Tüpraş’tan 2 Yeni Dev Yatırım!

Tüpraş, ülkemizde ve dünyada tüketimi hızla azalan yüksek kükürtlü fuel oil'i işleyerek Euro V standartında motorin ve benzin gibi beyaz ürûnlere dönüştürmek üzere Fuel Oil Dönüşüm Projesini gerçekleştirecektir.

En gelişmiş rafineri teknolojisi ile tasarlanan projenin tamamlanması sonucu, rafinerilerimizde üretilen değeri düşük yaklaşık 4,2 milyon ton siyah ürün (fuel oil, asfalt ve atmosferik díp), Avrupa Birliği standartlarında 3,5 milyon ton daha değerli ve çevreci beyaz ürûnlere dönüştürülecek.

Tüpraş'ın bir diğer yatırımı ise çevre ve insan sağlığına önem veren, Ülke ekonomisine katkı sağlayan, zorlu şartlarına dayanabilen üst düzey performansa sahip donanıyan motorin üretimini gerçekleştirmiş olmasidir.

Kuruluşların hizmet ettikleri toplumla büyübileceklerine inanan Tüpraş, Ülke ekonomisine katkı sağlayan, çevre ve insan sağlığına duyarlı yatırımlarını aralıksız sürdürecek!
Interfacial and Structural Properties of sputtered HfO$_2$ layers
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Abstract—Magnetron sputtered HfO$_2$ layers formed on heated Si substrate were studied. It is shown that formation of a SiO$_x$ suboxide layer at the HfO$_2$/Si interface is unavoidable. XRD spectra show that the deposited HfO$_2$ film has (111) monoclinic phase, also supported by FTIR spectra.

Hafnium oxide (HfO$_2$) is one of the best materials to be replaced by SiO$_2$ [1]. Since interfacial properties play crucial role in the electrical properties of the devices, the film system is better to be analyzed in depth by chemical diagnostic techniques like XPS [2].

HfO$_2$ thin film was grown on chemically cleaned p-type Si (100) substrate having a resistivity of 7–17 Ω-cm by reactive DC magnetron sputtering technique in high vacuum. Target to substrate distance was 7.4 cm of magnetron sputtering chamber. O$_2$, Ar gases were 12, 30 sccm respectively. 99.9% pure Hf target was pre-sputtered for 3 min to remove the possible surface contaminations. Substrate temperature and DC power were kept at 200 °C and 30 W respectively for 5 min sputtering time for this growth process.

Figure 1 (a) shows FTIR spectrum taken between 400 and 4000 cm$^{-1}$ of Hf oxide layer. Since OH peaks (around 3300–3400 cm$^{-1}$) and hydrocarbon absorption peaks (around 3000–1600 cm$^{-1}$) cannot be detected, this region is not shown.

The broad and very intense absorption band can be decomposed into two intensive peaks around 1060 and 1020 cm$^{-1}$ corresponding to Si-O stretching vibration mode and hafnium silicate (HfSi$_x$O$_y$), respectively [2]. The intensive peak infers that there is a very thick hafnium silicate layer. However, having close location but not around the exact position of natural oxide of SiO$_2$ (1075 cm$^{-1}$) implies that this interfacial oxide layer is in the suboxide form of Si, i.e. SiO$_x$ with $x\approx 2$. The main peaks around 595, 550, 527, 506, and 720 cm$^{-1}$ are due to Hf-O chemical bonds. It can be concluded that the presence of sharp phonon bonds in the low wavenumber region (600–400 cm$^{-1}$) is the result of the crystalline structure of HfO$_2$ film. The C-O vibration mode detected at its expected position ~670 cm$^{-1}$ is a result of measurement in air environment. The broad peak around 28° of inset XRD picture shows that the microcrystalline structure, predicted also from the sharpness of the phonon spectrum in the 400 to 600 cm$^{-1}$ of FTIR spectrum, has been just started to be formed. The other two intensive peaks around 33.3° and 62.1° are the signals coming from the Si (100) substrate.

The film system was modeled for SE as Air/ HfO$_2$/SiO$_2$/c-Si(100) in 300–850 nm. Thickness of SiO$_2$ film, and thickness and refractive index ($n$) of HfO$_2$ thin film were fitting parameters of Cauchy dispersion relation. Thickness and refractive index of HfO$_2$ is, respectively, 7.3 nm and 1.98 (Figure 1 b). A very thick SiO$_x$ interfacial layer of 20.8 nm is formed between the Si substrate and HfO$_2$ film.

Figure 2 shows the depth profile results from XPS spectrum. Elemental Si$^0$ is started to be seen at the very surface layers and continued till the depth of the oxide. The existence of this thick layer was also supported by FTIR. Shift of Si peaks infers as the oxide containing HfO-Si, i.e. Hf silicate (HfSi$_x$O$_y$). The energy state of O centered ~530 eV for the very surface layer is attributed to oxygen bonds in HfO$_2$. At deeper layers, the peak is shifted to higher binding energy levels to ~531.5 eV which is explained as the detection of O bonds in non-stoichiometric HfSi$_x$O$_y$ [2]. After the very surface layer, the main peak is decomposed into two sub-peaks, centered ~531.5 and 533 eV corresponding to Hf silicates (HfSi$_x$O$_y$) and SiO$_x$. Simultaneously, the peaks are shifted to 533 eV corresponding to Si-suboxide till the 12th etching cycle. Hf 4f has a spin-orbit splitting of 1.6 eV at 16.90 and 18.50 eV for 4f$_{7/2}$ and 4f$_{5/2}$ respectively for HfO$_2$, all levels containing Hafnium oxide can be decomposed into two contributions. However, these peaks shift to higher binding energies in the vicinity of Si, i.e. to 17-17.5 eV, for Hf 4f$_{7/2}$, which can be attributed to HfSi$_x$O$_y$. It is shown that reactive sputtered Hf atoms consume the oxygen atoms from the underlying SiO$_2$ to form HfO$_2$ leaving Si-Si bonds behind.

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Integrated angle resolved photoelectron spectroscopy for 300 mm wafers

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Abstract— A special photoelectron spectrometer, a so called integrated XPS-module will be introduced. It is the first XPS-module, which has been integrated in a typical semiconductor manufacturing cluster tool for 300 and 200 mm wafers. This allows in-line analysis of processed wafers. But all other kinds of samples thinner than 1 cm can be loaded and analysed, too. Special attention was paid on depth profiling in the nanometer range by the feasibility of angle resolved XPS measurements (ARXPS). ARXPS allows non-destructive analysis up to about 5 nm depth. For deeper depth analysis a sputter device is available. Measurements on layered and buried structures will be presented and discussed.

For a long time photoelectron spectroscopy (XPS) is known as a very powerful tool for chemical analysis of surfaces and thin layers. The qualification for thin layers and surfaces is evoked by the measurement information depth in a range of about 5 nm [1]. Non-destructive depth profiling in a 5 nm range is possible with angle resolved XPS (ARXPS) [2]. Therefore, this technique is very well suited for process control measurements in semiconductor manufacturing. The dimensions of semiconductor devices become smaller and smaller, while the productivity is growing year by year. That requires new or better measurement methods with higher spatial resolution. Hence, ARXPS is very appropriate to monitor layer deposition of layers in the nm range.

In the clean room of Fraunhofer IISB, a new cluster tool for 200mm and 300 mm wafers has been installed. One of the attached modules is the XPS tool (see figure 1) for process control measurements. The whole cluster unit is used for R&D purpose in an industry compliant environment [3, 4].

The XPS-module has an Al-X-ray tube with a monochromator, and therefore a high energy resolution of up to 300 meV is verifiable. The X-ray microspot has a diameter of about 200 μm, which gives the lateral resolution of investigation. The manipulator operates with an accuracy of better than ±20 μm. It is designed for 300 and 200 mm wafer, in addition smaller samples not thicker than 1 cm can easily be loaded into the measurement chamber, when mounted on a wafer.

Angle resolved measurements are performed without any sample tilt or analyzer turning. Instead, the analyzer has a lens system, which collects the electrons from a solid angle of 60°. This solid angle is displayed on a detector array in such a way that a particular angle interval can be related to particular detector channels.

The performance and effectiveness of the XPS-module will be demonstrated in this talk by measurements on layered structures and buried layers [5]. The measurements shown in figure 2 are taken from a tempered layer structure, which is constructed by deposition of TaN and TiN with changing concentrations in successively deposited layers. Measuring a depth profile of the layer sequence specifies not only the concentration ratio of the compounds as function of depth, but due to the very high energy resolution it shows also the resulting chemical bonds. This will be discussed in detail in this presentation.

Figure: 1 The XPS module with the spherical analyzer and the x-ray tube with monochromator in the front. On the very left side the connection to the transfer chamber of the cluster tool can be seen.

Figure: 2 XPS spectra taken from a tempered layer system

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Preparation and Microstructural Characterization of Oriented Titanosilicate ETS-10 Thin Films on Indium Tin Oxide Surfaces

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Abstract—Oriented polycrystalline ETS-10 thin films (average thickness ~1.50–1.75 μm) were prepared on the ITO glass substrates using secondary growth of ETS-10 multilayers with a partial a(b)-out-of-plane preferred crystal orientation. After secondary growth, the films showed a columnar grain microstructure, and a significantly increased degree of a(b)-out-of-plane orientation. This orientation is desirable for advanced applications of ETS-10 films. The prepared films were strongly attached to the ITO glass substrates as evidenced by the absence of discernible differences in the substrate coverage with film after a 60-min ultrasonication in water.

Zeoite and zeolite-like (zeotype) materials with their unique tetrahedral framework structures and compositions, uniform pores, well-defined acidity, cation exchange selectivity, and good thermal stability are widely used as commercial catalysts, ion exchangers, and adsorbents [1]. There is an increasing number of investigations involving titanium-containing zeotype and related microporous titanosilicate molecular sieve materials for optoelectronic, photovoltaic, and photocatalytic applications [2,3]. One of these materials, ETS-10, is a synthetic microporous (pore size 4.9 x 7.6 Å) titanosilicate with framework built of corner-sharing TiO₆ octahedra and SiO₄ tetrahedra [4]. These building units are uniquely arranged to form monatomic, linear, orthogonal, non-intersecting, semiconducting Ti–O–Ti–O–Ti chains that run in the crystal a and b directions. These chains are effectively separated from each other by the silica matrix, and are regarded as a 1D quantum-confined form of titania with a band gap energy of ~4.03 eV [5]. Thus, ETS-10 crystals may find potential applications in nanoscale electronic devices [6], and photovoltaic solar cells [7].

For use in advanced and device-oriented applications, zeotype and related molecular sieve crystals need to be supported on a substrate. However, investigations on the attachment and/or formation of zeotype thin films on transparent conductive oxide (TCO) substrates, which is crucial for testing these materials for use in many advanced applications, are limited [7,8]. Indium tin oxide (ITO) is one of the most intensively studied TCO materials due to its high optical transparency, good electrical conductivity, low cost, high thermal stability, and chemical inertness [9]. Thus, the attachment and growth of zeotype crystals on the ITO substrates might lead to a more extensive characterization and wider utilization of these materials in advanced applications [8].

In the present investigation, secondary growth of the seed crystals with the highly anisotropic shapes and submicrometer sizes was used to prepare a(b)-out-of-plane oriented ETS-10 thin films (average thickness smaller than ~2 μm) on the conductive and transparent ITO glass substrates.

The prepared films retained integrity after a 60-min substrate sonication in water; this suggests strong film bonding to the ITO glass substrates. It is believed that the ability to grow oriented ETS-10 films on the ITO glass substrates will open new directions for investigations of ETS-10 in advanced applications.

Fabrication of TiO$_2$ nanotubes by Anodization of Ti Thin Film

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Abstract—Ti thin films are anodized in an aqueous HF electrolyte (0.5 wt %) to form TiO$_2$ nanotube array. Ti films were deposited on microscope glass substrates, and then anodized. Anodization is performed at potentials ranging from 5 V to 20 V and at temperature ranging from 0 to 20°C. The films were studied using scanning electron microscopy (SEM), Energy dispersive X-ray analysis (EDX) before and after anodization. It is observed that anodization of deposited films resulted in nanotube type structures with diameters in the range of 30-80 nm for an applied voltage of 5-20 V.

In the past decade, nanoscale one-dimensional materials, such as nanotubes, nanowires, nanorods, and nanofibers, have attracted interest due to their high surface-to-volume ratios and size dependent properties. So, these materials have been used many technological applications especially gas sensors and photovoltaic devices. After Dr. Iijima discovered carbon nanotubes in 1991, many researchers focused on the synthesis of one-dimensional structures of other substances and chemical compounds. One-dimensional nanostructures have been fabricated by variety of methods such as chemical vapors deposition, deposition into a nanoporous alumina template, sol–gel transcription using organo-gelators as templates, hydrothermal processes and anodization techniques, etc. Nano-structured metal oxides has a great attention because of especially their gas sensing applications. Nano-structured titanium dioxide (TiO$_2$) has a great attention, because TiO$_2$ has many applications such as photocatalysis, dye-sensitized solar cells, self-cleaning, electrochemical devices, batteries, gas sensors, displays and photochromic devices and wettability applications [1, 2]. Previously, we fabricated TiO$_2$ nanotubes by anodization of Ti foil and investigated hydrogen sensing properties of TiO$_2$ nanotubes [3]. In this study, we synthesize highly-ordered TiO$_2$ nanotubes depending on anodization voltage and temperature by anodic oxidation of Ti thin films in an aqueous solution containing 0.5 wt% HF.

The Ti thin film was evaporated in a Leybold Univex 450 coater system equipped with an Inficon Deposition Monitor (XTM/2), with a thickness of 500-700 nm. The anodization was carried out in an aqueous electrolyte of 0.5 wt% HF using a DC power supply and a platinum foil as cathode in a thermostated bath at temperature range of 0-20°C. All solutions were prepared from reagent grade chemicals and deionized water (18 MΩ). The distance between the anodic and cathodic electrodes was 20mm. Before the experiments, the solutions were stirred using a magnetic stirrer. After the anodization, the samples were rinsed in deionized water, dried and characterized. To characterize the morphology, the diameter, and the length of the TiO$_2$ nanotubes, scanning electron microscopy and energy dispersive X-ray analysis (SEM, Philips XL 30S) were used. Figure 1 shows the SEM images of anodized Ti thin film in an aqueous HF electrolyte (0.5 wt %) at the temperature of 0 °C with a constant anodization voltage of 10 V.

![Figure 1. SEM images of the top view at different magnifications of anodized Ti thin film with a constant anodization voltage of 10 V at anodization temperature of 0 °C.](image)

In summary, fabrication of TiO$_2$ nanotubes by anodization of Ti thin film was reported depending on anodization voltage and temperature in details.

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Angular Dependence of a Powerful THz Emission from Intrinsic Josephson Junctions of High-Tc Superconductors Bi2212

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Keywords: Terahertz radiation, Intrinsic Josephson Junctions, high Tc superconductors, Bi2212

Abstract: Since the discovery of strong terahertz emission from the mesa of a high temperature superconductor Bi2Sr2CaCu2O8+d single crystal, a great deal of interests have been arisen in the development of powerful terahertz emitter for many practical applications. Among them, various kinds of imaging, spectroscopy, pharmaceutical development, bioscience and technology, diagnostics, ultra-highspeed communication, environmental studies, social security issues, etc. are the examples.

So far, we have studied mostly the fundamental features of the strong terahertz radiation from high-Tc superconductors and explored the nature of terahertz radiation. One of the most interesting question to be answered is how the electromagnetic wave is generated in the mesa due to perhaps the ac Josephson effect, since the Josephson relation seems to be fulfilled in any cases. We have measured the angular dependence of the radiation power at far-field, then understood what sort of electromagnetic waves are generated inside the mesa by a model calculation, which contains two radiation sources; one is the ac Josephson effect and another is the cavity mode. Two sources are necessary to explain the experimental data. It was found that the ac-Josephson currents is the basic radiation sources, rather than the cavity modes, although the mixing parameter indicates a considerable cavity radiation mode. I will show the detailed results the angular dependence measurement not only in the rectangular mesas but also cylindrical mesas, and argue the mechanism of the terahertz radiation. Possible methods to boost up the emission power will also be proposed.
From Carbon to Boron: Changing and Probing Nanostructures with Light and Sound

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Abstract—Ab initio calculations indicate that irradiation by monochromatic light or ions may be used as a unique tool for nanostructure engineering, since the electronic excitations following such perturbations modify the force field and open up new reaction pathways. The possibility to break or to form new bonds may help to heal atomic-scale defects in nanotubes, convert graphite to diamond or graphene, and create boron nanostructures with an unusual geometry. Changes in sound absorption on the sub-nanometer scale can be used to probe efficiently structural changes in the surface and subsurface region.

Precise structural control in nanostructures is impossible to achieve by top-down approaches due to their inadequacy on the atomic scale. This is a serious drawback, since atomic-scale defects in carbon or boron nanostructures, which include atomic vacancies and Stone-Wales defects, are known to significantly degrade the stability, the electrical and thermal conductance of these unique systems. It is an unfortunate fact that formation of such defects can not be avoided during the synthesis of carbon and boron nanostructures that involves very high temperatures in most cases. Consequently, it is imperative to understand the nature and effect of most likely defects, investigate ways to detect them, and find ways to control or selectively remove them without causing further damage to the nanostructure. Since the associated atomic-scale processes are hard to control by experimental means, computer simulations in the electronic ground and excited state are a welcome alternative to gain insight into the underlying Physics [1].

Not all defects are to be avoided, since their presence may have beneficial side-effects. Structural defects such as dislocations may initiate conversion of scrolls to nanotubes [2] or fusion of nanotubes [3]. Differences in atomic-scale roughness at the edges of graphene nano-ribbons may fundamentally modify spin quantum transport of these nanowires and turn them into spin valves [4].

Other defects, including atomic vacancies, Stone-Wales defects and covalently bonded impurity atoms, are highly undesirable at any time due to their adverse effect on electric transport and structural toughness. Whereas chemical treatment and thermal annealing are rather unspecific and likely to cause additional damage, irradiation by monochromatic light and ion beams turns out to be highly selective and efficient. The reason for this unexpected benefit is the long lifetime of electronic excitations and associated changes in the force field. New reaction pathways open up with often very low activation barriers. Calculations based on a combination of ab initio time-dependent density functional theory (TD-DFT) and molecular dynamics simulations indicate that carbon nanotubes with bare [5] or oxygen-terminated [6] atomic vacancies may be efficiently and selectively healed (see Fig. 1) in presence of electronic excitations. Also structural changes induced by Focused Ion Beam (FIB) irradiation are efficiently assisted by the presence of electronic excitations [7]. Finally, an efficient way to synthesize boron nanostructures with unusual shapes [8] also involves the presence of excitations in the plasma (see Fig. 2).

Besides removing defects, monochromatic light may be used to deliberately induce structural changes. Irradiation of graphite by femtosecond laser pulses gives rise to intriguing atomic motion, including oscillations in the interlayer distance [9], caused by the intermittent population of initially empty p_z orbitals that can modify the interlayer interaction. Even though the observed contraction of the interlayer separation in the initial experiments was rather small, photo-transformation to diamond appears a viable possibility when the pulse shape and intensity would be optimized. Such an optimization was performed when investigating the possibility to detach an isolated graphene monolayer from graphite by light [10], as a non-intrusive alternative to mechanical exfoliation by a Scotch tape. Computational results indicated this possibility,
Ab initio study on Ge/Si and Si/Ge core/shell nanowires
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Abstract—We study the structural, electronic, and optical properties of Ge/Si and Si/Ge core/shell nanowires using first-principles plane wave calculations within the density functional theory in the generalized gradient approximation. In the case of the heterostructure nanowires that we considered, the valence band maximum and conduction band minimum wavefunction localizations are analyzed, showing a clear tendency for a strong charge separation in a wide range of compositions which is highly preferable for solar energy devices. The details for the band gap properties and absorption spectra of these systems are discussed.

One-dimensional nanowires (NWs) have been extensively investigated because of their potential applications in photovoltaic cells [1,2]. These significant interests in the optical properties of NWs have basically aimed to improve the efficiency and decrease the cost and size of solar cell devices. After the experimental study on core/multishell NWs by Lauhon [4] Ge-Si core/shell structures have been thought to have promising applications on nanowire-based devices.

In this work, we first studied passivated Ge and Si NWs with different diameters ranging from 0.6 nm to 3.5 nm with [110] and [111] directions to understand the effect of surface reconstructions. Then we studied deeply the core/shell NWs in order to investigate the spatial localizations on core and shell atoms. In the field of renewable energy applications, including solar cells, the spatial charge separation between the lower conduction and upper valence states is highly preferred. Because of this fact, we mainly worked on NWs with [110] orientation rather than [111] direction which did not supply relevant information for solar cell applications.

It is found that the quantum confinement effect (QCE) played an important role in the band gap energies. Ge NWs were calculated to have direct band gaps at Γ-point which was in accordance with other studies. On the other hand, small diameter Si NWs (with d≤2.4 nm) were found to have direct band gap at Γ-point and larger diameter Si NWs have appeared to have indirect band gaps for which valence band maximums (VBMs) were located at around 0.1 Γ-Z. We can conclude that for Si NWs with [110] direction the critical diameter at which direct to indirect transition occurs was 2.8 nm. Furthermore, as the size of the Ge and Si NWs increased, band gap energies decreased as expected due to the QCE.

In order to model the core/shell structures we first systematically doped Si atom(s) on the surface of Ge NWs. Increasing the number of Si atoms caused to form core/shell NWs. The favorable doping positions were found to be the sites at which Ge-Ge bond lengths were on average shorter than around the other sites. The increase in Si atoms resulted in increment in the band-gap energy which was expected because the band gap of bulk Si is larger than that of Ge.

QC had also affected the band gap energies of the core/shell structures; as the diameter increased the NWs with the same number of core atoms had smaller band gap energies. Moreover, the same core concentrations with x<0.5 have lead Ge/Si core/shell NWs to have higher band gap energies than Si/Ge core/shell wires. Since Si NWs have larger band gaps, when Ge core concentration was smaller than 50% Si atoms played an important role in the increment of the NW band gap.

To understand the contributions of the atoms to the valence and conduction bands, the spatial localizations of the wave functions are plotted and presented in Fig. 1. The HOMO and LUMO localizations of the core/shell NWs have different properties than that of pure NWs. It can be clearly seen that while Ge/Si core/shell NWs had LUMO localizations in the Si shell, HOMOs were confined to the Ge core. For the Si/Ge core/shell NWs, electrons were localized in Si core and holes were confined to Ge shells. On the other hand, for both types there were small overlaps in the core/shell interfaces which did not create a danger but because of this overlap a longer carrier lifetime has been expected and the absorption at the fundamental band gap has been preserved. The interested readers are referred to Ref. [5] for more details.

\[ \text{Ge}_{x}\text{Si}_{1-x}H_{2} \quad x = 0 \text{ or } 1 \]

Figure 1: Cross sectional views of HOMOs and LUMOs in Ge/Si and Si/Ge core/shell NWs with diameters 2.9 nm along [110] direction.

The imaginary dielectric functions were calculated within RPA. The figure of merits for which the solar spectrum was taken as a reference revealed that Ge/Si core/shell NWs had better efficiencies than Si/Ge core/shell NWs. Furthermore, as the diameter of the NWs increased the efficiency increased for both of the core/shell types.

In summary, we found that Ge and Si NWs exhibited a strong QCE which remained significant upon the formation of core/shell NWs. The importance of the orientation has been also emphasized for the optical properties of NWs since the wave-function spatial localizations of the uppermost valence and lowest conduction bands were extremely different according to the wire axis orientation. Therefore, the [110] oriented Ge/Si core/shell wires appeared to be the most promising ones due to their spatial separation of carriers in terms of their potential applications in optical and electronic areas. This work was supported by the Belgian FNRS through the FRFC Convention No. 2.4505.09.

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Vibrational Characteristics of Cu Nanowires

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Abstract—We have investigated local density of states (LDOS) of Cu nanowires with \(<100>\) and \(<111>\) axial orientations and considered the effect of axial strain. The interactions between the atoms in model systems are defined using the embedded atom method (EAM) and the LDOS are calculated through a real space approach based on the real space Green’s function method. Results for unstrained case show similar characteristics for both \(<100>\) and \(<111>\) axial oriented nanowires: an increase in high frequency modes as the cross-sectional area decreases. The LDOS of a strained nanowire, on the other hand, exhibit quite distinctive characteristics as it points out to the existence of high frequency modes above the bulk band even for small strain of 2.5% for both types of the nanowires.

Metallurgical materials at nanoscale have been the focus of experimental and theoretical works as they display distinctive mechanical, electrical, thermal, and magnetic characteristics compared to their bulk or surface counterparts [1]. Except for a few studies, most of theoretical works, ranging from molecular dynamic simulations to first principles calculations, are devoted to determination of elastic, electronic, and structural properties of metal nanowire. On the other hand, the vibrational characteristics of nanowires, specifically in the radial direction, are likely to be modified, compared to the bulk system for symmetry reasons. In addition to the issue of unavoidable size effect, the vibrational characteristics are expected to differ from those of bulk system and strain-free nanowire, when the wire is under a strain. In this work it is, therefore, our aim to show, through reliable and accurate calculations, that vibrational properties of Cu wires change significantly when the nanowire is exposed to a constant axial strain.

In our simulations for examining the size effect on vibrational spectrum, we first construct the \(<100>\) and \(<111>\) axially oriented Cu nanowires with square and hexagonal cross-sectional area, respectively, in their bulk terminated positions and then allow the atoms in computational cells to interact through a semi-empirical and many-body type potential obtained from the embedded atom method (EAM)([2]). Next, the standard conjugate gradient method is used to fully minimize the total energy of the system. Then a series of strain ranging from 0% to 10%, with an increment of 0.5%, is applied. We have finally calculated the local vibrational density of states (LDOS) corresponding to any specific atom in our model system using an accurate method, the real space Green’s function technique ([3,4]).

In Figure 2, we present LDOS of a center atom at the cross-sectional area of both types of nanowires as the wire is constantly exposed to a strain with an increment of 0.5% along the axial direction. For a comparison we have also included the LDOS for a strain-free nanowire (strain of 0%). As seen in the figure, the LDOS of a CA along x and z direction exhibits quite different response to the applied strain: While the mid frequency modes along the z direction are overall shifted to the lower frequencies, the high frequency modes along the x direction are strikingly shifted towards the higher frequencies right above the bulk band as the axial strain increases and these characteristics are independent of the axial orientation of the wire.

In short, we have investigated the size and strain effects on the local vibrational properties of Cu nanowires through realistic calculations and showed that regardless of axial orientation, the vibrational characteristics are strongly affected by the size of wire and the applied strain.

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References:
III-V nanowires of wurtzite structure
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Abstract- Pure and Mn-doped III-V semiconductor (GaAs and InAs) nanowires are studied theoretically by ab initio methods. The calculations show that in such one-dimensional structures the crystal structure depends on the diameter of the nanowire. Moreover, in doped structures the distribution of Mn ions as well as their mutual spin alignment depends crucially on the crystallographic structure of the nanowire.

The analysis of crystal stability of GaAs and InAs nanowires is based on the comparison of their so called free energies. The free energy, \( E_{\text{free}} \), reflects the energy cost per cation–anion pair of creating the nanowire lateral surfaces. \( E_{\text{free}} \) is defined as a difference between the nanowire total energy divided by the number of atomic pairs in the wire and the energy per anion–cation pair of the bulk material. Since it is possible to grow III-V nanowires of different crystal structures, nanowires of both zinc-blende and wurtzite structures with different diameters and along different crystallographic directions are considered. We consider infinite wires, which are cut out from the bulk material of either zinc-blende or wurtzite structure. The model wires have dimensions ranging from 6 to 50 Å. The periodic boundary conditions are employed along the nanowire growth axis. A plane wave basis set has been used in the calculations. We also use periodic conditions in the other directions, with the unit cell dimensions which ensure that minimum separation between neighboring wires is not less than 10 Å. The energies of these wires are calculated by ab initio method, based on the density functional theory (DFT). All the calculations are performed within the Vienna ab initio simulation package (VASP) [1,2]. For each of the initial structure the minimum energy atomic configurations are determined by allowing relaxation of all atomic positions and of the unit cell dimension in the growth direction. A full reconstruction of the of the nanowire surfaces is performed.

The calculation show that for the diameters of up to 50 Å the most stable nanowires adopt the wurtzite <0001> structure. In very thin zinc-blende nanowires along any crystallographic axis, the free energy is much larger than that of the wurtzite <0001>. However, among zinc-blende nanowires thicker than 30 Å, the ones <111> oriented are energetically favorable, with the free energy difference from that of the wurtzite <0001> nanowires diminishing with diameter. The extrapolation of these results to larger diameters, presented in the Figure, shows that this difference becomes negligible for diameters larger than 10 nm. It is suggested that the diameter dependent competition between the energy cost of establishing the side surfaces (lower for wurtzite) and the tendency to adopt the zinc-blende structure, favorable in bulk III-V materials, is responsible for the stacking faults which occur during the growth of these nanowires and which are expected to impede the transport and optical properties of the wire. The theoretical result that thin wires on the order of 10 nm are bound to be wurtzite and free of stacking faults was confirmed by experimental findings. Using this result we have suggested that such wires can be used as a core for further lateral growth of thicker wires with a pencil shape morphology. In as much as stacking faults can form only along the <0001> axis, in principle the lateral expansion of nanowires growing in the <0001> direction cannot introduce any new stacking faults; the lattice structure is dictated already during the growth of the "core". It was shown [3] that by such procedure wurtzite III-V nanowires as thick as a few tens of nanometers with considerably reduced number of stacking faults can be grown.

Next, using the same method we study the III-V nanowires doped with magnetic, i.e., Mn ions. In both, zinc-blende and wurtzite, structures we look for the most energetically favorable atomic positions of the Mn impurities and the Mn-Mn mutual spin alignment which minimizes the energy. In zinc-blende nanowires we obtain that the Mn ions prefer to be located at the side surfaces of the wire, substituting the cations with additional dangling bonds. The lower energy was obtained for the antiferromagnetic alignment of Mn spins. In contrast, in wurtzite nanowires the Mn atoms prefer taking cation positions close to the center of the wire and to be ferromagnetically coupled. These results allow us to propose a procedure of growing ferromagnetic Mn-doped III-V semiconductor nanowires, which is based on the method presented in Ref. [3].

In summary, we have shown that in III-V semiconductor nanowires of wurtzite structure the number of stacking faults can be considerably reduced. Our calculations suggest also that the growth conditions leading to wurtzite crystal structure should be preferred in order to avoid accumulation of Mn ions at the surface during the growth of Mn-doped III-V wires and to obtain ferromagnetism in such nanostructures.

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Electronic Properties of Graphene Nano-Ribbons
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Abstract- In this study we present a theoretical work on the electronic structure of several graphene nano-ribbons (up to the system with more than 1000 atoms) including all types (armchair, zigzag and chiral) using tight binding approach both in 1D and 0D. To handle the dangling bonds, we saturated the ribbon by the introduction of hydrogen atoms. We saw that the band gap of the ribbons depend both on the length of the ribbon and the angle of chirality. However, there is no simple function to fit the data as there is for Carbon Nanotubes.

After the isolation of Graphene as a single layer in 2004 by Novoselov et al [1], the theoretical works became possible to be checked. Therefore, it became much more popular amongst both experimentalists and theorists. Having zero band gap, graphene cannot be used directly in applications as a semiconductor. However, Graphene Nano-Ribbons (GNRs), finite sized graphenes, can have a band gap different from zero. This band gap changes with the change in length and chirality angle of the ribbon. As the ribbon gets smaller, band gap increases.

There are some works on 1D AGNRs and ZGNRs in the literature showing great agreement with ours results which tells us that our parameters work fine [3,4]. 0D ZGNRs show zero HOMO-LUMO gap whatever its length is, whereas, HOMO-LUMO gap of 0D AGNRs show an exponential behavior increasing as the length of the ribbon decreases. Band gap of 1D CGNRs depend on the chirality angle and length of the ribbon. In determining the HOMO-LUMO gap of 0D CGNRs, however, in addition to those variables, width of the ribbon is also effective.

Although there is a simple function, as indicated by Yorikawa and Muramatsu [5], for Carbon nanotubes showing how the band gap changes with chirality and length, we were not able to find such a function for CGNRs. However, in all GNRs, the band gap increases as the size of the ribbon decreases.

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Modifying the physical properties of carbon nanotubes: Chemistry on defects

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Abstract— The surface of carbon nanotubes offer a larger area for chemical reactions. However, the reactivity of the nanotube surface when perfect. The chemical functionalization of defective nanotubes offer new chemistry on carbon nanotubes. Our density functional theory calculations show that both the adsorbates and defects go through structural changes. We investigate the atomic and electronic structure, and energetics of the adsorption of -SH, radicals, halogens, and the hydrogen atom. We found that H and F form very strong directional covalent bonds while Cl binds less aggressively. The structural deformations are strong in H and F functionalized carbon nanotubes. Our electronic structure calculations reveal that that some of the defect levels can be eliminated by exposing the nanotubes to halogens or hydrogen. We speculate that halogen and hydrogen chemistry can be used to probe defects, and also tune the electrical and thus optical properties of nanotubes. The silane-based radicals bind to defective carbon nanotubes with several configurations following the structural transformations of the radical. Our total energy results show that bonding between the carbon nanotube and a Si substrate is improved at defect sites.

The most common point defects in carbon nanotubes are mono- and di-vacancies, of which the di-vacancy has unexpectedly low formation energy [1, 2]. The defects modify the physical and chemical properties of materials. In carbon nanotubes, defect states appear near the Fermi level, and alter the transport properties adversely. In addition to nano-device applications, the carbon nanotubes offer new opportunities for chemical reactions due to their large surface area. Here, we compare the chemical reactivity of defective and pristine nanotubes in order to exploit the use of both defects and chemical functionalization for tuning the physical properties of carbon nanotubes. Among the functionalizing agents, the halogens and hydrogen are frequently encountered. In this work, we concentrate on Cl, F, and H adsorption on nanotube walls. We also use -SiHn radicals as adsorbates, which help us to understand the intercation of defective nanotubes with a Si substrate. Although the functionalization by these agents is sometimes undesirable, a controlled path for selective functionalization is viable [3,4].

We used ab initio density functional theory calculations to investigate the atomic and electronic structure of functionalized pristine, and defective nanotubes. The exchange-correlation approximation (LDA) level in the Perdew-Zunger parametrization, as implemented in the SIESTA code. A double-ζ basis set augmented by polarization orbitals is employed for expanding the wave functions. The interaction between the core and valence electrons were handled by norm-conserving pseudopotentials.

In our ab initio density functional theory calculations for the chemical reactivity of pristine and defective carbon nanotubes that interact with halogens and hydrogen. We first investigated the H, Cl, and F adsorption on pure carbon nanotubes, and observed structural and electronic modifications. We found that H and F form very strong directional covalent bonds while Cl binds less aggressively. The structural deformations are strong in H and F functionalized carbon nanotubes. Second, we have investigated the effect of Cl, F, and H adsorption on the reconstruction of defects. The point defects in carbon nanotubes reconstruct to reduce the number of dangling bonds. However, as we find, based on our adsorption energy values, the defect sites are more reactive for halogen and hydrogen adsorption. Moreover, the atomic structures of the defects are modified by the adsorbants. This atomic rearrangement is followed by electronic structure modifications. We find that

![Figure 1: The atomic structure of point defects in carbon nanotubes. (a) The reconstructed mono-vacancy with a dangling bond and (b) the reconstructed di-vacancy that is self-healed with no dangling bonds are depicted as ball-and-stick models. The new bonds that form during the self-healing is indicated by blue color.](image1)

![Figure 2: The structural transformation of the divacancy after successive hydrogen adsorption. (a) Dissociative adsorption of a hydrogen molecule may break the reconstructing bond that is shown in blue in Fig. 1. Two configurations in (a) are energetically degenerate. (b) A successive dissociative adsorption of a hydrogen molecule converts the hydrogenated divacancy in the right panel to a different atomic structure. This structural transformation is found to be energetically favorable by 1.3 eV.](image2)
Abstract—In this paper we have investigated the interactions between the monomer of a polymer (Poly[(phenylene)-co-(9,9-bis-(6-bromohexyl)fluorene)]) and graphene sheet by using pseudopotential plane-wave calculations based on density functional theory (DFT). To find the most favorable binding configurations, the monomer under investigation is placed at different orientations on graphene. In order to gain further insight into the binding interactions of polymer-graphene system, we have also calculated the binding energy for the structure in which the polymer is attached to graphene sheet via an atomic oxygen. Considering the graphene impurity we also further investigated the Br atom doping from polymer chain onto graphene. However our results demonstrated that the interaction between the (Poly[(phenylene)-co-(9,9-bis-(6-bromohexyl)fluorene)]) polymer and graphene is weak, mostly dispersive, and graphene is not flat but exhibits around 0.5 ~ 0.6Å corrugations.

Graphene, which consists of a single atomic sheet of conjugated $sp^2$ carbon atoms, the long-range $\pi$ conjugation yields extraordinary thermal, mechanical, and electrical properties, which have long been the interest of many theoretical studies and more recently became an exciting area for experimentalists[1]. However, the detailed reactivity of graphene is still not well understood[2]. The functionalization of graphene offers an alternative approach for their applications. Perhaps the largest application of functionalized graphene lies in the area of polymer nanocomposites.

In this work, we investigated the recently synthesized polymer attached graphene system. Our calculations are performed within first-principles DFT under the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE)[3]. The Vienna Ab-initio Simulation package (VASP) is used to perform all calculations[4,5].

Polymers may interact with graphene via strong covalent or electrostatic interactions, $\pi$ stacking, or hydrogen bonding. Alternatively, polymer and graphene may interact via generic weak van der Waals interactions. The binding energies obtained for the backbone side and the rotated ring side interactions of polymer with the graphene sheet are $43\text{meV}$ and $100\text{meV}$, respectively. Pure graphene is hydrophobic and has no appreciable solubility in most solvents[6]. However, recently, Bai et al.[7] reported that graphene functionalized by conjugated polymer sulfonated polyaniline (SPANI) is soluble in water and has good air stability and electrochemical activity. The interactions are due mainly to the strong $\pi - \pi$ interaction between the backbones of SPANI and the graphene basal planes. In that sense we also studied two water molecules connected polymer on graphene sheet. We found no improvement for the binding energies that is agree with ref[8] in which they state that the effect of water strongly depends on properties of the substrate such as the amount and types of defects. Furthermore, in order to obtain further inside into the binding interactions of polymer-graphene system, we calculated the binding energy for the two structures: in one structure the polymer is attached to graphene sheet via an atomic oxygen and the binding energy is improved to $133\text{meV}$, in another structure the Br atom from polymer chain side is doped into graphene sheet.

In conclusion, we found that the interaction between the polymer and graphene is weak van der Waals type interaction and the closest $C - C$ distance from polymer to graphene range $3.5 ~ 3.7\text{Å}$. This means that, most probably, bulk graphene without defects will be stable enough with respect to the polymer, at least at room temperature. This project is supported by TUBITAK (Grant No: TBAG-1077892) and European Union 7. Framework project Unam-Regpot (Grant no: 203953).

As shown in figure, in order to find the most favorable binding configurations, the polymer under investigation is placed at different orientations with respect to graphene plane. First we studied the polymer chain side interaction with graphene, for which we found that the binding energy is $40\text{meV}$. The binding energy was extracted from the difference in graphene and polymer energy with the total energy:

$$E_{\text{binding}} = E_{\text{total}} - E_{\text{graphene}} - E_{\text{polymer}}$$

First-Principles Investigation of Polymer Binding to Graphene and Carbon Nanotubes

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Dynamics and friction in double walled nanotubes
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Abstract— Nanotubes have exceptional physical properties, they are as tough as diamond and excellent heat and electricity conductors. On the other hand their cylindrical shape suggests the possibility of using them as mechanical parts at the nanoscale. Recent experiments showed that oscillators or rotational axes could be manufactured and controlled. Moreover the motion was observed to be wearless and with extremely low friction. We present analytical and numerical results on the dynamics and friction in those systems. The results show that the empirical law stating that friction is proportional to the area of contact is very well verified. Moreover, friction increases with temperature. These dependencies can be easily interpreted. Indeed, if the temperature is large enough so that electronic effects can be negligible, then dissipation is only due to the phonons. Consequently, if the temperature increases, the coupling between the phonons and the rotational or oscillatory motions increases, as well as friction. In the same manner, when the area of contact increases, the number of available phonons to transport energy increases, resulting in a higher friction force.

Since the pioneering work of Iijima on nanotubes [1], research on their electronic and mechanic properties has been rapidly growing. Very high electric and thermal conductivities were observed and the nanotubes were shown to be as stiff as diamond in their axial direction with Young modulus of the order of TPa. These observations make the nanotubes promising candidates for nano-electrical and nano-mechanical devices. The experiments on the translational motion in multi-walled nanotubes of Cumings and Zettl [2] and rotational motion of Fennimore et al. [3] and Bourlon et al. [4] showed the feasibility of such devices. For both systems no wear or fatigue, and extremely fast operating speeds were observed, thus further motivating their use as mechanical parts at the nanoscale. However the dissipation mechanisms or detailed dynamics could not be measured because of the short time scales and small dimensions.

This work is devoted to the study of these devices, thanks to statistical mechanics arguments and molecular dynamics simulations, we show that the dynamics of the oscillatory motion, is ruled by [5],

$$\frac{d^2 r}{d t^2} = F(r) - \gamma \frac{d r}{d t} + F_{\text{fluct}}(t), \quad (1)$$

where $r$ is the distance between the centers of mass of both nanotubes, $\mu$ their relative mass, $F(r)$ is the restoring force due to the van der Waals interactions, $\gamma$ the damping coefficient. On the other hand the rotational dynamics is very well described by a simple Langevin equation [6],

$$I \frac{d \omega}{d t} = -\chi \omega + N_{\text{fluct}}(t), \quad (2)$$

where $\omega$ is the relative angular velocity of the nanotubes, $I$ their relative moment of inertia, and $\chi$ the damping coefficient. Thanks to the relations (1) and (2) and systematic molecular dynamics simulations we evaluate the dependence on temperature and area of contact of friction. In both cases the results show that if the systems are large enough, the friction force $F_k$ increases linearly with the area of contact, in agreement with the macroscopic observation $F_k = s A$, where $s$ is a velocity dependent shear stress. Moreover we show that friction increases linearly with temperature for the translational motion and as a power $3/2$ for the rotational dynamics. Both increases in friction can be interpreted by either an increase in the number of phonons or an increase in the coupling between the phonons and the large scale motion.

Finally, we study the limitations of both models. The results show that while for the rotational motion, Eq. (2) is valid for frequencies up to 1 THz, a novel mechanisms is observed in the oscillatory dynamics. Indeed, at some specific velocities, a resonance between the translational motion and some specific phonon modes arise and greatly enhance friction [7].

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A bio-safe approach to prepare ZnO nanorods: Growth and properties

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Abstract—We will present a novel, economical and soft synthesis of hexagonal-shaped zinc oxide (ZnO) nanorods at very low temperature of ~80°C simply by using metallic zinc foil and de-ionized (DI) water without the use of any additives or surfactants. The formation of ZnO structures by the reaction of metals with DI water is suggested to occur due to the oxidation of metallic zinc in presence of water. The synthesized ZnO products were characterized in terms of their structural and optical properties. By the morphological investigations using FESEM, it was observed that the grown products are hexagonal-shaped ZnO nanorods with the diameters and lengths in the range of 50-60 nm with several micrometers. The EDS and XRD pattern confirmed the composition and crystallinity of the grown nanorods and revealed that the grown products are pure ZnO with the wurtzite hexagonal phase. The optical properties of grown products were characterized by room-temperature photoluminescence spectroscopy which confirmed the good optical properties for the grown products. The product is believed to be bio-safe and bio-compatible and can be readily used for medicine.

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Formulation of Thermoelectric Nanostructures by Electrochemical Atom-by-atom Codeposition

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Abstract—Nanostructures of Bi$_2$Te$_3$, Sb$_2$Te$_3$ and PbS were electrodeposited using a novel and practical electrochemical method, based on simultaneous underpotential deposition of precursors of target compound from the same solution at a constant potential. These nanostructures are characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), energy dispersive spectroscopy (EDS) and reflection absorption-FTIR (RA-FTIR) to determine structure, morphology, composition and optic properties.

Synthesis of nanomaterials with controlled size, shape and crystallographic orientation has become an important issue in material science research. Since the properties of semiconductor nanocrystals, which possess many novel properties that differ considerably from those of the bulk [1,2], depend both on dimension and superlattice structure. Therefore, the development of synthetic methods that enable their precise control is expected to have a significant impact on progress. Bi$_2$Te$_3$ and Sb$_2$Te$_3$ with a narrow band gap and other V-VI group semiconductors are best-known materials for TE applications at room temperature and are widely used for thermoelectric (TE), biomedical and optoelectronic applications as heat pumps, power generations, solid state refrigeration, cooling IC chips, biochips, infrared sensors, optoelectronic sensors, photo detectors, and so on. Recently, we have developed a new electrochemical process, based on co-deposition from the same solution at the upd of the precursors of the target compound, which have been used for the electrochemical deposition of PbS, PbTe, ZnS, and CdS in the single crystal form [3-6]. The appropriate electrodeposition potentials based on the underpotential deposition potentials (upd) of precursors have been determined by the cyclic voltammetric measurements. In the present study, we illustrated the detailed growth process of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ [7] nano films and Bi$_2$Te$_3$ nanorod-structured films on single crystalline Au(111) electrodes by using Atomic Force Microscopy (AFM), X-ray Diffraction (XRD), Electron Dispersive Spectroscopy (EDS), and UV-vis-NIR Spectroscopy techniques. We found out that that the growth direction (orientation) and thickness of nanostructured Bi$_2$Te$_3$ can be readily controlled by pH, composition of the solution, and the time of the electodeposition.

The morphological investigation of Bi$_2$Te$_3$ nanostructures revealed that the film growth follows 3D and 2D nucleation and growth mechanism in acidic and basic solutions, resulting in nanofilms and nanowires, respectively. XRD results show that single crystalline nanostructures of Bi$_2$Te$_3$ are highly preferentially orientated along the (015) for nanofilms and (110) for nanowires. The growth of Sb$_2$Te$_3$ nanofilms follows the nucleation and three-dimensional (3D) growth mechanism resulting in high crystalline films of Sb$_2$Te$_3$ (110) in hexagonal structure, which were grown at a kinetically preferred orientation at (110) on Au (111). Highly strong quantum confinement effect, for both Sb$_2$Te$_3$ and Bi$_2$Te$_3$ nanostructures, was observed.

Moreover, we applied a new modified electrochemical method [8] to deposit nanostructure of PbS on a thiol modified Au(111) surfaces. Electrochemical deposition was carried out after the stripping of thiol from the surface at different potential pulses. We showed that the size of the PbS nanostructures could be controlled by the electrochemical deposition time and pulse width.

In summary, structural and morphological studies indicate that growth of these nanostructures follows atom by atom growth mechanism resulting in highly crystalline nanostructures grown at a kinetically preferred orientation. Absorption measurements as a function of thicknesses indicated that the band gap of the nanostructures increase as the thickness decreases.

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The Use of Anodized Aluminum for Preparing Non-spherical Nanocarriers
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Abstract—Anodized Aluminum Oxide (AAO) membranes are ideal templates for the production of various 1D nanostructures due to the available array of monodisperse nanopores with adjustable pore diameter, depth and porosity. Here, we describe two different uses of AAO for the preparation of novel nanocarriers. First application employs the template synthesis of silica nano test tubes within AAO pores. The second is an indirect application of AAO where composite polymeric nanorods were created from nanoporous silicon molds that were fabricated via AAO etch masks.

In the biomedical research field, there is a great current interest for the utilization of differently shaped nanoparticles, including spherical, cubical, and tubular geometries.[1,2,3] Spherical nanoparticles are more widely used because this shape is easy to make, and spherical particles can be synthesized from a diverse range of materials, such as liposomes, polymers, dendrimers and various inorganic compounds. In contrast, the lack of fabrication methods to simultaneously and precisely control the size and shape of non-spherical nanoparticles causes a dramatic limitation for the use of such particles in biomedical applications.[4]

We have recently described two different approaches that use anodic aluminum oxide (AAO) (Figure 1a) structures to address these challenges.[4,5] The first one utilizes AAO membranes as a template material to produce monodisperse silica nano test tubes (Figure 1b) via surface sol-gel chemistry. Combination of the template synthesis and surface sol-gel chemistry allows the preparation of silica nano test tubes with controllable dimensions and tube thickness. These nanostructures are potential candidates for biomolecule delivery due to their controllable large inner volumes and chemically modifiable surfaces for special targeting studies.[5] Multifunctional silica nano tubes can also be obtained by the independent modification of the inner vs. outer tube surfaces. When biofunctionalized by a cancer-specific antibody, these silica nano test tubes can specifically recognize breast carcinoma cells (Figure 1c, d).[5]

In the second approach, nanoporous Si molds are created from AAO etching masks (Figure 2a) via inductively coupled plasma and subsequently used in a nanoimprinting setup to fabricate free-standing composite polymeric nanorods (Figure 2b).[4] Using Si molds with different depths, one can control the dimensions of the resultant nanorods by simply varying the thickness of the functional polymer layer (Figure 2c). The sacrificial PMMA layer allows the release of free nanorods which are not connected by a residual layer.

We have presented two novel applications of AAO for the fabrication of tubular and rod-shaped nanoparticles with potential biomolecule delivery applications. Currently we are investigating the utilization of such structures for targeted drug delivery of certain anticancer drugs to designated cell types. This work was partially supported by NSF, Montcrief Foundation, and Marie Curie International Reintegration Grant within the 7th European Community Framework Programme.

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Figure 1. (a) Scanning Electron Micrograph of AAO membrane. (b) Transmission Electron Micrograph (TEM) of silica nano test tubes. Confocal fluorescence images of MDA-MB-2881 breast carcinoma cells incubated with target (c) and non-target (d) antibody-modified silica nano test tubes.[5]

Figure 2. (a) Production of nanoporous Si mold. (b) Preparation of polymeric nanorods. (c) TEM (left, scale bars are 500 nm) and Confocal fluorescence (right) of different polymeric nanorods.[5]
pH-Responsive Functional Layer-by-Layer Films

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Abstract—We have shown that micelles of poly[2-(N-morpholino)ethyl methacrylate]-block-poly[2-(diisopropylamino)ethyl methacrylate] (PMEA-b-PDPA) could be self-assembled at surfaces through layer-by-layer technique based on hydrogen bonding interactions between PMEA corona and tannic acid (TA). Functional molecules can be loaded into such multilayer films and the release of encapsulated cargo can be tuned via controlling pH and/or temperature at the post-assembly step.

Layer-by-layer technique is a powerful way of fabricating ultrathin films to modify and functionalize surfaces or prepare free-standing ultrathin films. It is based on alternating immersion of the substrate into solutions of interacting polymers.[1,2,3] Due to possibility of using aqueous solutions, there has been a growing interest in the use of layer-by-layer films in biomedical applications, specifically for controlled delivery systems. However, including hydrophobic drugs within multilayers at high capacities has been an issue due to low solubility of hydrophobic drugs in aqueous loading solutions, as well as low binding affinity of relatively hydrophilic polymer multilayers towards hydrophobic drugs.

Recently, amphiphilic block copolymers which self-assemble into micelle-like structures above a certain concentration have attracted great attention due to their potential use as drug carriers.[4] One can produce functional surface coatings with higher loading capacities through incorporation of self-assembled block copolymer micelles into multilayers. Moreover, block copolymer micelle containing multilayers may enable engineering surfaces with multiple functionalities by encapsulating both hydrophilic and hydrophobic molecules in one system by taking advantage of the presence of hydrophobic micellar cores and relatively hydrophilic film matrix.

In this work, we have shown that poly[2-(N-morpholino)ethyl methacrylate]-block-poly[2-(diisopropylamino)ethyl methacrylate] (PMEA-b-PDPA) can be self-assembled into micelle-like aggregates above pH 6.5 with PMEA block forming the corona and PDPA block forming the core. Such aggregates were assembled at surfaces using tannic acid (TA) through layer-by-layer technique. TA has 25 phenolic hydroxyl groups and it is capable of forming hydrogen bonds with hydroxyl accepting polymers.[5,6] Figure 1 shows evolution of film thickness as a function of layer number (Figure 1A) and corresponding AFM images of PMEMA-b-PDPA micelles/TA films with TA (Figure 1B) and PMEMA-b-PDPA micelles (Figure 1C) as the top layer, respectively.

We have also studied the effect of post-treatment conditions on controlled release profile of functional molecules encapsulated in the cores of PMEMA-b-PDPA micelles. We found that decreasing pH resulted in release of the encapsulated cargo, while increasing temperature significantly affects the amount of cargo released from the surface.

In summary, we have shown that layer-by-layer technique is an efficient way to prepare ultrathin films with relatively high loading capacity using block copolymer micelles as building blocks. Our results are promising and constitute a model study to prepare thin films for controlled delivery applications from surfaces.

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Peptide Self-Assembly

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Abstract-The self-assembly of the trifluoroacetate salt of the short peptide (ala)6-lys (A₆K) in water has been investigated by Cryo-transmission electron microscopy and small angle X-ray scattering. For concentrations below ca. 12 %, the peptide does not self-assemble but forms a molecularly dispersed solution. Above this critical concentration, however, A₆K self-assembles into several micrometer long hollow nanotubes, with a monodisperse cross-section radius of 26 nm. Since the peptides carry a positive charge, the nanotubes are charge stabilized. Because of the very large aspect ratio, the tubes form an ordered phase that presumably is nematic and upon increase in concentration goes from closed packed hexagonal to multi-shelled cylinders. Nanotubes are shown to disintegrate upon increase in temperature using SAXS.

Peptide self-assembly structures not only have importance for medical applications [1, 2] due to their biological origin, but also used in different fields [3, 4]. Understanding peptide self-assembly is not only important to design novel materials but also gain insight for disease, which lowers the quality of life and lead to death.

In this study, we demonstrate our results for the extensive study of self-assembly structures of short synthetic oligopeptide A₆K in water. In our previous work [5], we studied the self-assembly structures, including the formation of nematic ordering. The self-assembly structures were investigated using cryo-transmission electron microscopy (Cryo-TEM) and small angle X-ray scattering (SAXS). In this part of the work, the studies were extended to higher concentrations of the peptide.

In Figure 1, SAXS patterns obtained at peptide concentrations from \( q \cdot g^{-1} = 0.12 \) to \( q \cdot g^{-1} = 0.43 \), are presented. At lower \( \phi \) values, scattering pattern supports the presence of hollow nanotubes whereas at higher \( \phi \), the oscillations smear out, although not completely vanish, and at higher q values oscillations start to build up. This kind of scattering pattern is associated with concentric cylinders. After reaching the hexagonal phase, as \( \phi \) increases, nanotubes go through a transition from a single wall to multishell structure. The theoretical model shows the scattering pattern of a system with cylindrical shells, which contain a maximum of 5 shells, each shell has a thickness of 1 nm and the distance between the shells is 3 nm.

The phase transition from nematic to isotropic phase upon increasing the temperature is also studied for \( \phi = 0.11, 0.12 \) and 0.13.

![Figure 1. SAXS patterns obtained from \( \phi = 0.12 \) to \( \phi = 0.43 \)](image)

In Figure 2, SAXS pattern for \( \phi = 0.13 \) is shown. In temperature studies with SAXS, it is seen that the form factor for hollow cylinder disappears between 70-75°C. In summary, we have investigated nanotube nematic to hexagonal phase transition upon increase in concentration and nematic to isotropic upon increase of temperature. This simple system lends itself for systematic investigations of peptide self-assembly including e.g. investigation of the effect of counterion on the nanotube formation and investigation of self-assembly of slightly different peptides such as A₆R.

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Abstract—In this work, the use of electrospun nanofibrous as highly responsive fluorescence quenching-based optical sensors for Hg(I) and Hg(II) ions is reported. The mercury sensing agent Y-8 (4-(dimethylamino)benzaldehyde2-[4-cyanophenyl]methylene]hydrazone) was doped into ethyl cellulose (EC) and poly-methyl-methacrylate (PMMA). Optical chemical sensors were fabricated by electrospinning technique.

The design of new, sensitive and accurate sensors allowing field analysis for mercury ions is of great interest in different areas. In these designs, different dyes have been used for spectral Hg (II) detection either in free or in thin film form.

Recently, the electrospinning technique has been found to be a unique and cost-effective approach for fabricating large surface area materials for a variety of sensor applications [1]. Electrospinning is a process by which high static voltages are used to produce an interconnected membrane-like web of small fibers, with the fiber diameter in the range of 10-1000 nm. This technique can be used with a variety of polymers to produce nanoscale fibrous membranes. Electrospun nanofibrous materials can have approximately 1 to 2 orders of magnitude more surface area than that found in continuous thin films [2].

In this work, we adapted the electrospun nanofibers to conventional optical chemical sensing approach. It is expected that this large amount of available surface area has the potential to provide unusually high sensitivity and fast response time in sensing applications[3].

The fluorescence quenching-based optical chemical sensors were produced by the electrospinning technique. The Hg(I) and Hg(II) sensitive dye 4-(dimethylamino)benzaldehyde2-[4-cyanophenyl]methylene]hydrazone (y-8) has been used as sensing agent. (See Fig.1). Polymer solutions were prepared by mixing 240 mg of ethyl cellulose, 1 mg Y-8 dye, equivalent amount of phase transfer agent, varying amounts of plasticizer (DOP) and ionic liquid in 1.5mL of tetrahydrofuran (THF). PMMA based solutions were prepared by a similar protocol and characterized by Scanning Electron Microscopy (SEM). Electrospinning was performed at 25 kV voltage and at 1 mL/h flow rate. SEM micrographs of EC and PMMA based nanofibers were shown in Fig. 2 and Fig. 3, respectively. The fiber diameters were measured between 484 nm - 2.78μm for 40% DOP, 10% IL and 50% EC containing composites and 6.40-8.35 μm for 25% DOP, 25% IL and 50% PMMA containing ones. Upon exposure to the Hg(II) solutions, the y-8 dye exhibited a decrease in fluorescence intensity at 580 nm. The observed relative signal change was 90%.

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Inferring the Aharonov-Bohm phase of particles and quasi-particles at semi-conductor based interferometers

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Abstract—Here, I report on the on going experimental and theoretical investigations to obtain Aharonov-Bohm phase of particles and quasi-particles considering a two dimensional topology, induced on semi-conductor materials. The high perpendicular magnetic field yields formation of compressible and incompressible strips which propagate along the interference device. These so-called edge-states are utilized to transmit electrons coherently, which I will be discussing in detail.

Recent low-temperature transport experiments, utilizes the quantum Hall based interferometers to investigate the quantum nature of particles. Particularly, the Aharonov-Bohm (AB) interference experiments became a paradigm [1,2], which infers the AB phases of both the electrons and the quasi-particles.

Most interestingly, two dimensional topology enables experimentalists to investigate the statistical properties of composite "quasi" particles [3], in the fractional quantum Hall effect regime. In the integer quantized Hall regime, the single particle edge-state picture is used to describe transport, meanwhile electrostatics is enriched by interactions and both are used to explain the observed AB oscillations [2].

Figure: The spatial distribution of incompressible edge states at different magnetic field values, indicated on each figure. The interference pattern is only observed at B=8.0 T, where two states come close enough and also the current carrying strip is no longer incompressible.

However, the actual spatial distribution of the edge-states is still under debate for real samples, since handling the full electrostatics is a formidable task, although, several powerful techniques are used [4]. By full electrostatics we mean both handing the crystal growth parameters and the "edge" definition of the interferometer, i.e. gate, etched or trench-gated.

In this talk, I report on a semi-analytical scheme to model AB interferometers induced on a two dimensional electron gas (2DEG) by solving the 3D Poisson for the given heterostructure [5]. Our calculation scheme also takes into account the lithographically defined surface patterns to obtain the electron and potential distributions under quantized Hall conditions [6,7].

The distinct part of our calculation is that we can handle both gate and etching defined geometries. Our findings show that the etching defined samples provide a sharper potential profile than that of gate defined [7,8]. In addition we can define the structure with trench gating, which is the case for the experiments, and show that the formation of the edge-states is strongly influenced.

The fractional edge-states and their effect on AB phase is discussed at the end, together with its importance on the fractional charges.

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References:
Formation of Graphene Sheets and Carbon Nanotubes on SiC
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Abstract— We studied the formation of carbon nanostructure on single crystalline 6H SiC by vacuum decomposition at 1400-1900°C. Produced nanostuctures were characterized by using scanning electron microscopy, transmission electron microscopy, Atomic Force Microscopy and Raman spectroscopy.

Control over the structure of materials on nanoscale can open numerous opportunities for the development of materials with controlled properties. Carbon, which is one of the most promising materials for nanotechnology, can be produced by many different methods. One of the most versatile, in terms of a variety of structures demonstrated (graphite, porous amorphous carbon, nanotubes, graphene and diamond), is selective etching of SiC and other carbides [1-3]. Since the Si atoms are extracted layer by layer, atomic level control of the carbon structures can potentially be achieved without changing the size and shape of the sample. Carbon produced by this method is called Carbide-Derived Carbon (CDC).

In this work, CDC formation was studied on single crystalline 6H-SiC wafers by vacuum decomposition at high temperatures with the goals to better understand the mechanism of carbide-to-carbon transformation and determine conditions for synthesis of desired carbon structures. The transformation mechanism of the SiC surface to carbon was discussed in detail accounting to the effects of processing parameters (temperature, and composition of the environment), and material parameters (surface conditions, surface chemistry, crystal face, etc.). The characterization of the carbon structures was performed by using scanning electron microscopy (SEM), Raman spectroscopy, transmission electron microscopy (TEM) and Atomic Force Microscopy (AFM).

We found that the transformation from SiC to carbon is conformal, preserving the morphology of the initial sample[5]. This shows that the CDC synthesis technique can generate uniform carbon coatings on carbide substrates of complex shape. Thin graphene layers formed parallel to surface on the Si face upon vacuum annealing (Fig.1a,b,c). It is important to mention that graphene sheets, while producing high-quality Raman spectra with a weak or no D-band, always contained wrinkles. Since vacuum decomposition of SiC is widely used to produce graphene, this may affect its electronic properties.

Accelerated CNT formation on both Si and C faces of SiC wafers was observed by vacuum annealing in the presence of oxygen (Fig.1d). This was explained by additional processes such as active oxidation of SiC and carbon transport through the gas phase, in addition to accelerated SiC decomposition by introducing oxygen into the system. The role of carbon transfer through the gas phase in CNT growth on both wafer faces was observed when CO2 and CO were added to the furnace. Both led to the formation of CNTs on Si and C faces (Fig.1e).

CNTs synthesized on the Si face were characterized in detail. Strongly pronounced RBM modes in Raman spectra and TEM images that show formation of small-diameter nanotubes with 1-4 graphene walls.

Figure 1 (a) AFM and (b) SEM image of graphene layers formed on Si face of SiC annealed for 4 h in vacuum at 1400°C. Wrinkles (0.5-2 nm in height) are occasionally observed near the surface steps (steps are almost invisible). (c) SEM image of the Si face annealed for 4 h in vacuum at 1900°C. Fracture surface in shows that bright lines in (b) are wrinkles. SEM micrographs of CNTs formed on Si face (d) after 4 hr at low vacuum (10−4 Torr) at 1900°C by annealing for 4 hrs at 1700°C in CO.[4].

CNT brushes grown on SiC have a significantly higher density than CVD nanotubes, leading to improved mechanical properties of the brush. They are catalyst free and have a high oxidation resistance upon heating in air, withstanding temperatures of 100-150°C higher than DWCNT or MWCNTs produced by catalytic CVD growth.

We also showed that patterns of graphite and catalyst-free nanotubes can be grown simultaneously and directly on a semiconductor SiC wafer.

In summary, we showed that different structures are formed on the Si (0001) and C(000-1) faces of SiC by vacuum decomposition depending on the initial surface morphology, chemistry and carbon transport through the gas phase. While graphene sheets were produced parallel to the crystal surface, carbon nanotube arrays formed vertically. The nanotube arrays formed by this technique have a very high density and are catalyst-free with no internal closures. They show a higher oxidation resistance and better mechanical properties compared to CNT carpets deposited by catalytic chemical vapor deposition. Their integration with graphite or silica layers on SiC wafers is possible in a simple 2-step process and opens new horizons in nanoscale device fabrication.

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Abstract - In this study CNTs were synthesized using Fe thin film catalyst on Si/SiO$_2$/Al$_2$O$_3$ substrates by thermal chemical vapor deposition (CVD). With the addition of CO$_2$ to hydrogen pretreatment, catalyst particles were reduced from oxide form to metal form. Reduction process was studied using several different CO$_2$ flow rates which varied during both in pretreatment and in growth process. The effects of CO$_2$ pretreatment and CO$_2$ flow rate on CNT structural properties were analyzed. This study showed that added small amount of CO$_2$ resulted in decrease in CNT average diameter. However, further increasing CO$_2$ ratio and time, CNT average diameter started to increase. It was also observed that adding controlled small amount of CO$_2$ assisted to improve CNTs structural quality.

In order to analyze catalyst thin films structural properties scanning electron microscopy (SEM), atomic force microscopy (AFM), and profilometer were used. These grown carbon nanotubes structural properties, diameter and length were defined by SEM.

We observed that CO$_2$ had a critical effect on CNT growth. With the addition of CO$_2$ the average diameter of CNTs were decreased from about 16 nm to 10 nm. From SEM images we saw that the pretreatment time also affected the diameter of CNTs. With decreasing pretreatment time, CNTs diameter range was narrowed. The optimal results were obtained for 2 min. and 5 min. pretreatment time. SEM images also revealed that more effective growth was occurred for low CO$_2$ flow rates during pretreatment (Figure 1). CO$_2$ flow rate study for CNT growth process has the same effect with at pretreatment study. We saw that for 2 min pretreatment process, when CO$_2$ flow rate reduced by half, CNT average diameter decreased by 3 nm.

Figure 1. SEM picture of sample CNT537. Scale bar: 5 μm.

In summary, by adding an appropriate amount of CO$_2$ during both pretreatment and growth process in the thermal CVD, catalyst metal nanoparticles sizes can be decreased and hence, diameters of CNTs can also be decreased. We also observe that the presence of a small amount of CO$_2$ yielded high purity CNTs. However, efficiency window for CO$_2$ was very narrow requiring strict control of the parameters. This study was supported by TUBITAK with a project number 109T534.

Carbon nanotubes, due to their superior mechanical and physical properties, have been an important subject of research since 1991 [1], and find use in many applications.

A correlation exists between the size of the catalyst particle and CNT diameter [2]. The catalyst particle size is strongly affected by the pretreatment conditions and the growth temperature. There are conflicting reports whether metal or metal oxide particles contribute efficient growth of CNTs [3]. It is generally agreed upon that catalyst particles in metallic form can easily coalesce and form larger particles which results in CNT diameters with wide range of distribution, which in turn affect CNT properties since the diameter is very important parameter to decide electronic, mechanical, and structural properties of CNTs. During growth an oxidizing environment helps to have efficient growth by removing amorphous carbon coverage over catalyst particles. If amorphous carbon accumulates over catalyst particle it becomes inactive in CNT synthesis. CO$_2$ provides the regeneration of the catalyst [4], and yield more uniform CNTs [5]. It has similar effects with O$_2$ and water on CNT growth [6]. H$_2$ also is used for reduction of catalyst particle from oxide form to metal form but some study claim that it causes a reversible reaction, and so it may decelerate the CNT formation [7].

In this study CO$_2$ to provide a mild oxidizing environment both during pretreatment and growth. It provides controlled reduction of metal oxide so fast coalescence occurs during this stage. We also studied the effects of controlled small amount of CO$_2$ on CNT characteristics.

We used Fe films grown on commercially purchased Si (100) wafers covered with 200 nm SiO$_2$ by thermal oxidation to have CNT growth. 15 nm Al$_2$O$_3$ buffer layer was grown by magnetron sputtering. We used thermal CVD method for CNT growth. Our main study parameter was CO$_2$. Firstly we synthesized CNTs without CO$_2$, then we synthesized CNTs using CO$_2$ without changing the other parameters. We studied CO$_2$ effect on both pretreatment process and growth process. All growth runs were carried at atmospheric pressure and at 740 °C temperature. Ultra high purity Ar was used as a carrier gas at 150 sccm throughout the whole growth sequence. For pretreatment H$_2$ and CO$_2$ mixture was sent to the system at four different durations. Various flow rates of CO$_2$ were also examined during pretreatment process. Our carbon precursor was ethylene, and its flow rate was constant for all growths and 180 sccm. During CNT growth also CO$_2$ flow continued but flow rate of gas was decreased, and different CO$_2$ flow rates were studied at also during CNT growth process. Finally, system was cooled to room temperature under 150 sccm Ar flow after the growth.
Carbon Nanotube Growth by Chemical Vapor Deposition on Co-Mo/MgO Catalyst

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Abstract - The effects of pretreatment and growth conditions in the growth of carbon nanotubes (CNTs) by chemical vapor deposition was investigated by using hydrogen, argon and the mixture of these two gases during both pretreatment and CNT growth on Co-Mo/MgO catalyst. This study showed that increasing hydrogen ratio has a good effect on the quality of CNTs. However, hydrogen ratio also affected the diameter of CNTs, with increasing hydrogen ratio the CNT diameter also increased. On the other hand temperature also had a very important effect on CNT yield and at this study the maximum obtained yield was 2000%, and average diameter range was between 5-15 nm.

Carbon Nanotubes (CNTs) with their unique one-dimensional highly-ordered structure [1] and nanometer scale in diameter possess excellent mechanical flexibility and chemical stability [2]. Therefore they take part in high strength composite materials, interconnections, and functional devices in molecular electronics [3]. There are several methods to synthesize CNT, the most common ones are arc discharge [4], laser ablation [5] or chemical vapor deposition (CVD) [6] methods. Among these CVD is the most promising technique for large-scale synthesis of high-quality SWCNTs and DWCNTs.

To synthesize CNTs, catalyst particles are needed for growth initiation in CVD. Metal-supported catalysts are appropriate for CNT growth. As support, inorganic porous materials such as silica (SiO₂), alumina (Al₂O₃), zeolites and magnesium oxide (MgO) are generally used [7]. MgO support is widely preferred because it provides a high yield of surface, clean SWNTs and DWCNTs and is easily removed by a simple acid treatment [8]. The dispersion of catalyst increases with high BET surface area, and in order to increase specific surface area different organic compounds can be used such as tartaric acid, citric acid, ethylenediamine tetraacetic acid (EDTA), and sorbitol. Among these organic additives sorbitol derived catalyst gave the highest specific surface area and the smallest metal particle size [9].

In this study, Co-Mo/MgO catalyst was prepared using sorbitol as organic additive with gel-combustion method and analyzed in order to find the most efficient pretreatment and growth conditions for high quality CNT growth. To produce Co–Mo/MgO catalyst, Co(NO₃)₂.6H₂O, (NH₄)₂MoO₄.24H₂0, and Mg(NO₃)₂.6H₂O salts with a molar ratio of Co:Mo:MgO;0.5:0.25:10 and sorbitol were dissolved in 10 ml distilled water by stirring until a clear solution was obtained and the solution was dried at 100 °C for 3 hours to form a uniform gel, followed by a flash calcination of obtained gel in oven at 550 °C for 30 minutes. Then it was ground into a powder with particle size between 75-250 μm. Catalyst was characterized with X-ray diffraction (XRD) scans, scanning electron microscopy (SEM) and N₂ adsorption (BET surface area). CNTs were synthesized by CVD method at atmospheric pressure in a 1 inch diameter quartz tube. 15 mg catalyst used for a growth. Catalyst pretreatment was investigated with Ar, H₂ and Ar-H₂ mixture keeping the total gas flow 200 sccm for 1 hour. CNT growth also was investigated with Ar, H₂ and Ar-H₂ mixture keeping the total gas flow 250 sccm for 40 minutes. Growth temperature in the range of 850 to 1000 °C was another studied parameter. Finally, as-grown CNTs were purified with 4M HCl acid treatment.

Purified and unpurified CNT samples were analyzed with SEM, thermo-gravimetric analysis (TGA), Raman spectroscopy, transmission electron microscopy (TEM).

SEM images showed that increasing hydrogen/argon ratio in CNT growth and in pretreatment process positively affected the quality of CNT, and caused higher yield of product. Obtained CNTs were in a narrow diameter range between 5-15 nm. Parameter study of temperature showed that when the temperature decreased CNT yield reached up to 2000 % and average diameter of CNTs decreased below 10 nm. However, CNT had poor structural quality with decreasing temperature.

Figure 1. SEM image of sample MgOCNT513 grown under H2:CH4 200:50 sccm and 1000 °C conditions.

In conclusion, the optimal growth parameters were studied in order to obtain high quality and high yield CNTs and this study revealed that hydrogen had a very important role on quality of CNTs and when growth and pretreatment took place in hydrogen atmosphere alone, without argon, it gave optimal CNT growth.

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New Technique of Producing Polymer Nano-Fibers by Electrospinning Process

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Abstract- The main goal of this research proposal is to realize and validate an innovative nanofiber electrospinning production system of simple design, low cost, safe operation and relatively high production rate. This system was introduced by Abdel Hady[1]. The new system is capable of overcoming some of the existing process drawbacks such as beads, fiber breakage, whipping, and low productivity. It will allow the production, with low cost, of high-value, high-strength fiber from biodegradable polymers.

Many variables affect the process of electrospinning: polymer (type, concentration), solvent (type, vapor pressure, diffusivity in air), solution (conductivity, viscosity, surface tension, feed rate), electric field (strength, shape), the apparatus design (nozzle radius, distance from nozzle to collector plate), ambient condition, etc.

Several works studied the electrospinning process and the effect of variables through mathematical modeling (Thompson [2]). Dzenis [3](2000) and Spivak and al. [4] formulated the process by the three governing equations (mass balance, momentum balance, electric charge balance). In this formulation they ignored the gravity as an external source on the momentum balance equation which plays an important roll in explaining the random scatter of the fibers at the collecting electrode.

This research covers two essential subjects. The first is a comprehensive study of the process of electrospinning in order to produce polymer nanofibers with controllable morphology and properties. This study is achieved through finite element modeling taking into consideration the three-coupled sciences: fluid flow, mechanics and electrostatics. The second is to introduce a new upward spinning principle in vacuum environment and to validate its functionality by both experimental and analytical approaches. In the proposed new upward electrospinning system the instability is eliminated due to three facts: 1- the process is performed under vacuum environment, 2- the electric field is modified to take a nearly normal direction to the ground electrode starting from the pipette nozzle, 3- the gravitational force is always in the opposite direction of the electrostatic force. Moreover, as the fiber formation is produced upwards the gravitational force and surface tension will work against the electrostatic force (before fiber separation from the main fluid), which introduces more stretching to fiber thus producing smaller fiber diameter than in the case of downward formation (Fig.1). As the fiber separates from the main fluid, acceleration will be gained upwards that will add more stretching or even put the fiber under stretching force until it reaches the ground electrode.

In the new upward system, the fiber is always under two balanced forces during its course of travel (electrostatic and gravitational forces). This makes the fiber collection at the ground electrode take a uniform pattern instead of random orientation as produced with downward method. In addition, because the fluid flow is mainly controlled by the amount of fluid sucked out from the pipette by the electrostatic force, the formation of beads will not occur as in the case of using pressure to force the fluid out in the downward process.

A schematic diagram of the new proposed electrospinning system is shown in Figure 2. The spinning chamber and the polymer reservoir are connected together to have the same pressure environment acting on both the surface of the polymer and the nozzle of the pipette.

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Single Molecule Spintronics
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Abstract- In this contribution I will review the current state of the art of the theory of spin-transport and manipulation in organic materials. In particular I will discuss how to manipulate and how to read the spin configuration of a magnetic molecule.

The weak spin-orbit and hyperfine interaction make the spin-lifetime ($\tau_s$) of organic molecules and molecular solids reaching up to the second mark. However organic materials in general have also poor mobility, so that their spin-diffusion lengths ($l_S$) are rather short. These peculiar characteristics position organic molecules in a unique space within Spintronics and one should envision applications where the spins are manipulated close to where they are injected [1]. This is the realm of single molecule spintronics.

Then I will move to discuss the consequences of such effects on the transport properties of the molecules, addressing both the temperature dependence of the electron transport and the description of the low-bias spin-flip inelastic spectra. In particular I will demonstrate that there is a critical voltage, where the current becomes independent from the temperature. This corresponds to the voltage needed to make the singlet and the triplet state of the molecule degenerate.

Finally I will present results for spin-transport in Mn$_{12}$ and demonstrate that the magnetic state of the molecule can be read electrically with a single I-V read-out obtained by using non-magnetic electrodes [3]. This is achieved by translating the spin-information of a molecule into orbital information, which in turns produce characteristics fingerprints in the I-V curve. The mechanism is general and can be extended to other molecular systems not necessarily magnetic.

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Structural Vibration Analysis of Single Walled Carbon Nanotubes with Atom-Vacancies

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Abstract—It is known that any amount of imperfections lead to significant changes in mechanical, electrical or optical properties of Carbon Nanotubes (CNT). This study mainly focused on the investigation of effects of different amounts of atomic-vacancies on vibrational characteristics of single walled CNT. It is interesting to note that with a vacancy amount of approximately %8, the first natural frequencies can be reduced about %30.

Ever since Iijima [1] reported the new kind of long and slender types of fullerene, carbon nanotubes opened promising research opportunities. Recent investigations in nanotechnology show that carbon nanotubes have one of the most significant mechanical [2], electrical [3] and optical [4] properties. Also interactions between these three fields widen the potential of CNT to be used as sensors [5]. Those unique characteristics are built by mainly the atomistic structure of the carbon nanotubes. Atomistic [6] and continuum [7] models were developed to understand the structural dynamics of CNT. On the other hand since it is reported [8] that any kind of imperfections significantly affects the characteristics of nanotubes, it is worthy to analyze the vibrational properties of nanotubes with vacant atoms.

In this study, we aimed to develop a code in order to construct the atomistic structure of any kind of zigzag or armchair nanotubes and induce any amount of atomic vacancies. Establishing a linkage between molecular mechanics and structural mechanics [6], system stiffness matrices, $K$, and system mass matrices, $M$, can be found and used to find the vibrational properties of nanotubes. Fixed-fixed (bridged) and fixed-free (cantilevered) support mode shapes and natural frequencies can be calculated and visualized for either defect-free or vacancy-induced single walled nanotubes. (See Fig 1)

Figure 1: (a) A mono atomic-vacency located in a (5,5) CNT. (b) First mode shape of a fixed-free supported CNT. (b) Third mode shape of a fixed-fixed supported CNT. (d) The plot of the percent of reductions in the first fixed-free natural frequencies of zigzag nanotubes with increasing number of randomly induced vacancies.

Since it is possible to dislocate a C atom from the side walls of a nanotube and create different amount of atomic-vacancies with experimental methods, the first part of our study is aimed to induce increasing percentages of randomly positioned vacancies. A linear trend was observed in the reductions of the first natural frequencies for any kind of nanotubes. (See Fig 1) Extending this work, similar analyses were conducted on the second natural frequencies which shows slightly parabolic trend in the reductions. Also results exhibit large variations in the amount of reduction for any particular percentage of atomic-vacancies. This may stem from accumulation of vacancies as large holes or the influence of the position/closeness to the supports of the defect.

Also, the effects of mono-vacancies with consecutive positions on the side walls along the axis of the nanotubes are studied. By this way we manage to calculate the altering effect of mono-vacancies and plot the variations in the first five natural frequencies. Since we observe the significance of the position vacancies, valuable conclusions were made regarding the variations in the change of natural frequencies. Expectedly found that any extraction of atoms close to the support atoms decrease the frequencies comparatively more. Also as an interesting finding we showed that extraction of atoms at the free end of a cantilevered nanotube or in the middle section of bridged nanotube behave more like a removal of mass rather than a stiffness element. Hence it shows that depending on the position of defect is possible to increase the natural frequencies of CNT just by inducing an atomic-vacancy. Also the favored mode shapes of a defect-induced nanotube are presented which indicates the availability to tune a nanotube to have the desired mode shaped in the desired vibration plane.

In summary, we showed that vacancies have significant effect on the vibrational properties of nanotubes. Even though a defect-free CNT has outstanding material properties, its unique characteristics can be altered at the production stage or with the exposure of irradiation. Our results are beneficial for determining the amount of imperfections just by investigating the vibrational properties. Also we show that it is possible to tune the mode shapes and natural frequencies to desired value by inducing vacancies in correct positions.

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Characteristics of PFCVAD grown n and p-type ZnO Thin Films
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Abstract—Semiconducting n and p-type ZnO thin films were deposited employing Pulsed Filtered Cathodic Vacuum Arc Deposition System. The structural, optical and electrical properties of these were studied and the reliable results were obtained. The hetero and homo-junction diodes were successfully fabricated using these films.

Semiconductor ZnO thin films with wide band gap attract much interest due to their properties such as chemical stability in hydrogen plasma, high optical transparency in the visible and near-infrared region. Due to these properties ZnO oxide is a promising materials for electronic or optoelectronic applications such as solar cell (as an antireflecting coating and a transparent conducting material), gas sensors, surface acoustic wave devices. The purpose of this research is to improve the properties of n and p-type ZnO thin films for device applications. Polycrystalline ZnO is naturally n-type and very difficult to dope to make p-type. Therefore nowadays hardly produced p-type ZnO attracts a lot of attention. Nitrogen considered as the best dopant for p-type ZnO thin films [1,2].

The transparent, conductive and very precise thickness controlled n and p-type semiconducting nanocrystalline ZnO thin films were prepared by pulsed filtered cathodic vacuum arc deposition (PFCVAD) method. Structural, optical and electrical properties of these films were investigated. And also photoluminescence properties of these films were investigated.

Two different techniques had been used to produce p-type ZnO thin films. Firstly zinc nitride compound was deposited and annealed at different temperatures to convert it into p-type ZnO by thermal oxidation [3]. Second technique employed for producing p-type ZnO thin films is introducing dopant to the arc plasma. Different nitrogen concentrations were used to determine doping efficiency.

Transparent p-type ZnO thin films were produced by oxidation of PFCVAD deposited zinc nitride. Zinc nitride thin films were deposited with various thicknesses and under different oxygen pressures on glass substrates. Zinc nitride thin films, which were deposited at room temperatures, were amorphous and the optical transmission was below 70%. For oxidation zinc nitride, the sample was annealed in air starting from 350 °C up to 550 °C for one hour duration. XRD pattern of these films have diffraction peaks with (100), (101) and (110) orientations. These XRD patterns imply that zinc nitride thin films were converted to zinc oxide thin films with the same hexagonal crystalline structures of ZnO. The optical measurements were made for each annealing temperature and the optical transmissions of ZnO thin films were found better than 90% in visible range after annealing over 350 °C. By oxidation zinc nitride the film converted to p-type zinc oxide and the film became more transparent. During the oxidation process at each temperature Hall measurements were made to determine carrier type, carrier concentration, mobility and resistivity. The Hall effect measurements indicated that ZnO films were p-type, the reliable results obtained for carrier concentration and mobility. Hall effect measurements proved that after annealing at 350 °C up to 500 °C the film was p-type. By increasing the oxidation temperature over 550 °C the ZnO thin films turned into n-type due to the loss of N atoms in the film [4]. Room temperature photoluminescence measurements were performed to investigate doping and impurity level of these films.

The deposited best quality n and p type ZnO thin films were used to produce hetero and homo-junctions [5,6]. p-type ZnO deposited on the n-type Si substrate and aluminum or indium was evaporated as metal contacts (n-p). On the other hand n-type ZnO deposited on p-type Si substrate for p-n structure. In the case of homo-junction both n and p-type ZnO thin films were deposited on glass substrates with Al contacts. Current-Voltage characteristics of these devices were determined and the typical result for p-n hetero-junction was shown in the following Figure.

Figure. The Output Characteristics of p-n junction

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Nanorod networks and core-shell structures of doped ZnO

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Abstract-Al and Sn doped ZnO nanorods have been grown by a thermal evaporation-deposition method. The presence of Al has been found to favor the formation of three dimensional nanorod networks. Sn doped nanorods contain a complex defect structure, including nanochannels. Also tubular structures with either an empty core, or a core filled with Sn inside the ZnO shell.

The study of low dimensional ZnO structures is a subject of increasing interest due to their potential applications in fields such as nanoelectronics, optical nanodevices, gas sensing, catalysis and others. In this work, Sn and Al doped ZnO nanorods have been grown by a thermal evaporation-deposition method and their defect structure has been investigated by transmission electron microscopy. The nanorods have been also characterized by X-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy and cathodoluminescence in the scanning electron microscope.

Mixtures of ZnS and SnO$_2$ powders or of ZnS and Al$_2$O$_3$ powders were used as precursors of the Sn doped and the Al doped ZnO nanorods, respectively. The mixtures were milled in a centrifugal ball mill and the final powder was compacted to form disk-shaped samples of about 7 mm diameter and 2 mm thickness. Samples were then annealed under argon flow at 1280 °C. This process leads to the growth of ZnO doped nanorods or nanorod networks. This method has been previously used to grow different elongated structures of ZnO [1-3] and other semiconducting oxides [4-6].

Sn doped nanorods have typical sizes in the range of hundreds of nanometers wide and lengths of tens of microns. TEM investigations show that the rods have a complex structure of extended defects including voids, empty channels, precipitates and dislocations. In general, specific features appear to be characteristic of the central part, or core, of the rods. In particular, rods of voids of about 50 nm are aligned along the growth axis and connected with dislocations and small precipitates. Also tube shaped voids and long channels oriented along the axis are observed in many rods. In addition, dark elongated regions forming the core of a core-shell structure, appear connected with empty tubular parts of the rod, as shown in figure 1. EDS measurements reveal that the shell is ZnO and the core is a Sn rich region. Selected area electron diffraction (SAED) shows the presence of metallic Sn and of ZnO, and dark field TEM images show that Sn is in the core region. Heating experiments by focusing the TEM electron beam, lead to melting and expansion of the Sn core inside the ZnO shell. The expansion of the Sn core could be directly recorded during observation in TEM. When the Sn core is not connected with empty space, the electron beam induced thermal stress causes the break of the tubular structure and spreading of Sn nanodrops as a consequence of the nano-explosion. Mobile Sn filling inside the ZnO tube has potential nanothermal and nanoelectrical applications.

Figure 1. TEM image of the core-shell structure. The dark core is Sn and the outer region is ZnO. By heating, the core expands into the empty space.

Al doped nanorods grow with a nearly 4-fold symmetry hierarchical structure, shown in figure 2, or form three dimensional nanorod networks.

Figure 2. SEM image of Al doped nanorod array.

SEM and TEM investigations indicate that the star-like structures, as that of figure 2, give rise to the three dimensional networks, by the growth of lateral branches during the thermal treatment, related to the dopant incorporation. The influence of Al on the luminescence of the structures has been assessed by SEM-CL.

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