Phonon engineering in nano-devices and virus-based nano-templates

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ABSTRACT

Phonons, i.e. quanta of lattice vibrations, manifest themselves practically in all electrical, thermal, optical and noise phenomena in semiconductors and other material systems. Reduction of the size of electronic devices below the acoustic phonon mean free path creates a new situation for the phonons propagation and interaction. From one side, it may complicate heat removal from the downscaled devices. From the other side, it opens up an exciting opportunity for re-engineering phonon spectrum in nanostructured materials, and achieving enhanced operation of nano-devices. Since phonon-assisted tunneling and carrier scattering on phonons affect the charge carrier transport, modification of the phonon spectrum is also expected to influence noise level in nano-devices. This paper reviews the development of the phonon-engineering concept and discusses its device applications. The focus of this review is on tuning the phonon spectrum in acoustically mismatched nano- and heterostructures in order to change the ability of semiconductors to conduct heat and electric current. New approaches for the electron – phonon scattering rates suppression and the carrier mobility enhancement are also discussed. The last section of this review describes our recent results on phonons in the rod-shaped viruses used as biological nano-templates for self-assembly of nanoelectronic circuits.

Keywords: confined phonons, phonon engineering, acoustically mismatched nanostructures, virus nanotemplates, hybrid bio-inorganic nanostructures

1. INTRODUCTION

Phonons[1] are quantized modes of vibration occurring in a rigid crystal lattice, such as the atomic lattice of a solid. One can speak of a gas of phonons, which are quasi-particles of the energy $\hbar\omega$ and quasi-momentum $p=\hbar q$ obeying Bose-Einstein statistics [1]. Phonons manifest themselves practically in all properties of materials. For example, acoustic and

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[1] Plenary invited talk at the SPIE conference Noise and Information in Nanoelectronics, Sensors, and Standards III.

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optical phonons limit electrical conductivity. Optical phonons strongly influence optical properties of semiconductors while acoustic phonons are dominant heat carriers in insulators and technologically important semiconductors. Long-wavelength phonons gives rise to sound waves in solids, which explains the name phonon. Phonons also affect the noise levels in electronic devices. Although, depending on the noise type the role of the phonons and their importance vary. For example, different theoretical descriptions of the low-frequency noise include phonon in rather different capacity.

Similar to electrons, one can conveniently characterize the properties of phonons by their dispersion $\omega(q)$, i.e. dependence of the phonon frequency ω on its wave vector q. In bulk semiconductors with g atoms per unit cell, there are $3g$ phonon dispersion modes for every value of q. In the limit of long waves, three modes describe the motion of the unit cell, and form the three acoustic phonon branches. The other $3(g\text{-}1)$ modes describe the relative motion of atoms in a unit cell, and form the optical phonon branches. Acoustic phonons in bulk crystals have nearly liner dispersion, which can be written as $\omega=V_S q$ (where V_S is the sound velocity). Optical phonons, in general, are nearly dispersion-less for small q values (long-wavelength approximation) and have a small group velocity $V_G=d\omega/dq$.

Spatial confinement of acoustic phonons in hetero- and nanostructures can strongly affect the phonon dispersion and modify phonon properties such as phonon group velocity, polarization, density of states as well as affect phonon interaction with electrons, point defects, other phonons, etc. Modification of the acoustic phonon dispersion is particularly strong in freestanding thin films and nanostructures or in nanostructures embedded into elastically dissimilar materials. Such modification may turn out to be desirable for some applications while detrimental for others. Thus, nanostructures offer a new way of controlling phonon transport via tuning its dispersion relation, i.e. *phonon engineering* [2]. The concept of engineering the phonon dispersion in nanostructures has the potential to be as powerful as the concept of the band-gap engineering for electrons, which revolutionized the electronic industry. In this paper I focus on confined acoustic phonons in hetero- and nanostructures. The first sections of this review deals with conventional semiconductor materials while the last section describes phonons in viruses used as nano-templates for nanofabrication.

2. SPATIAL CONFINEMENT OF THE ACOUSTIC PHONONS

The idea of looking at the changes that acoustic phonon spectrum experiences in heterostructures has a rather long history. In 50s, Rytov published a series of theoretical papers [3] where he analyzed acoustic vibrations in "artificial thinly-laminated media" (something, which now would be referred to as a superlattice) and described folded phonons in such media. The folded acoustic phonons were later observed in quantum well superlattices made of different semiconductors [4]. In 80s and early 90s there have been large amount of theoretical work done aimed at calculating the confined acoustic phonon – electron scattering rates in freestanding thin films and nanowires. Some notable examples of this work include papers from the research groups of Stroscio [5], Mitin [6], Nishiguchi [7] and Bandyopadhyay [8]. Many papers on the subject used the elastic continuum approach for calculating phonon dispersion and adopted solution techniques developed in acoustics and mechanics. The prime motivation was to see if the spatial confinement and quantization of the acoustic phonon modes in freestanding thin films or nanowires produces noticeable effect on the deformation potential scattering of electrons. The opinions were split about how important the acoustic phonon

confinement in the description of electron transport in low-dimensional structures. Some theorists argued that the phonon-confinement induced changes for macroscopic characteristics, such as carrier mobility, are not pronounced [7, 9]. Others have found that the deformation potential scattering can be substantially suppressed for certain electron energies [6, 8].

The interest to the subject has been renewed when Balandin and Wang [10] pointed out that the confinement-induced changes in the acoustic phonon dispersion may lead to strong effect on the lattice thermal conductivity. Decreased averaged phonon group velocity in freestanding thin films or nanowires leads to the increased acoustic phonon relaxation on point defects (vacancies, impurities, isotopes, etc.), dislocations, as well as in three-phonon Umklapp processes [11]. Thermal conductivity reduction, being a bad news for thermal management of downscaled electronic devices, is good news for the thermoelectric devices, which require materials with high electrical conductivity and low thermal conductivity [12]. Subsequently, it has been have theoretically shown [13-14] that in the thin films or nanostructures embedded in the "acoustically fast" materials (materials with larger sound velocity), the phonon group velocity and thermal conductivity can be enhanced along certain directions (see Fig. 1). A possibility of forming phonon stop-bands in quantum dot superlattices and inhibition of the thermal conductivity, beneficial for thermoelectric applications has also been predicted [15]. As a result, the concept of phonon engineering has been expanded to include tuning of the acoustic phonon transport to achieve the desired thermal conductivity of the material. Due to the continuing reduction in the electronic device feature size and increased integration densities, the thermal management at nanoscale gains a particular importance.

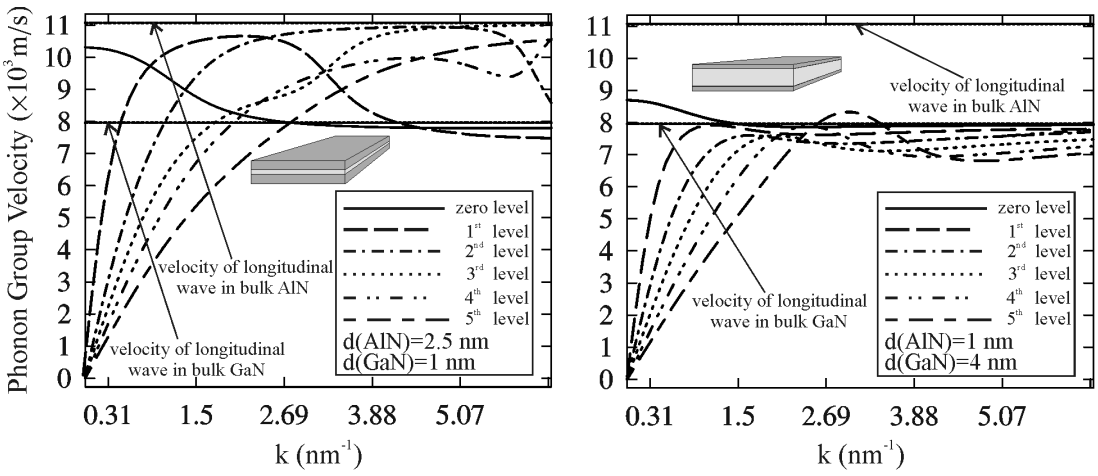

Figure 1: Phonon group velocity for confined potential acoustic phonon branches as a function of the phonon wave vector in a three-layered heterostructure. The results are shown for (left panel) the "thin core-layer – thick cladding layers" structure, and for (right panel) the "thick core-layer – thin cladding layers" structure. Inset shows the geometry of the heterostructures. Longitudinal sound velocities in constituent bulk semiconductors are indicated with straight lines. Note in the left panel that the phonons in the cladding layer are accelerated compared to bulk owing to the presence of the acoustically hard cladding (barrier) layers. After A.A. Balandin *et al*. [13, 14].

More recently, the idea of engineering the phonon – electron scattering rates received a new impetus. It has been theoretically demonstrated [13, 16-18] that the effect of the phonon confinement could be made stronger if one considers a hetero- or nanostructure coated with elastically dissimilar material. The acoustic-phonon properties of the materials are characterized by the acoustic impedance $Z=\rho V_s$, where ρ is the mass density of the material and V_s is the sound velocity in given material. The material with larger Z is referred to as acoustically harder. The mismatch between sound velocities in materials forming nanostructures and heterostructures is also important. In the acoustically mismatched hetero- and nanostructures, the phonon depletion (and scattering rate suppression) can be achieved in acoustically harder materials [17], while phonon accumulation happens in the acoustically soft material (see Fig. 2). This effect can be used in the design of the nanoscale transistors, vertical MOSFETs, alternative-gate dielectric transistors, etc. As the transistor feature size W reduces well below the acoustic phonon mean free path (MFP), which is on the order of 50 nm – 200 nm in Si at room temperature, the possibilities for engineering phonon dispersion to improve the carrier and heat transport increase tremendously.

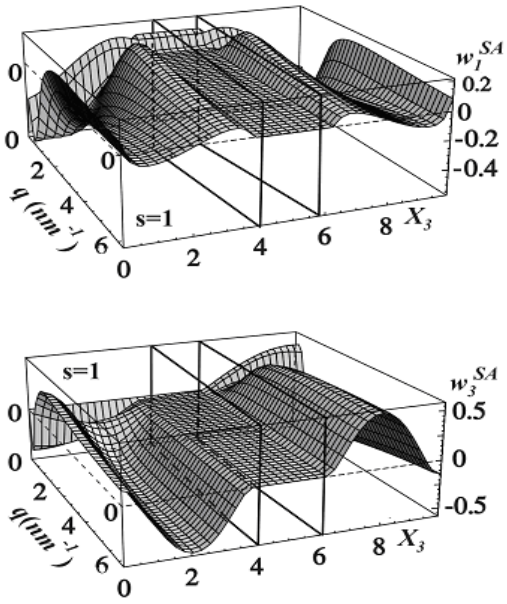

Figure 2: Illustration of the phonon depletion effect showing the redistribution of the displacement components in the acoustically mismatched heterostructures with acoustically hard core layer and acoustically soft barrier cladding layer (*Zcore> Zcladding*), which leads to the higher amplitudes of vibrations in the cladding layers and lower in the core layer. Results indicate that the amplitudes of the lattice vibrations in the acoustically harder core layer are near zero for the wide range of the phonon wave vectors. Phonon depletion in the core layer may result in the enhanced charge carrier mobility [17].

3. ENGINEERING PHONON THERMAL CONDUCTION IN NANOSTRUCTURES

The change in the thermal conductivity of semiconductors due to the phonon confinement bares important consequences for electronic industry in a view of continuous miniaturization. Heat in technologically important semiconductors is mostly carried by acoustic phonons. The feature size of the state-of-art transistor is already well below the room-temperature phonon MFP in Si. In hetero- and nanostructures with feature size W smaller than the phonon MFP, the acoustic phonon spectrum undergoes strong modification and appears quantized provided the structures are free standing or embedded within material of different elastic properties [14, 17]. This modification is particularly strong when the

structure feature size becomes much smaller than the phonon meat free path, W<<MFP, and approaches the scale of the dominant phonon wavelength $\lambda_d \cong 1.48 V_S \hbar / k_B T$. Here k_B is the Boltzmann constant, T is the absolute temperature, $\hbar$ is the Plank's constant, and V_S is the sound velocity. For many crystalline materials λ_d is on the order of 1.5 nm – 2 nm at room temperature, which is about the size of the transistor gate dielectric thickness. The decrease of the thermal conductivity with corresponding local temperature increase has detrimental effect on the device performance through mobility degradation, increased thermal noise, breakdown, etc.

Thermal conductivity in plane of thin films or along the length of nanowires can decrease for two basic reasons. The first is the co-called classical size effect on thermal conductivity related to increased phonon – rough boundary scattering [19]. This effect is pronounced when W is on the order of phonon MFP. It can be observed even in bulk samples at low temperature when the phonon MFP is long. If the structure dimensions W << MFP, another more interesting effect takes place [10]. Due to flattening of the dispersion branches, the population average phonon group velocity in freestanding nanowires decreases leading to the increased phonon scattering on defects and in Umklapp processes [10-11]. As a result, the thermal conductivity in freestanding thin films or nanowires can be significantly reduced (see Fig. 3). As one can see in Fig. 3, the acoustic phonon confinement leads to the reduction of the thermal conductivity even in a nanowire with ideally smooth surface. At the same time, embedding nanostructures into acoustically harder barrier (cladding) layers can cure the situation to some degree (see Fig. 1). In the described phenomena, the lateral (cross-plane) confinement of acoustic phonon modes in structures with W<<MFP affects the in-plane (along the length) phonon and heat transport.

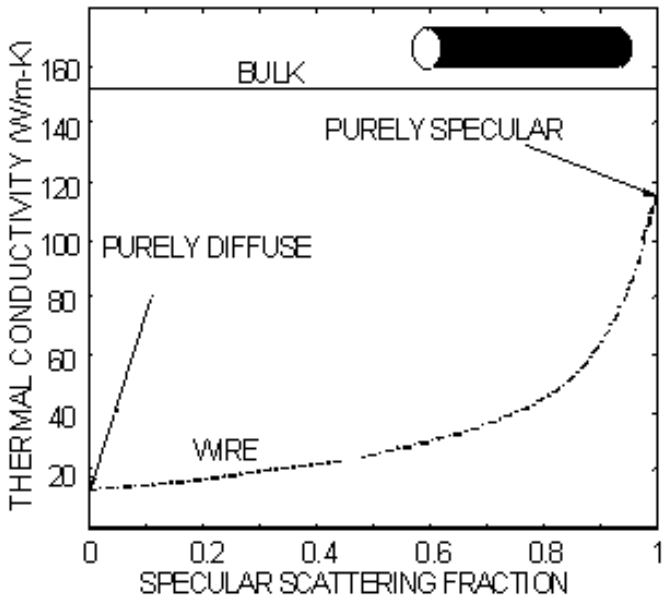

Figure 3: Thermal conductivity of Si nanowire with diameter D=20 nm as a function of the boundary roughness parameter p (p=1 corresponds to the ideally smooth surface), defined as a fraction of the specular scattered phonons. Acoustic phonon confinement effect leads to the reduction of the thermal conductivity even in a nanowire with ideally smooth surface. Overall one can observe a strong reduction of the thermal conductivity compared to its bulk value indicated by the horizontal straight line. After Zou and Balandin [11].

Another factor, such as thermal boundary resistance (TBR) at the interface between two materials, also referred to as Kapitza resistance, affects the cross-plane thermal transport. The significance of TBR in thermal management of electronic circuits increases due to the increasing number of layers (and interfaces) in ICs, the use of dissimilar materials,

and the fact that the larger thermal gradient in ICs is across the layers. It is also believed that TBR plays an important role in the experimentally observed decrease [20] of the thermal conductivity in quantum dot superlattices together with the phonon spectrum modification (see Fig. 4).

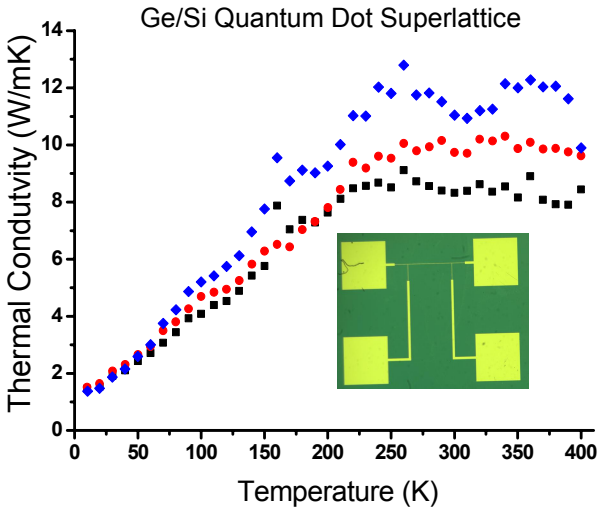

Figure 4: Measured cross-plane thermal conductivity in Ge/Si quantum dot superlattice. Three curves correspond to Ge dots of different height. The Si layer thickness is 20 nm in all three samples. Note a strong decrease of the thermal conductivity and shift of the peak value to higher temperatures as compared to bulk. The measurements were carried out by the differential 3ω method using the thermometer- heater deposited on top of the sample (shown in the inset). Experimental data is after W.L. Liu and A.A. Balandin, Nano - Device Laboratory, 2004.

Recently, Li *et al.* [21] reported on fabrication and measurement of the thermal conductivity in a single crystalline free-surface Si nano-wires with diameters as small as 22 nm. The experimentally observed strong decrease of the thermal conductivity K in such nanowires down to $K \sim 9$ W/cmK at T=300 K was in excellent agreement with the earlier theoretical prediction of Zou and Balandin [11], which calculated the value of K for 20 nm Si nanowire to be 13 W/cmK at T=300 K. The strong reduction of the thermal conductivity from its bulk value of around 150 W/cmK was explained by the acoustic phonon confinement in nanowires and boundary scattering [11].

4. PHONON DEPLETION AND ACCOUMULATION IN NANOSTRUCTURES

Spatial confinement of acoustic phonons in nanoscale structures with the large mismatch of the sound velocities or acoustic impedances $\eta=\rho V_S$ (ρ is the mass density and V_S is the sound velocity in the given material), at the boundaries can strongly affect the phonon spectrum and substantially modify the electron - phonon interaction in comparison with bulk. In such structures, both confinement of electron states and acoustic phonons should be taken into account while calculating the scattering rates. The change in the electron – phonon scattering rates, in its turn, can affect electronic conduction and noise characteristics in nanoscale devices. We have [17] recently shown theoretically that the phonon population in thin films or nanowires embedded into acoustically softer materials can be depleted, and the carrier – phonon scattering rate is suppressed. The latter is achieved if the nanostructure parameters (diameter, interface, mass density) are properly tuned and $\eta_{inside} > \eta_{matrix}$. This effect can be used to suppress the inelastic scattering in nanowires and increase electron carrier mobility (see Fig. 2). The latter may have a strong effect on the noise level in nanoscale

transistors. Svizhenko *et al.* [22] suggested that the acoustic phonon confinement in freestanding GaAs quantum wire leads to pronounced changes in Johnson noise.

4. PHONONS IN VIRUS-BASED TEMPLATES AND BIO-INORGANIC NANOSTRUCTURES

The rod-shaped viruses, such as tobacco mosaic viruses (TMV) have been utilized as biological templates in the synthesis of semiconductor and metallic nanowires [23]. They were also proposed as elements in the hybrid nanoelectronic circuits. TMV viruses have very convenient cylindrical shape and dimensions: TMVs are 300 nm long, 18 nm in diameter with a 4 nm in diameter axial channel (see Fig. 5). It is expected that genetically programmed viruses will contribute to the next generation of nanoelectronic circuits [24].

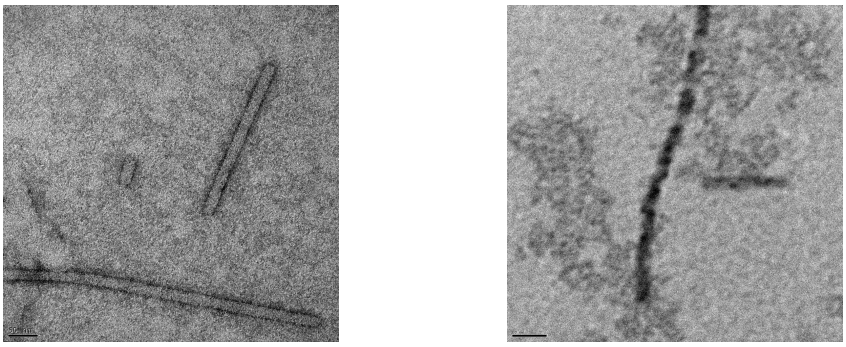

Figure 5: TEM micrograph of the pure TMV virus and virus end-to-end assembly used as templates for nano-fabrication (left panel), metal-coated TMV end-to-end assembly. After A.A. Balandin and W.L. Liu, 2005.

Since TMV viruses have the diameters of the same order of magnitude as diameters of semiconductor nanocrystals and nanowires, elastic vibrations of TMV should manifest themselves in low-frequency Raman scattering spectra. The knowledge of the low-frequency vibrational modes of the viruses is important for interpretation of Raman spectra and monitoring the template-based self-assembly processes. For example, low-frequency vibrational modes of pure TMV and silica coated TMV are different. The same can be said about low-frequency vibrational modes of a single functionalized TMV nanorod and end-to-end connected assembly of TMV nanorods, which form a nanotubular superstructure (see Fig. 5). Thus, signatures of these unique vibrational modes observed in Raman (Brillouin) spectra can be used to monitor and help to control the process of virus functionalization, i.e. coating with different materials, and self-assembly, i.e. attachment to other objects such as quantum dots, carbon nanotubes, etc., or forming the end-to-end superstructures. Information, which can be obtained with the help of Raman spectroscopy, is particularly valuable since other direct characterization techniques, such as transmission electron microscopy (TEM), are difficult to carry out and require special treatment of the samples. Recent developments in instrumentation for Raman spectroscopy have strongly increased the usefulness of the micro-Raman spectroscopy for gaining insights into internal virus structure, viral assembly pathways, and phonon modes in the hybrid bio-inorganic nanostructures.

Interpretation of measured Raman spectra of the hybrid bio-inorganic nanostructures requires theoretical analysis and modeling of phonon dispersion in such systems. Fonoberov and Balandin have theoretically studied the low-frequency vibrational modes of TMV and M13 viruses used for nanoelectronic self-assemblies [25-26]. The radial breathing modes of TMV and M13 viruses in air are found to be 1.85 cm^{-1} and 6.42 cm^{-1}, respectively. If the viruses are in water, the above frequencies become 2.10 cm^{-1} and 6.12 cm^{-1}, respectively. The confined phonon dispersion in pure TMV virus in air and water is shown in Fig. 6.

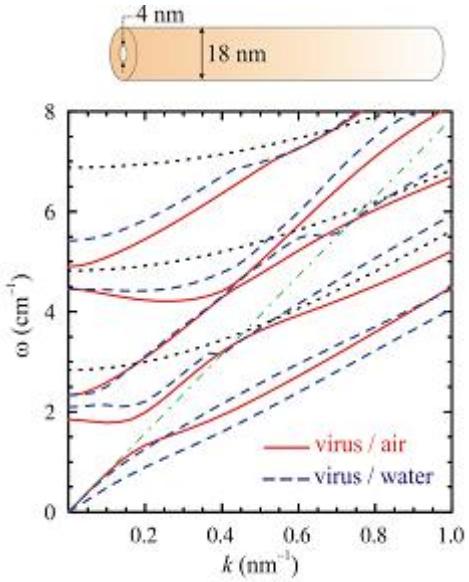

Figure 6: Dispersion of the lowest vibrational frequencies with m = 0 for cylindrical viruses without (a) and with (b) an axial canal. Solid (dashed) lines correspond to radial-axial vibrations of the virus in air (water). Dotted lines correspond to torsional vibrations. Dash-dotted lines mark the speed of sound in water. After V.A. Fonoberov and A.A. Balandin [25].

The modelling results for water are important since this is the medium of virus synthesis, purification and assembly processes. Water is also a notoriously strong infrared (IR) absorbing medium, and generally samples can be investigated more favorably by Raman (see Fig. 7) rather than by Fourier transform infrared (FTIR) methods.

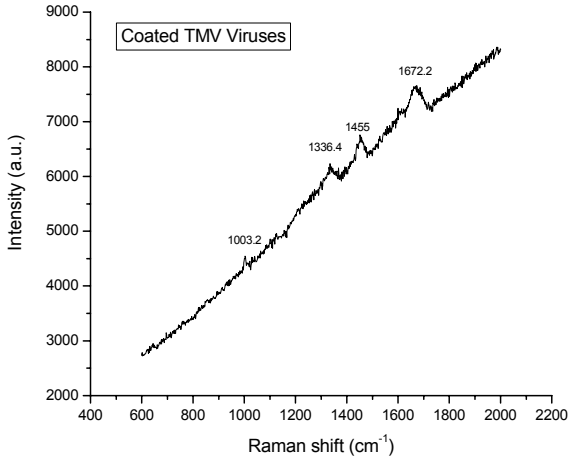

Figure 7: Raman spectrum of the metal-coated TMV viruses under the visible laser excitation. Measurements indicate consistent shift in the position of several phonon peaks for coated viruses compared with the pure ones. Results are after A.A. Balandin and W.L. Liu, Nano-Device Laboratory, 2004 [26].

In Fig. 7 we show Raman spectrum of the metal-coated TMV viruses under the visible laser excitation. Measurements indicate consistent shift in the position of several phonon peaks for coated viruses compared with the pure

ones. A combination of the experimental Raman spectroscopy and theoretical investigation of phonon spectrum in coated viruses may shed new light on transport properties of hybrid bio-inorganic nanostructures as well as better understanding of bio-inorganic interfaces.

5. CONCLUSIONS

In this paper we reviewed our resent results on phonon transport in semiconductor and hybrid bio-inorganic nanostructures. The focus of this review is on modification of the acoustic phonon spectrum in acoustically mismatched nano- and heterostructures. Spatial confinement of the acoustic phonon modes in nanostructures leads to significant changes in the thermal and electronic transport with consequences for heat removal, electrical conductivity, electronic noise, etc. The last section of the review describes our recent theoretical and experimental results pertinent to phonons in the rod-shaped viruses used as biological templates for nanoelectronic self-assembly.

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