the island of about 20% can be estimated in this case.

The diffraction measurements obtained with sample B are reported in Fig. 2. Figure 2(a) shows a cross section electronic microscopy image. The islands of sample B do not exhibit the same flat shape as in sample A but rather a conic shape. The angle measured from the [001] direction is around 9°. The island shown in Fig. 2(a) is about 6 nm high at the top and 90 nm wide at its base. Again, the observation of the electron diffraction pattern clearly indicates that the deformation in the islands is quadratic. Figure 2(b) shows the splitting existing between the two 228 spots which stem from the silicon matrix and from the island. A composition of about 40% of germanium is deduced in this case. The spot associated with the island is narrower than that observed in the previous sample. The gradient of the composition can be estimated to be around 10%.

We emphasize that these results significantly differ from recent results reported on uncapped Ge islands grown by chemical vapor deposition.[14] In the latter case, no significant alloying was observed. The present transmission electron diffraction measurements underline the prominent role played by the capping of the islands.

The photoluminescence spectrum of sample A was reported in Ref. 6. The photoluminescence associated with the Ge islands was maximum at 780 meV. It is obvious that this value is not compatible with that of pure strained Ge islands. The data provided by the diffraction patterns bring a new insight on this value. Following Ref. 15, the band offset in the valence band between strained $Si_{0.5}Ge_{0.5}$ alloys and Si is around 420 meV. The confinement energy associated with the quantum dots can be approximated by the confinement energy of a 5 nm thick quantum well for sample A. The lateral confinement associated with the in-plane direction can be safely neglected. For a $Si_{0.5}Ge_{0.5}$ alloy, the confinement energy of a 5 nm thick quantum well is around 43 meV. Assuming a mean Ge composition of 50% for the islands of sample A, the photoluminescence is therefore expected to be maximum around 775 meV for a type II recombination. We emphasize that this value represents a rough estimate which neglects any band-mixing effects. The inhomogeneous composition of the island along with its size dependence is likely to introduce some variation for this theoretical estimate. However, the predicted photoluminescence value of 775 meV is very close to the experimental value. We conclude that the significant intermixing in the island is at the origin of the high-energy photoluminescence measured for the self-assembled quantum dots grown by chemical vapor deposition. It is worth noting that the influence of SiGe intermixing on the photoluminescence energies has already been emphasized.[16]

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[1] L. Goldstein, F. Glas, J. Y. Marzin, M. N. Charasse, and G. Le Roux, Appl. Phys. Lett. **47**, 1099 (1985).
[2] Y. W. Mo, D. E. Savage, B. S. Swartzentruber, and M. G. Lagally, Phys. Rev. Lett. **65**, 1020 (1990).
[3] P. Schittenhelm, M. Gail, J. Brunner, J. F. Nützel, and G. Abstreiter, Appl. Phys. Lett. **67**, 1292 (1995).
[4] H. Sunamura, N. Usami, Y. Shiraki, and S. Fukatsu, Appl. Phys. Lett. **66**, 3024 (1995).
[5] M. Goryll, L. Vescan, K. Schmidt, S. Mesters, H. Lüth, and K. Szot, Appl. Phys. Lett. **71**, 410 (1997).
[6] V. Le Thanh, P. Boucaud, D. Débarre, Y. Zheng, D. Bouchier, and J.-M. Lourtioz, Phys. Rev. B **58**, 13 115 (1998).
[7] T. I. Kamins, E. C. Carr, R. S. Williams, and S. J. Rosner, J. Appl. Phys. **81**, 211 (1997).
[8] D. J. Eaglesham and M. Cerullo, Phys. Rev. Lett. **64**, 1943 (1990).
[9] T. I. Kamins, G. Medeiros-Ribeiro, D. A. A. Ohlberg, and R. S. Williams, Appl. Phys. A: Mater. Sci. Process. **67**, 727 (1998).
[10] S. A. Chaparro, J. Drucker, Y. Zhang, D. Chandrasekahr, M. R. McCartney, and D. J. Smith, Phys. Rev. Lett. **83**, 1199 (1999).
[11] C. Hernandez, Y. Campidelli, D. Simon, D. Bensahel, I. Sagnes, G. Patriarche, P. Boucaud, and S. Sauvage, J. Appl. Phys. **86**, 1145 (1999).
[12] V. Le Thanh, V. Yam, P. Boucaud, F. Fortuna, C. Ulysse, D. Bouchier, L. Vervoort, and J.-M. Lourtioz, Phys. Rev. B **60**, 5851 (1999).
[13] E. Kasper, A. Schuh, G. Bauer, B. Holländer, and H. Kibbel, J. Cryst. Growth **157**, 68 (1995).
[14] P. D. Miller, C. P. Liu, W. L. Henstrom, J. M. Gibson, Y. Huang, P. Zhang, T. I. Kamins, D. P. Basile, and R. S. Williams, Appl. Phys. Lett. **75**, 46 (1999).
[15] C. G. Van de Walle and R. M. Martin, Phys. Rev. B **34**, 5621 (1986).
[16] O. G. Schmidt, C. Lange, and K. Eberl, Appl. Phys. Lett. **75**, 1905 (1999).