Phonon pressure coefficient as a probe of the strain status of self-assembled quantum dots

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The built-in strain in self-assembled quantum dots has large impact on their physical properties, but both its average value and degree of anisotropy are often unknown. The authors demonstrate that the pressure coefficient of optical phonons might be used as probe for the strain status of the dots. This method was applied to the case of Ge dots capped with Si layers of different thicknesses. The authors observe a transition from a strictly biaxial stress situation for uncapped dots to a status of quasihydrostatic strain for cap-layer thicknesses larger than a critical value of the order of the dot height. © 2007 American Institute of Physics. [DOI: 10.1063/1.2773958]

Self-assembled quantum dots (QDs) are fundamental building blocks in optoelectronics nowadays¹ for their electronic, optical, and transport properties can be tailored by controlling dot parameters such as size, shape, and composition.² Another key parameter which is inherent to self-assembled growth and which has large influence on the optoelectronic properties of the dots is the residual built-in strain. Unfortunately, the strain status of the dots in the ready device is usually unknown. In this respect, Raman scattering has been demonstrated to be a powerful tool for measuring strain in compound semiconductor microstructures.³ For the most frequent case of Raman measurements in backscattering geometry from the (001) surface, the strain is directly determined from the frequency shift of the Raman-allowed *singlet* component of the optical phonons according to^{4,5} $\omega_s(x, \varepsilon) = \omega_0 + b_s \varepsilon_{\parallel}$, where x is the alloy composition, $\varepsilon_{\parallel}$ is the in-plane strain, and b_s is the so-called strain-shift coefficient given by

$$b_s = \omega_0(-\tilde{K}_{11}\alpha/2 + \tilde{K}_{12}). \quad (1)$$

Here, ω_0 is the frequency of the unstrained phonon mode, $\tilde{K}_{ij}$ are the dimensionless phonon deformation potentials, as defined in Ref. 3, and $\varepsilon_{\perp} = -\alpha\varepsilon_{\parallel}$ is the relation between in-plane strain and that in the growth direction.

Equation (1) was deduced for the case of a strictly biaxial stress like that in quantum wells, for which $\alpha = 2C_{12}/C_{11} \approx 1$, where C_{ij} are the elastic constants of the material. It also holds for a purely hydrostatic strain just by setting $\alpha = -1$, because in this case all three strain components along the principal axes are the same. In the general case of dealing with a mixed stress tensor containing a hydrostatic and a biaxial component, one might, in principle, still be using Eq. (1) but with an unknown value of the parameter α lying between ± 1 . Such is too often the situation for self-assembled QDs depending on the aspect ratio and cap-layer thickness. Thus, it is not surprising to find in the literature a wide spread of values for the strain-shift coefficient b_s . For Ge/Si thin films and/or QDs, for instance, b_s ranges from about -400 to -800 cm^{-1} .⁵⁻¹² The conclusion is that in order to obtain sound quantitative results from Raman

scattering for the residual strain in QD systems, it is crucial to know the strain situation, i.e., which is the pertinent value for α .

In this letter, we show that the pressure coefficient of the longitudinal optical phonon ($d\omega_s/dP$) can be regarded as a probe of the strain status of quantum dots. The main reason for using the pressure derivative of the phonon frequency instead of the frequency itself is that the former is to a very good approximation only sensitive to the strain distribution rather than QD composition, size, or even the presence of dislocations. For that purpose we have studied systematically the hydrostatic pressure coefficient of the optical phonon of a series of carbon-induced Ge dots capped with a layer of Si with different thicknesses ranging from 0 to 200 nm. With increasing cap-layer thickness we observe a steep decrease of the phonon-pressure coefficient followed by saturation. Based on the results of a simple elastic model which accounts for the pressure dependence of the phonon frequency, we interpret this behavior as indication of a transition from a purely biaxial stress situation for uncapped dots to a status of quasihydrostatic compression for dots embedded in the Si matrix.

Samples were grown by molecular beam epitaxy on Si(001) substrates according to the following sequence: after deposition of a 100-nm-thick Si buffer layer, a 4.8 Å thick Ge wetting layer was grown before depositing 0.1 ML of carbon to control the shape and density of the QDs.¹³⁻¹⁵ In the next step, 15 Å of Ge were grown at 500 °C leading to dot formation. Finally, the Ge QDs were capped with either 0, 3, 10, 50, or 200 nm of Si also at 500 °C. The reference sample without cap layer was used to determine the dot shape and density using atomic force microscopy (AFM). As shown in Figs. 1(a) and 1(b), the average dot height is about $h = 14 \text{ nm}$, the base length is $b = 120 \text{ nm}$, and the areal density is about $40 \text{ dots}/\mu\text{m}^2$. In Fig. 1(c), we show a representative transmission electron microscopy (TEM) image of a Ge dot. The cap layer can be easily identified, as it copies the QD shape.

Raman spectra were collected with a LabRam HR800 system in backscattering geometry at room temperature using the 514.5 nm line of an Ar⁺ laser. Raman peak positions are determined with an error of less than 0.5 cm^{-1} . Measurements under pressure were carried out using the diamond

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FIG. 1. (a) Topographic image by AFM of the uncapped sample and (b) line scan across a representative carbon-induced Ge quantum dot. (c) TEM image of the sample with 10-nm-thick cap layer showing one Ge dot in cross section.

anvil cell (DAC) technique. A 4:1 mixture of methanol and ethanol was employed as the pressure-transmitting medium. Pressure was monitored *in situ* by the shift of the Si longitudinal optical phonon, which was previously calibrated using the pressure shift of the ruby R1 line.¹⁶ Samples loaded into the DAC were previously thinned to about 30 μm by mechanical polishing.

Figure 2 displays the dependence on hydrostatic pressure of the frequency of the Raman peak corresponding to the Ge optical phonon for five samples with cap-layer thickness, as indicated in the legend. We show only data in the pressure range up to 5 GPa, in which the pressure dependence of ω_s is well described by a straight line. The solid lines in Fig. 2 represent the results of least-squares fits to the data points using a linear relation.¹⁷ The fit results are listed in Table I. The phonon pressure coefficient ($d\omega_s/dP$) obtained from the fitted slopes exhibits a clear decreasing trend with increasing cap-layer thickness.

In Fig. 3 we have plotted the tabulated values of the phonon pressure coefficient as a function of cap-layer thickness. A fast exponential reduction of $d\omega_s/dP$ is observed for thicker Si caps. Preliminary results on smaller Ge QDs were published elsewhere.¹⁸ To explain this behavior we developed a simple elastic model which takes into account the effects of the wetting layer (WL) and dot capping on the dot residual strain. We consider three contributions to the coefficient $d\omega_s/dP$. The obvious one is from the external hydrostatic pressure and the two arise from changes in the built-in strain of the QDs indirectly induced by the applied pressure due to the different compressibilities, i.e., bulk modulus of

FIG. 2. Dependence on pressure of the frequency of the Ge longitudinal optical phonon mode for five samples with cap layer thicknesses of 0, 3, 10, 50, and 200 nm. Solid lines are results of least-squares fits to the data points using linear relations.

TABLE I. Coefficients describing the pressure dependence of the Raman-allowed optical phonon of Ge dots capped with a Si layer of different thicknesses t obtained from fits of a linear expression $\omega_s = \omega_0 + (d\omega_s/dP) \cdot P$ to the experimental data. Error bars are indicated in parenthesis.

Cap (nm)	ω_0 (cm^{-1})	$d\omega_s/dP$ ($\text{cm}^{-1}/\text{GPa}$)
0	301.4(1)	3.72(4)
3	302.4(2)	3.54(3)
10	304.2(2)	3.29(3)
50	305.2(2)	3.16(3)
200	304.7(2)	3.20(3)

the dot and surrounding material which we labelled hereafter B and A, respectively. From the latter contributions one corresponds to the biaxial deformation caused by the wetting layer and the other comes from the recompression of the dots during capping.

For hydrostatic pressures up to a few gigapascals, the reduction in relative volume is proportional to the applied pressure, $\Delta V/V \approx -P/B_0$, where B_0 is the bulk modulus. The corresponding contribution to the phonon pressure coefficient is simply given by

$$\frac{d\omega_s^{(P)}}{dP} = -\frac{a}{B_0^B}, \quad \text{with } a = \frac{\omega_0}{6}(\tilde{K}_{11} + 2\tilde{K}_{12}), \quad (2)$$

the hydrostatic phonon deformation potential.³ For $B \equiv \text{Ge}$ is $-a/B_0^{\text{Ge}} \approx 4 \text{ cm}^{-1}/\text{GPa}$,¹⁹ which constitutes an upper bound for the phonon pressure coefficient of the dots.

Although the residual QD strain is not known *a priori*, the way it varies by applying hydrostatic pressure due to the different elastic properties of the dot and surrounding material is readily estimated as $d\epsilon_{\parallel}/dP = 1/3(1/B_0^B - (1/B_0^A))$. In the present case, we have $A \equiv \text{Si}$ with $B_0^{\text{Si}} = 98 \text{ GPa}$ and $B \equiv \text{Ge}$ with $B_0^{\text{Ge}} = 75 \text{ GPa}$.²⁰ Let us first consider the case of uncapped dots, for which there is a strictly biaxial stress situation due to the constraint of isomorphism to the Si substrate. Since such stress is transduced to the dot through the wetting layer, we call it the WL contribution. The dot, however, relaxes its strain by expanding laterally, as it grows in height h . Thus, the measured blueshift of the QD phonon would be smaller by a phenomenological factor φ than is mandatory after Eq. (1). This factor is expected to depend on aspect ratio and WL composition but not on pressure. Hence, the contribution of the biaxial stress to the phonon pressure coefficient can be written as

FIG. 3. Phonon pressure coefficient of Ge optical mode of the dots vs cap layer thickness as obtained from the slopes of the fits in Fig. 2. The solid curve represents the result of a fit to the data points using Eqs. (2), (3), and (5) with λ as adjustable parameter.

$$\frac{d\omega_s^{(WL)}}{dP} = \varphi b_s \frac{d\varepsilon_{\parallel}}{dP} = \frac{\varphi b_s}{3} \left(\frac{1}{B_0^B} - \frac{1}{B_0^A} \right). \quad (3)$$

The effect of capping the dots with a layer of thickness t is twofold: On the one hand, the cap layer produces a hydrostatic recompression of the dots and, on the other hand, the expansion in the growth direction due to the biaxial compression induced by the WL is gradually suppressed with increasing t . The latter supposes for the parameter φ a phenomenological dependence on t , $\varphi = \varphi_0 e^{-t/\lambda}$, with λ a critical cap-layer thickness. The amount of recompression caused by capping is a function of the ratio of the cap layer volume V_c to the volume of the dot V_d , in order to minimize the total elastic energy of the dot/cap system. Inspired by TEM pictures like that of Fig. 1(c) we consider for the calculation of the elastic energy a dot shape of a half revolution ellipsoid with an aspect ratio $f = b/h$ surrounded by a Si layer of thickness t ($g = t/h$). The minimum energy is attained for a dot strain of

$$\varepsilon_d = \frac{\varepsilon_{\parallel}}{1 + (V_d/V_c)(B_0^B/B_0^A)}, \quad \frac{V_d}{V_c} = \frac{f^2}{(f+g)^2} \frac{(1+g)^2}{(1+g)^3 - 1}. \quad (4)$$

Considering this strain as hydrostatic, it yields for the contribution of the cap layer to the phonon pressure coefficient the term

$$\frac{d\omega_s^{(cap)}}{dP} = \frac{a}{1 + (V_d/V_c)(B_0^B/B_0^A)} \left(\frac{1}{B_0^B} - \frac{1}{B_0^A} \right). \quad (5)$$

The solid line in Fig. 3 is the result of a least-squares fit to the experimental data of $d\omega_s/dP$ using the function which consists of the three terms given by Eqs. (2), (3), and (5). Here, λ is the only adjustable parameter, since φ_0 is determined by comparing the value of $d\omega_s/dP$ for the uncapped dots to that of bulk Ge. In spite of the crudeness of the model, we obtain a good description of the behavior of the phonon pressure coefficient with cap-layer thickness for $\lambda = 8$ nm. Even more important is the fact that the model provides further insight into the strain status of self-assembled dots, leading to a deeper understanding of the high pressure results. For example, the meaning of the saturation value of the pressure coefficient is the following: When $t \rightarrow \infty$, $\varphi \rightarrow 0$ and $V_d/V_c \rightarrow 0$ too. The term $d\omega_s/dP^{(WL)}$ vanishes and the other two yield $d\omega_s/dP = -a/B_0^A \approx 3.2 \text{ cm}^{-1}/\text{GPa}$ ($A \equiv \text{Si}$), which is the pressure coefficient calculated with the hydrostatic deformation potential of Ge but using the bulk modulus of the Si matrix. In fact, a similar pressure coefficient has been reported by Teo *et al.* for a sample with Ge QDs capped with 200 nm of Si.²¹ This led us to the conclusion that there is an abrupt transition from a strictly biaxial stress situation of uncapped dots to a fully hydrostatic (isotropic) three-dimensional compression state of the dots for cap layers thicker than the critical value λ (8 nm in the present case). We emphasize that this result is independent of the model; the latter is helpful to understand the underlying physics.

Obviously, λ depends on f . For very flat dots one expects $\lambda \rightarrow \infty$, thus, the dots, capped or uncapped, are always in a state of biaxial compression like the wetting layer. In fact, Raman measurements from the cleaved edge of a QD sample containing very flat dots ($h \approx 2$ nm) exhibit a clear singlet-doublet splitting,^{6,8} which is evidence of biaxial

strain. On the contrary, our sample with a 200-nm-thick cap layer does not display any splitting, being indicative of a hydrostatic (isotropic) compression of the Ge dots.

The practical importance of this work is to provide a means to infer the proper strain situation which applies for a given quantum dot structure, independent of the material system. Our pressure experiments indicate that for QDs with heights larger than about 5 nm or with steep facets like dome-shaped dots, if the cap layer is of the order of the dot height or above, then to consider a quasihydrostatic strain status is appropriate. On the contrary, for very flat or uncapped dots their deformation is better accounted for using a biaxial stress tensor. This would allow for the proper use of Eq. (1) with the correct value of the parameter α for the determination of the mean dot strain by Raman scattering.

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