Controlling a Nanowire Quantum Dot Band Gap Using a Straining Dielectric Envelope

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Supporting Information

ABSTRACT: We tune the emission wavelength of an InAsP quantum dot in an InP nanowire over 200 meV by depositing a SiO₂ envelope using plasma-enhanced chemical vapor deposition without deterioration of the optical quality. This SiO₂ envelope generates a controlled static strain field. Both red and blue shift can be easily achieved by controlling the deposition conditions of the SiO₂. Using atomistic empirical tight-binding calculations, we investigate the effect of strain on a quantum dot band structure for different compositions, shape, and crystal orientations. From the calculations, we estimate the applied strain in our experiment. This enables engineering of the band gap in nanowires with unprecedented possibilities to extend the application range of nanowire devices.

KEYWORDS: Nanowires, quantum dots, strain, photoluminescence, band gap engineering

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strain is a powerful parameter to control a wide range of physical properties in semiconductors. It was recently shown that strain can make direct transitions observable in germanium, an indirect material when unstrained. In addition, large biaxial strain can reverse the heavy hole–light hole order with important applications in quantum communication. Modifying the band structure with strain allows also for very large tuning ranges of frequency as shown for core–shell nanowires (NWs) with applications in photon detection and light sources. Additionally, strain is used to increase mobilities with tens of percentages. These examples show how strain can drastically engineer the band structure of a semiconductor.

Recently, NWs have been shown to be good photon detectors and can be used as single photon sources when containing a quantum dot (QD) with high light extraction efficiencies. NWs allow the growth of material combinations that could not exist in bulk or thin films, allowing new possibilities for the design of nanodevices. The small NW dimensions allow for band structure engineering by growing a shell of a material with different lattice constant or envelope, where an envelope is grown in a different growth environment from the NW (ex situ).

Not only is the band structure engineering of NWs of interest, but also, band structure engineering of QDs has gained a lot of attention. In particular, it is useful to shift the QDs’ energy to telecom wavelength or to couple the QD emission energy to another single photon emitter. It is well-known that the emission energy of QDs can be altered using electric fields, magnetic fields, or temperature. Using electric fields, typical red shifts in the PL are 2.5–3 μeV/mV. However, the range of the shift is limited because the oscillator strength of the optical transition quenches, due to the decreasing spatial overlap of the electron–hole wave function. Also, electric fields may alter the change state of the QD. Another method to tune the quantum dot emission energy is with magnetic fields. The energy shift for III–V QDs depends on both the g-factors and the diamagnetic coefficient; however, it usually does not exceed 100 μeV/T. The tuning range is limited to only one direction (blue shift) and also practically limited by the available magnetic field. Yet another degree of freedom to control the band gap of the QD is the temperature. Although large modifications in the band gap can be achieved, this is of little use for QDs because high temperatures, at which QDs are poor emitters, are required to obtain significant shifts.

Recently, it was shown that the band gap of QDs can be engineered using strain, for example, induced with piezoelectric actuators. Advantages of using this technique is that both red and blue shifting are possible. Also, the method is dynamic, allowing for precise and fast tuning. However, the tuning range is limited by the breakdown of the piezo material. Today, the maximum tuning range reported is about 20 meV.

Although all of these methods allow for precise tuning of the QD, the range over which the QD can be tuned is very limited. Here, we demonstrate a large tuning of the band gap of a NW–QD system using a simple SiO₂ envelope. We explore this new

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technique to engineer the band gap of an InAsP QD in an InP NW. A SiO₂ envelope is deposited using plasma-enhanced chemical vapor deposition (PECVD) to generate a static strain field that can be controlled with the deposition conditions. By using photoluminescence (PL) measurements, we show that this allows tuning the emission of the QD and NW over almost 200 meV without affecting the optical quality of the QD. We show that the emission can be both blue- and red-shifted without any broadening of the linewidth. By removing the SiO₂ envelope, we recover the original NW and QD emission, showing that this technique is reversible. Using atomistic empirical tight-binding (TB) calculations, we estimate the strain and study the behavior of the band structure for different QD shapes and compositions.

Not only is our tuning method interesting from a scientific point of view, but our method could also find its application in tuning LEDs or solar cells to desired wavelength, as our method is easily scalable and straightforward to implement.

**Experimental Methods.** We study bottom-up grown InP NWs containing a single InAsP QD (Figure 1a). The geometry of the NW is controlled during growth to have a high collection efficiency: the diameter is chosen to optimize the waveguiding properties for the QD emission, and the NWs are tapered toward the top to allow an adiabatic transfer of the guided mode into free space. Details on the growth can be found elsewhere. A typical scanning electron microscope (SEM) image of an as-grown NW can be seen in Figure 1b.

The NWs were measured in a microphotoluminescence setup at 10 K under nonresonant excitation with a laser of \(\lambda = 532\) nm and a spot size of \(\sim 1\) μm. The emission was collected with an objective with 0.75 NA, sent to a spectrometer, and detected with a CCD camera. The density of the NWs is 6 \(\times\) \(10^{10}\) cm\(^{-2}\), which made it possible to study single as-grown standing NWs. Marks allow measurement of the same NW before and after SiO₂ deposition.

**Results.** We first examine how a SiO₂ envelope deposited with the standard growth conditions influences the emission of the NW and the QD. The results are shown in Figure 2. In Figure 2a, the emission from the as-grown NW and QD (NWA) is shown. The emission detected at 1.32 eV is from the QD, and the emission at 1.40 eV is from the NW. The NW emission results from the fact that it consists of many zinc blende (ZB) and wurtzite (WZ) sections, all contributing to the PL.\(^{27-29}\)

We deposit a SiO₂ envelope on NWA using PECVD. The SiO₂ was deposited at 300 °C with a silane flow of 8.5 sccm and a RF power of 20 W. The PL of NWA was measured under the same conditions after deposition of the SiO₂ envelope, and the result is shown in Figure 2b. The PL of the NW and QD is red-shifted by 59 meV for the NW and 83 meV for the QD. In (c), the SiO₂ envelope is removed, and the PL for the same NW as in (a) and (b) shifts back to its original energy.

**Figure 2.** (a) Photoluminescence (PL) of an as-grown InP NW with an InAsP QD, (b) same NW as in (a), but now with a SiO₂ envelope. The PL is red-shifted over 59 meV for the NW and 83 meV for the QD. In (c), the SiO₂ envelope is removed, and the PL for the same NW as in (a) and (b) shifts back to its original energy.
expect that depositing an envelope should have an effect on these surface states. We propose the following explanation for the fact that the change in the linewidth is negligible.

After the NW growth, a thin native layer of oxide is formed on the NW. Surface states are then mainly expected at the interface of the InP NW and the native oxide layer. As we directly grow our SiO2 envelope without any preprocessing, the SiO2 envelope has no direct influence on these surface states and, therefore, the charge traps will have the same contribution to the spectral broadening. Moreover, the SiO2 envelope is amorphous and contains impurities which can serve as charge traps. However, from the data, we observe that these have a negligible effect on the linewidth of the QD emission, and we conclude that these additional charge traps do not modify the QD linewidth.

Furthermore, alternating ZB and WZ segments in the NW, called stacking faults, can trap charges which can lead to broadening of the linewidth of the QD. However, the SiO2 envelope does not alter the number of stacking faults in the proximity of the QD, and therefore, the broadening of the linewidth due to stacking faults is expected to be minimally influenced by the SiO2 envelope.

From Figure 3, also the intensity of the X and XX before and after deposition of a SiO2 envelope can be compared. Although changes in the intensity were measured for QDs before and after SiO2 deposition, no clear trend for improvement or decrease of the intensity was observed. However, the intensity with and without the SiO2 envelope was always on the same order of magnitude.

It is possible to modify the magnitude of the QD energy shift since changing the SiO2 deposition conditions alters the properties of the SiO2 (see Supporting Information). By changing the deposition conditions, one can influence the density and the percentage of H incorporation. Especially, the density has an influence on the intrinsic stress. Dense films will have a small angle between their Si–O–Si bonds leading to increased stress. Figure 4 shows how changing the deposition condition alters the energy shift of the QD. In Figure 4a,c,e, three NW PL spectra are shown before the SiO2 envelope was deposited. The SiO2 envelope of the NW in Figure 4a (NWB) was deposited under the same growth conditions as the SiO2 envelope of NWA by only increasing the silane flow from 8.5 to 15 sccm. Then, the PL of NWB was remeasured, and the results are shown in Figure 4b. The PL of NWB is red-shifted by 52 meV and the QD by 45 meV, which is a smaller shift compared to the deposition condition with 8.5 sccm silane flow.

A SiO2 envelope was also deposited on the NW in Figure 4c (NWC) using again the same growth conditions as the SiO2 envelope of NWA, but now the RF power was increased from 20 to 40 W. The results are shown in Figure 4d. The NW and QD are strongly red-shifted by 110 and 116 meV, respectively.

Figure 4f shows the PL of the exact same NW as in Figure 4e (NWD) with a SiO2 envelope that is deposited using TEOS-PECVD, which makes use of tetraethylorthosilicate (TEOS) instead of silane to deposit SiO2. Comparing the PL of Figure

![Figure 3](https://example.com/figure3.png)

**Figure 3.** PL from the QD (a) before and (b) after deposition of the SiO2 envelope. The linewidth and intensity of the exciton (X) and biexciton (XX) line are barely influenced by the SiO2 envelope.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** By changing the deposition conditions of the SiO2 envelope, the energy of the band gap can be tuned: (a) PL of the NW before SiO2 deposition, (b) PL of the same NW as in (a) with a SiO2 envelope deposited with increased silane flow. The PL is red-shifted for the NW with 52 meV and for the QD with 45 meV. (c) PL of the NW before SiO2 deposition and (d) same NW as in (c) with a SiO2 envelope deposited with increased RF power. The PL is red-shifted for the NW over 110 and 116 meV for the QD. (e) PL before SiO2 deposition and (f) same NW as in (e) with a SiO2 envelope deposited with TEOS-PECVD. The PL is now blue-shifted over 55 meV for the QD and 35 meV for the NW.
Figure 5. Evolution of the ground electron ($e_i$) and hole ($h_i$) energies and the single particle gap ($E_{gap} = e_i - h_i$) as a function of externally applied (lateral) biaxial strain for (a) InAs/InP NW−QD of 3 nm height and (b) alloyed InAs$_{0.2}$P$_{0.8}$/InP NW−QD of 8 nm. (c) Relative energy shift compared to the unstrained system for different QD configurations. Positive values correspond to tensile biaxial strain, while negative values correspond to compressive biaxial strain. The dotted lines correspond to the pseudomorphic cylinder external strain model.

4e,$fi$, it can be seen that the PL has now blue-shifted. The QD PL is blue-shifted by 55 meV and the NW PL by 35 meV.

From the measurements shown in Figure 4, we conclude that we can tune the band gap depending on the deposition conditions of the SiO$_2$ envelope. Normal SiO$_2$ PECVD deposition results in a decrease of the band gap, which is observed by a red shift of the PL. The shift can also be tuned: increasing the silane flow during the deposition decreases the red shift, while increasing the RF power leads to larger red shift. Increasing the band gap can be achieved by using TEOS as a reaction gas, which is observed as a blue shift in the PL.

Theoretical Calculations. These large shifts in PL can be explained by considering the effect of strain exerted by the SiO$_2$ envelope on the NW and the QD. We use a TB approach to calculate the electronic properties of strained NW−QDs. The SiO$_2$ envelope is simulated by applying external biaxial strain to the NW−QD system. As the details of the SiO$_2$ envelope (e.g., density, intrinsic strain) are growth-dependent35,36 (see also Supporting Information), we vary external biaxial strain from the unstrained system for different crystal orientations: [001] and [111].

Relaxation of local strain (due to lattice mismatch) and applied strain (e.g., the applied strain with SiO$_2$ envelope) on the NW and the QD. We use a TB approach to calculate the electronic properties of strained NW−QDs. The theoretical calculations show the results of the calculations for disk-like In$_x$As$_{1-x}$/InP NW−QD of 8 nm height. Such size, shape, and composition correspond to the structural properties of the quantum dot experimentally studied in this work: the TB calculated excitonic emission is in good agreement with the observed value of $\sim$1.3 eV for the as-grown QD. Due to the alloying, the internal strain is reduced to a small value ($\sim$0.5%). The lack of a significant internal strain leads to a more pronounced gap evolution with respect to the external tensile strain for an In$_x$As$_{1-x}$/InP system. Already a tensile biaxial strain on the order of 0.75% is sufficient to induce a $\sim$50 meV red shift of the single particle gap, while 2% tensile strain red shifts the emission peak by almost 200 meV. However, in the compressive strain regime, we again notice a small gap variation due to the cancelation of the electron and hole contributions.

The optical gap observed in the experiment is dominated by the contribution from the single particle gap but is also reduced by the electron−hole Coulomb attraction. We thus calculated the electron−hole Coulomb integral for electron and hole in their ground states for the considered In$_x$As$_{1-x}$/InP QD system. We found this value to be close to 16 meV and not varying significantly with the external strain within the considered strain magnitudes.

In Figure 5c, we study the relative excitonic emission peak shift as a function of externally applied strain for several systems of different size and composition. The reference point matches the emission at zero external strain for each of the considered systems. As expected from the previous analyses, NW−QD systems with larger arsenic content reveal a smaller shift of the effective gap under external tensile strain due to the countering action of the internal strain. We also investigate the effect of strain for different crystal orientations: [001] and [111]. For
tensile strain, there is little quantitative difference between the two considered crystal orientations. However, for compressive strain, there is a noticeable difference between the two orientations due to different deformation potential values for large compressive [111] and [001] strains.

In Figure 5c, results obtained for an external strain model assuming strain distribution similar to that in an infinitely long cylinder are shown for an 8 mm InAs$_{0.6}$Ga$_{0.4}$As$_{0.3}$ InP$_{0.7}$ QD. Both models agree well for tensile strain, yet there is a pronounced difference for compressive strain.

The experimentally observed QD red shifts can be related to \sim 0.74, \sim 1.1, and \sim 1.35% strains for the observed 45, 83, and 116 meV shifts, respectively. For these magnitude shifts, the pseudomorphic cylinder model predicts \sim 0.55, \sim 1.0, and \sim 1.42% strains correspondingly.

The 55 meV blue shift observed for one of the samples is related to a compressive strain with a magnitude larger than 2%, should we assume external strain distribution analogous to that in a piezoelectric actuator. However, the same shift is achieved with only 0.66% compressive strain for an infinitely long cylinder model. As the proposed models are extreme cases, the strain in the real NW system is a combination of the two models. Therefore, the real compressive strain in the NW giving the observed blue shift is between 0.66 and 2%. For the measured red shifting of the QDs, the models predict similar values of strain.

**Conclusion.** We have used a very simple, but powerful, method based on a SiO$_2$ envelope deposition to red or blue shift the NW and QD emission energy over 200 meV. Such an extreme energy shift is achieved as a result of strain acting on the NW and QD. We demonstrate that our method preserves the QD optical quality. We observe no degradation of the linewidth within our spectral resolution and no large changes in intensity. Using TB calculations, we estimated the strain and we conclude that our technique allows one to vary the strain between a maximal 2% compressive and 1.42% tensile strain.

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