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Phonon Confinement Effects in Hybrid Virus-Inorganic Nanotubes for Nanoelectronic Applications

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ABSTRACT

Genetically modified viruses have been proposed recently as templates for the assembly of nanometer-scale components of electronic circuits. Here we show that, in addition to their role as nanotemplates, viruses can actually improve the electron transport properties in semiconductor nanotubes grown on them. In the considered hybrid virus-inorganic nanostructures, which consist of silica or silicon nanotubes deposited on tobacco mosaic viruses, the confined acoustic phonons are found to be redistributed between the nanotube shell and the acoustically soft virus enclosure. As a result, the low-temperature electron mobility in the hybrid virus-silicon nanotube can increase by a factor of 4 compared to that of an empty silicon nanotube. Our estimates also indicate an enhancement of the low-temperature thermal conductivity in the virus-silicon nanotube, which can lead to improvements in heat removal from the hybrid nanostructure-based nanocircuits.

In a continuous effort to the ultimate miniaturization of computer electronic circuits, nanowires, and nanotubes, as thin as a few atoms in diameter, have been employed recently.[1] The performance of such nanocircuits can be enhanced greatly by increasing the electron mobility and thermal conductivity in constituent nanowires and nanotubes. The former can be achieved by suppressing the inelastic scattering of electrons on phonons, whereas the latter can be achieved by properly tuning the acoustic phonon modes, which carry the bulk of the heat.[2−5] Genetically modified viruses, as "smart" nanotemplates for the chemical assembly of nanowire-interconnects and circuit elements, present one of the recent developments in the field.[6−8] Understanding the lattice vibration, that is, phonon, properties of such hybrid bioinorganic nanostructures is of great interest from the fundamental science point of view.

In this Letter we consider inorganic nanotubes grown on plant viruses, which are used as nanotemplates.[6,7] We show, for the first time, that the viruses, previously thought of only as nanotemplates, can actually improve the electronic and thermal properties of the inorganic nanotubes grown on them because of the phonon confinement and redistribution effects in the acoustically mismatched hybrid nanostructures. It is demonstrated that the electron−phonon scattering in such hybrid nanotubes can be suppressed at low temperature. Our results suggest that the genetically programmed viruses,[8] such as the tobacco mosaic virus (TMV), may serve not only as vehicles for the self-assembly[9,10] and ordering[11,12] of nanostructures for nanoelectronic circuits but may also enhance the performance of the resulting circuits via the proposed phonon engineering approach.

During the past few years there have been a number of reports on theoretical and experimental investigations of phonon modes in inorganic and organic nanowires.[2,4,13] The spatial confinement and quantization of phonon modes in such nanostructures was shown to influence their thermal and electronic properties.[14,15] At the same time, the phonon modes in coated nanowires, consisting of layers of materials with strongly dissimilar elastic properties, let alone in the hybrid bioinorganic nanostructures, have not been considered so far. It is well known that electronic states undergo strong modifications in such nanowires and quantum dots.[16−18] To answer the question if there are any unusual and practically important changes in the vibrational properties of hybrid bioinorganic nanostructures, we consider a real 3-nm-thick silica (silicon) nanotube grown on the 18-nm-in-diameter TMV.[6] In the following, we study the changes in the phonon dispersion, density of states, phonon spatial distribution, and low-field electron mobility of the hybrid virus/silica (virus/silicon) nanotubes in comparison to empty silica (silicon) nanotubes.[19,20] The TMV-based nanotubes were selected as example hybrid systems because of the promises of robust TMVs as nanotemplates for chemical nanostructure self-assembly.[6,7] The benefits of TMVs as nanotemplates include

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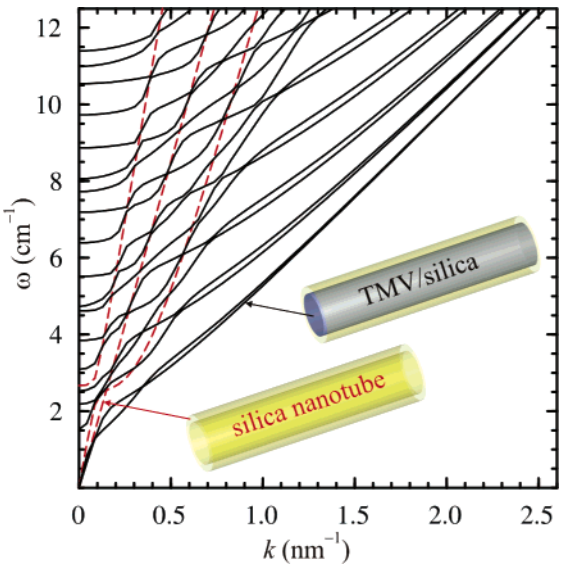

Figure 1. Dispersion of axially symmetric phonon modes ($m = 0$) for TMV/silica and empty silica nanotubes.

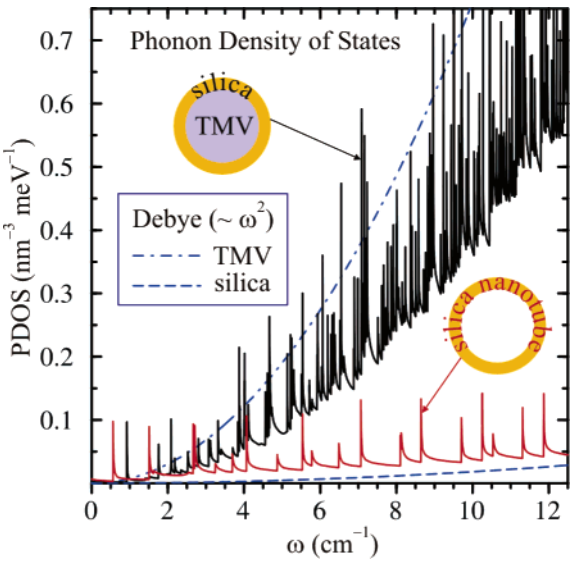

Figure 2. Phonon density of states (PDOS) for TMV/silica and empty silica nanotubes as a function of phonon frequency. PDOS within the Debye model is shown with the dash−dotted line for TMV and with the dashed line for silica.

the right size and shape, small size variation, ability to form end-to-end assemblies, as well as the attachment selectivity.

To understand the vibrational, thermal, and electronic properties of the hybrid virus-inorganic nanotubes, one has to know all of the quantized phonon modes for a given nanostructure. Following a standard technique,[21] we find the vibrational modes of the considered cylindrical heterostructures as eigenmodes of the equation of motion for the displacement vector **u**.[13,14] Because of the axial symmetry of the problem, the equation of motion can be solved analytically in cylindrical coordinates (r, ϕ, z) and the time-dependent displacement vector can be written as

$$\mathbf{u}(r,\phi,z,t) = \mathbf{w}_{m,n}(r,k)\exp(im\phi + ikz - i\omega_{m,n}(k)t) \quad (1)$$

where m is the angular quantum number, k is the axial wavenumber, n is the number of different phonon modes with the same m and k, ω is the phonon frequency, and **w** is the normalized radial vibration amplitude. The material parameters of the virus, silica (TEOS), and silicon used in the simulation are listed in ref 22. It can be shown (see ref 23) that no interface acoustic phonons appear in the considered hybrid nanotubes; therefore, all phonon modes are confined. We have calculated all of the relevant phonon modes as the functions of k for a large number of integer quantum numbers, m. The dispersion of the lowest axially symmetric phonon frequencies ($m = 0$) is shown in Figure 1 for the hybrid TMV/silica nanotube and for the empty 3-nm-thick silica nanotube. It is seen that the presence of the "acoustically soft" TMV core, which has a velocity of sound three times lower than that of the nanotube,[22] makes the phonon spectrum denser and decreases the slope of the dispersion curves. The phonon frequencies with $m \neq 0$ are twice degenerate with respect to the sign of m. Let us note that the dispersion of phonon frequencies with $m \neq 0$ is qualitatively similar to that of $m = 0$ frequencies and can be sketched as the curves from Figure 1 shifted to the larger frequencies by approximately $|m| \times 0.7$ cm^{-1}.

Once the phonon modes are known, it is straightforward to calculate the phonon density of states (PDOS) for the hybrid nanostructure using the definition

$$g(\omega) = \frac{1}{\pi S}\sum_{m=-\infty}^{\infty}\sum_{n=1}^{\infty}\int_0^{\infty}\delta(\omega - \omega_{m,n}(k))\,dk \quad (2)$$

where S is the total cross-section area and δ is the Dirac delta function. Figure 2 shows PDOS calculated from eq 2 for TMV/silica and empty silica nanotubes as a function of the phonon frequency. The van Hove singularities, characteristic of one-dimensional nanowires, are seen clearly in PDOS. As expected from Figure 1, the PDOS of the hybrid TMV/silica nanotube is much larger than that of the empty silica nanotube. It is illustrative to compare the calculated PDOS with PDOS resulting from the Debye model. In the Debye model, only three acoustic phonon modes are taken into account and PDOS is calculated as $g^{\text{Debye}}(\omega) = (\omega^2/2\pi^2)((1/V_l^3) + (2/V_t^3))$, where V_l and V_t are longitudinal and transverse sound velocities, respectively.[22] It can be shown that the Debye PDOS reproduces the PDOS of homogeneous nanowires fairly well, calculated using eq 2. Therefore, a strong deviation of PDOS of the hybrid and empty nanotubes from the Debye PDOS is an important feature of these nanostructures.

For the description of physical properties of the hybrid nanotubes, it is convenient for one to introduce three physical regimes that correspond to three partially overlapping intervals of the phonon energy. The low-energy regime describes phonons with the energies below ~3 cm^{-1}. In this regime the "acoustically hard" nanotube shell and the acoustically soft virus core are coupled strongly and move together (the stiffness is characterized by the acoustic impedance $\zeta = \rho V$, where ρ is the mass density and V is the sound velocity). As a result, one can see from Figure 2 that

the PDOS of the hybrid and empty nanotubes in the low-energy regime are close to each other and very different from the corresponding Debye PDOS. In this regime, the phonon modes of the hybrid system are considerably different from the modes of either the virus core or the nanotube shell alone.

The medium-energy regime includes phonons with the energies above ~3 cm^{-1} and below the Debye cutoff frequency of the acoustically soft virus core, which is about 50 cm^{-1} for organic crystals. In this regime, the nanotube shell and the virus core are rather decoupled from each other so that one can think of the system as having a core and a shell, which support their own separate vibrational modes. As a result, one can see from Figure 2 that the PDOS of the hybrid nanotube in the medium-energy regime is close to the volume average of the virus and nanotube Debye PDOS. Indeed, because the PDOS of the nanotube is much smaller than that of the virus and the volume of the nanotube is approximately equal to the volume of the virus, the volume average PDOS should be about one-half of the virus PDOS.

Finally, the high-energy regime deals with phonons with the energies above 50 cm^{-1} (this region is not shown in Figures 1 and 2). The nanotube shell and the virus core are still decoupled in this region. However, the acoustically soft virus will not support modes at these high energies (above the Debye cutoff frequency of the virus). Thus, all of the vibrational modes in this regime are localized in the nanotube and the presence of the soft core has no effect on the phonons in the nanotube. Because we are concerned mainly with the low-temperature physics of the hybrid nanotubes, the high-energy regime is not considered in this Letter.

To quantitatively characterize the phonon redistribution in the "acoustically soft core−acoustically hard shell" hybrid nanotube, we calculate the probability of finding a phonon at a given location as a function of the distance from the center of the nanotube. It is defined as

$$p(r,\omega) = \frac{r}{N_\omega} \sum_{m=-\infty}^{\infty} \sum_{n=1}^{\infty} |\mathbf{w}_{m,n}(r,k)|^2_{\omega_{m,n}(k)=\omega}$$

where N_ω is the number of phonon modes with frequency ω and $\mathbf{w}$ is determined from eq 1. Note that $\int_{R_1}^{R_2} p(r,\omega)\, dr$ is equal to unity, when $R_1 = 0$ and R_2 is the external radius of the hybrid nanotube. At the same time, when R_1 is the radius of TMV, the above integral gives the probability of phonon presence inside the silica (silicon) shell of the hybrid nanotube. The probability of finding a phonon inside the "hard" shell of the nanotube is plotted in Figure 3a as a function of the phonon frequency for TMV/silica and TMV/silicon hybrid nanotubes. It is seen that the probability of phonon presence inside the silica (silicon) nanotube is small and decreases inversely proportional to the phonon frequency. When the phonon frequency is only 10 cm^{-1}, the probability of finding a phonon in the shell is about 1/20 (1/40) for the hybrid silica (silicon) nanotube. In other words, the presence of the acoustically soft yet robust virus inside the acoustically hard silica (silicon) nanotube decreases the probability of finding a phonon in the nanotube by 20 (40) times compared to the empty nanotube.

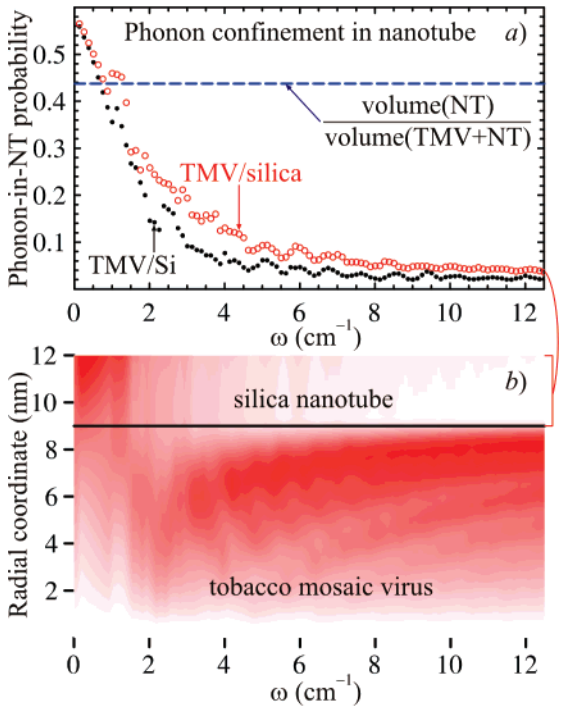

Figure 3. (*a*) Probability of finding a phonon inside the inorganic nanotube as a function of the phonon frequency for TMV/silica and TMV/silicon hybrid nanotubes. (*b*) Probability of finding a phonon as a function of the distance from the center of hybrid TMV/silica nanotube and phonon frequency. The intensity of the red color is proportional to the probability of finding a phonon.

The phonon-in-nanotube probability is lower for the silicon nanotubes than it is for silica nanotubes because of a higher sound velocity in silicon[22]. Figure 3b shows the distribution of the probability $p(r,\omega)$ for the hybrid TMV/silica nanotube. A substantial decrease of the phonon-in-nanotube probability is observed for phonon frequencies larger than 2 cm^{-1}. A very low probability of finding a phonon in the acoustically hard silicon shell and corresponding high probability of finding a phonon in the acoustically soft virus nanotemplate core holds promise for manipulating the thermal conductivity of hybrid nanostructures. If the phonons are present mainly in the virus core, then the thermal conductivity of the hybrid nanotube will be close to that of the virus. Following the prescription of ref 14, we have estimated the thermal conductivity of TMV to be 2−10 times larger than that of a silicon nanotube for temperatures up to 30 K. Modification of the thermal conductivity in the acoustically mismatched hybrid nanostructures can potentially be important for heat removal and biological applications.

The described effect leads to changes in the thermal conductivity but does not imply the increase of the charge carrier mobility in the silicon shell because the charge carriers are present mainly inside the silicon shell and, as mentioned above, the absolute number of phonons in the silicon shell does not decrease in the presence of the virus core. At the same time, the phonon spatial confinement and redistribution in the hybrid nanotube leads to the increase of the electron mobility in the low-energy regime for the acoustic phonons. To demonstrate this, we consider the carrier mobility in

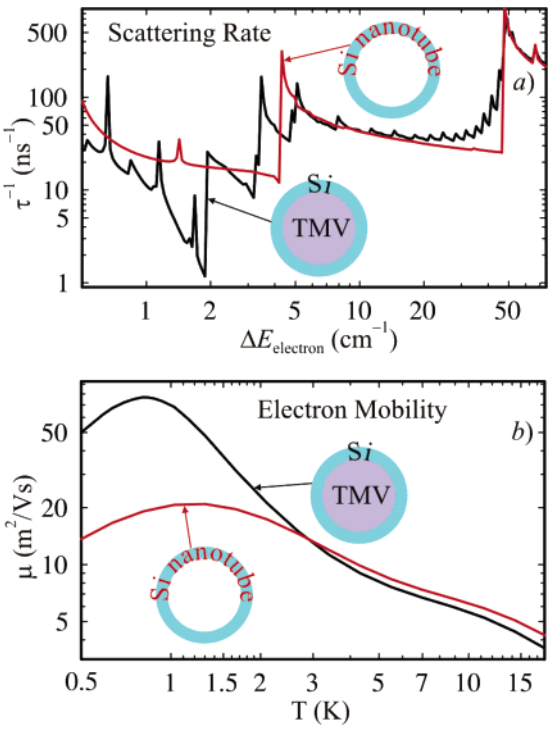

Figure 4. (*a*) log−log plot of the electron−phonon scattering rates ($T = 1$ K) for TMV/silicon and empty silicon nanotubes as a function of the electron energy above the band gap. (*b*) log−log plot of the low-field electron mobility for TMV/silicon and empty silicon nanotubes as a function of temperature.

silicon nanotubes, which is limited at low temperature by scattering on acoustic phonons.[24]

The low-field acoustic-phonon-limited electron mobility is calculated in the relaxation time approximation as $\mu = (e/m^*)\langle\tau\rangle$,[25] where e is the electron charge, m^* is the electron effective mass (see ref 22), and τ is the relaxation time (as a function of electron energy above the band gap). The electron−phonon scattering rate has been calculated according to ref 26 and using parameters from ref 22. In the calculation, we assumed that the electron wave function is localized in the nanotube and does not penetrate into the virus core because of the large potential barrier. Density function theories have been used to study electron transport in silicon nanowires.[27] The relatively large diameter and thickness of the silicon nanotubes allowed us to employ the effective-mass approximation, which is valid even for shells as thin as a few monolayers.[17]

Figure 4a shows the calculated electron−phonon scattering rate at $T = 1$ K. It is seen that the presence of the "soft" virus core leads to the strong scattering rate suppression in hybrid virus-inorganic nanotubes at the low electron energies above the band gap. The obtained scattering rate suppression translates into the increase of the low-temperature electron mobility, which is shown in Figure 4b. One can see that the electron mobility in the hybrid TMV/silicon nanotube becomes up to 4 times larger than the mobility of an empty silicon nanotube for temperatures around 3 K.

In conclusion, we investigated the confined acoustic phonon redistribution effects in the hybrid bioinorganic nanostructures such as silica (silicon) coated plant viruses. It was shown that the presence of the acoustically soft virus template inclusion leads to the strong decrease of the probability of finding a phonon inside the acoustically hard nanotube shells and results in the increase of the thermal conductivity. The observed phonon redistribution also leads to a completely new method for the charge carrier mobility enhancement in nanostructures made of acoustically mismatched materials. We demonstrated that the low-temperature electron mobility of silicon nanotubes can be enhanced up to 4 times in the presence of an acoustically soft core.

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