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Strong modification of the reflection from birefringent layers of semiconductor nanowires by nanoshells

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The propagation of light in layers of vertically aligned nanowires is determined by their unique and extreme optical properties. Depending on the nanowire filling fraction and their diameter, layers of nanowires form strongly birefringent media. This large birefringence gives rise to sharp angle dependent peaks in polarized reflection. We demonstrate experimentally the tunability of the reflection by adding shells of SiO_2 with thicknesses ranging from 10 nm to 30 nm around the nanowires. The strong modification of the reflection peaks renders nanowire layers as a promising candidate for sensing applications. © *2011 American Institute of Physics*. [doi:10.1063/1.3662393]

Recent progress in nanofabrication technology has opened avenues in the research of semiconductor nanowires. The high control of nanowire dimensions,[1] position,[2] growth direction,[3] and doping[4] results in effective media with unique optical properties. The large aspect ratio of nanowires results in a large optical anisotropy,[5–8] which leads to giant form birefringence in layers of aligned nanowires.[9] A consequence of the giant birefringence is a peak in the reflection contrast.[10,11]

In this manuscript, we demonstrate experimentally that the narrow peaks in the reflection contrast of birefringent layers of nanowires are sensitive to small changes in the refractive index of the medium surrounding the nanowires. Specifically, we determine a large shift of the reflection contrast as a function of angle of incidence by coating the nanowires with SiO_2 shells. Our results demonstrate that the layers of semiconductor nanowires are promising candidates for sensing applications.

We have grown layers of GaP nanowires on a GaP substrate using the vapor-liquid-solid growth mechanism[12] by metal-organic vapor phase epitaxy.[9] Figure 1(a) shows a cross-sectional scanning electron micrograph (SEM) of the nanowire layer. The thickness of the layer is 1 ± 0.1 μm, and the average nanowire diameter is 33 ± 9 nm. The average distance between nanowires is in the range of 100–200 nm. To determine the modification of the reflection from nanowire layers to small changes in their surrounding, we have cleaved the sample into five pieces and coated the nanowires in four of these pieces with SiO_2 shells of different thicknesses by plasma-enhanced chemical vapor deposition (PECVD). The fifth sample was left as a reference. The average SiO_2 shell thicknesses and its standard deviation, determined by performing transmission electron microscopy (TEM) on several nanowires, is 10.3 ± 1.3 nm, 16.7 ± 2 nm, 18.6 ± 1.1 nm, and 29.3 ± 4.7 nm. Figure 1(b) shows a TEM image of a coated nanowire. The SiO_2 shell has a constant thickness over the nanowire length, indicating a good infiltration of the nanowire layer during the PECVD. The nanowire contains defects, which are twin planes perpendicular to the growth direction. The gold particle used to catalyze the growth is visible on top of the nanowire. Both the defects and the gold have no effect on the properties discussed next.[9,11]

Layers of aligned nanowires form birefringent media with ordinary, n_o, and extraordinary, n_e, refractive indices for light polarized perpendicular and parallel to the nanowire axis, respectively.[9] We have measured the angularly resolved reflection contrast using linearly polarized light from a diode-pumped solid-state laser emitting at a wavelength of 532 nm. The sample and detector were mounted on two computer controlled rotational stages for measuring the specular reflection. A Glan-Taylor polarizer was placed in front of the detector for analyzing the polarization of the reflected light. The sample was rotated around the axis perpendicular to the nanowire elongation. The incident polarization was set at 45° with respect to the plane of incidence, defined by the

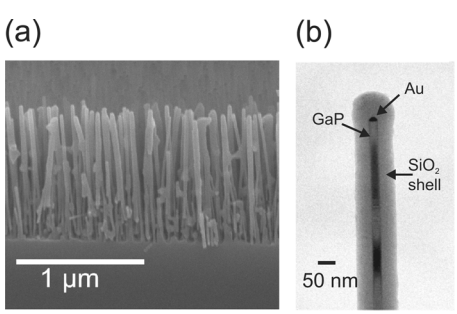

FIG. 1. (a) Cross-sectional SEM image of a sample of GaP nanowires. (b) TEM image of a nanowire covered with a thin shell of SiO_2.

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k-vector of the incident plane wave and the nanowire axis. Two measurements of the specularly reflected intensity were performed to determine the reflection contrast: the first measurement with the analyzer aligned nearly parallel, $I_{\parallel}$, and the second with the analyzer aligned nearly perpendicular, $I_{\perp}$, to the direction of the incident polarization. The reflection contrast is given by $I_{\perp}/I_{\parallel}$. To increase the reflection contrast, the orientation of the analyzer was optimized in order to achieve a minimum intensity for (nearly) parallel alignment and a maximum intensity for (nearly) crossed alignment. These small adjustments were necessary to compensate for the polarization dependent Fresnel reflection at the interfaces.

We have measured the reflection contrast of the samples as a function of the angle of incidence using a beam diameter of 2 mm. Figure 2(a) shows these measurements for the uncoated sample and for the coated samples with shell thicknesses of 10.3 ± 1.3 nm, 16.7 ± 2 nm, 18.6 ± 1.1 nm, and 29.3 ± 4.7 nm. The maximum reflection contrast of the uncoated nanowire sample is 162 and the full-width at half maximum (FWHM) is 1.8°. This maximum shifts to larger angles of incidence with increasing shell thickness. The peaks are due to the birefringence of the nanowire layer resulting from the large geometric anisotropy introduced by the nanowires and can be explained as follows. The incident light with a polarization at an angle of 45° with respect to the plane of incidence can be split into s- and p-components. S-polarized light has the electric field component oriented perpendicularly to the nanowire axis for any angle of incidence. The refractive index experienced by this polarization, $n_{s,}$ corresponds to the ordinary refractive index of the birefringent nanowire layer, i.e., $n_s = n_o$. P-polarized light has an electric field component perpendicular and another parallel to the nanowire axis, which varies with the angle of incidence. The refractive index for this polarization, n_p, depends on the angle of incidence (θ) and on the ordinary (n_o) and extraordinary (n_e) refractive indices according to the relation[13]

$$n_p = \sqrt{n_o^2 + \frac{n_e^2 - n_o^2}{n_e^2} \cdot \sin^2\theta}. \quad (1)$$

The difference between n_s and n_p introduces a phase shift between s- and p-polarized light while traveling through the nanowire layer. This phase shift depends on the layer thickness L, the vacuum wavelength λ, the refractive indices $n_{s,p}$,

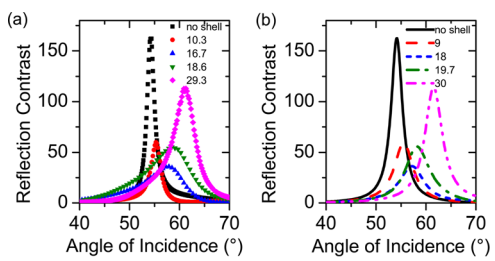

FIG. 2. (Color online) Measured reflection contrast as a function of the angle of incidence of a sample of GaP nanowires, and of similar samples in which the nanowires have been coated with SiO_2 shells. (b) Fits to the measurements.

and the internal angles of propagation $\theta_{s,p}$ for s- and p-polarizations, respectively, which are related to the angle of incidence by Snell's law. The phase shift is given by $\Delta\phi = \frac{4\pi}{\lambda} L(n_p \cos\theta_p - n_s \cos\theta_s)$.[10] If $\Delta\phi$ equals π, the nanowire layer forms a $\lambda/2$-plate and the polarization is rotated by $\pi/2$ rad, resulting in a maximum of $I_{\perp}$ and a concomitant minimum of $I_{\parallel}$. The reflection contrast in this case is maximum.

The reflection contrast can be quantitatively modeled using Maxwell-Garnett effective medium theory for core-shell cylinders[14] and Jones calculus for a three layer system consisting of air, nanowires, and the substrate.[15] The ordinary refractive index of core-shell cylinders surrounded by a dielectric medium can be determined by solving the static field equation (Laplace's equation), giving rise to the Maxwell-Garnett formula[14]

$$n_o = n_s = \left[1 - \frac{2f_{cs}}{\gamma_1 + f_{cs}}\right]^{\frac{1}{2}}, \quad (2)$$

with

$$\gamma_1 = \frac{r_c^2(\epsilon_s - \epsilon_c)(\epsilon_d - \epsilon_s) + r_s^2(\epsilon_s + \epsilon_c)(\epsilon_d + \epsilon_s)}{r_c^2(\epsilon_s - \epsilon_c)(\epsilon_d + \epsilon_s) + r_s^2(\epsilon_s + \epsilon_c)(\epsilon_d - \epsilon_s)}, \quad (3)$$

where r_c is the average radius and ϵ_c the permittivity of the core, r_s the average radius of the core-shell nanowire and ϵ_s the permittivity of the shell, surrounded by a dielectric with the permittivity $\epsilon_{d.}$ The filling fraction of the coated nanowires is calculated using $f_{cs} = \pi r_s^2/d_{nw}^2$ with d_{nw} the average distance between the midpoints of two nanowires. The Maxwell-Garnett formula is valid when the diameter of the core-shell cylinder is much smaller than the wavelength of the incident light. To determine the extraordinary refractive index, the following considerations have to be made.[18] The electric field is parallel to the core-shell cylinder axis, i.e., tangential to the nanowire interfaces. As the tangential component of the electric field is continuous at an interface, the electric field is the same in the dielectric and in the core-shell cylinder. The electric displacements in each region are defined by the product of the square of the respective refractive index and the electric field. The effective displacement is given by the geometrical average of the displacements in the core, shell, and dielectric. From the effective displacement, the refractive index can be determined as the square root of the ratio of the effective displacement and the electric field, resulting in Ref. 16,

$$n_e = \sqrt{f_c\epsilon_c + f_s\epsilon_s + (1 - f_c - f_s)\epsilon_d}, \quad (4)$$

with $f_c = \pi r_c^2/d_{nw}^2$ and $f_s = f_{cs} - f_c$.

We have determined the reflection contrast using the core radius, the average distance between the nanowires, the shell thickness, and angle of the polarizer as fitting parameters. Figure 2(b) shows the fit to the measurement for the uncoated nanowires. The core radius of the nanowires obtained from this fit is $r_c = 19.4 \pm 1$ nm, and the distance between the nanowires is $d_{nw} = 160 \pm 10$ nm. The error in these quantities is obtained by fitting them independently to achieve a good agreement with the measurements in the peak position and

width. The birefringence parameter $\Delta n = n_e - n_o$ can be derived with Eqs. (2)–(4) to be 0.19 ± 0.1.

Fits of the reflection contrast for core-shell nanowires are given in Figure 2(b). From the fits, we obtain shell thicknesses of 9 ± 1 nm, 18 ± 1 nm, 19.7 ± 1 nm, and 30 ± 1 nm. Within the uncertainty of these values, they are in agreement with the shell thickness determined from TEM images. The measurements and calculations show that a SiO_2 shell with a thickness of ~10 nm shifts the peak of the reflection contrast by ~1° (red circles and dashed curve). Therefore, the measurement of the reflection contrast allows an accurate determination of the thickness of nanoshells.

The refractive index of SiO_2 ($n = 1.45$) at 532 nm is similar to the refractive index of biomolecules in the visible.[17] Therefore, the strong dependence of the reflection contrast of nanowire layers by nanometric shells renders these structures very interesting as sensor for functionalized surfaces. To quantify the sensitivity of the reflection contrast to changes in the medium surrounding the nanowires, we have analyzed the peak shift as a function of the product of $\Delta n \cdot t$, being Δn the difference in the refractive index of the shell and the surrounding medium, i.e., air in our case, and t the shell thickness. Figure 3 shows the peak shift obtained from the measurements and from the calculations. The calculated shift follows a parabolic dependence. We have determined the sensitivity of the shift of the reflection contrast, with the change in the refractive index and the thickness of the shell, $\frac{d(\Delta\theta)}{d(\Delta n \cdot t)}$. The inset of Figure 3 displays this sensitivity as a function of $\Delta n \cdot t$. The sensitivity follows a line with a slope of ~0.05°/(nm · RIU), where RIU is a refractive index unit. Higher sensitivities are obtained with thicker shells of high index materials. The overall high sensitivity of the reflection contrast can be attributed to the large surface to volume ratio of nanowires, which allows probing minute changes in their surrounding.

Finally, it should be mentioned that the reflection contrast can be increased by reducing the size of the incident beam. This reduction allows the measurement of small sample areas in which inhomogeneities in the nanowire dimensions and density are less probable. Measurements with a beam diameter smaller than 1 mm (not shown here) on the nanowire layer without SiO_2 shell exhibit a maximum in the reflection contrast of 2450 and a FWHM of 0.63° in contrast with the maximum reflection of 162 and FWHM of 1.8° measured with a beam diameter of 2 mm (see Fig. 2). This extremely narrow peak in the reflection is sensitive to changes in the average nanowire diameter as small as one monoatomic layer.

In conclusion, we have demonstrated that the reflection contrast measured on birefringent layers of nanowires exhibits narrow peaks that are sensitive to changes in the surrounding of the nanowires. We have measured the shift of the reflection contrast peak by coating the nanowires with shells of SiO_2 with different thicknesses finding that a shell with a thickness of only ~10 nm shifts the reflection contrast by ~1°. The large sensitivity of the reflection from nanowire layers to minute changes in the medium surrounding the nanowires renders these layers as a promising material for sensing applications.

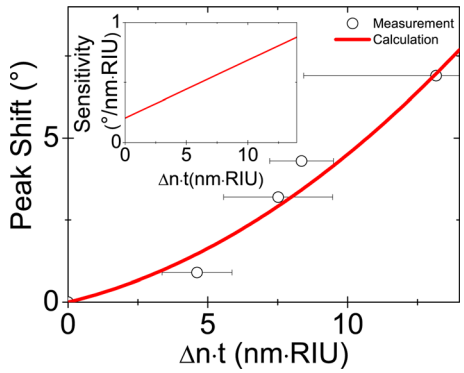

FIG. 3. (Color online) Measured and calculated shift of the peak in reflection contrast as a function of the product of the SiO_2 thickness, t, and the difference in refractive index Δn, between the shell and the surrounding medium. The inset shows the sensitivity of the shift as a function of $\Delta n \cdot t$.

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