Teflon target was characterized by an energy and a current fixed at 850 eV and 50 mA, respectively. The energy and the current of the ion-beam sputtering the Au target were 500 eV and 40 mA, respectively. The Au content in the Teflon-like composite layers was controlled by the deposition rates of the Au and Teflon species and checked by X-ray photoelectron spectroscopy (XPS) on reference samples. More details on the ion-beam sputtering deposition, and the structural and chemical properties of the Au nanoparticle/Teflon-like composite are reported elsewhere [16].

Vapor-Sensing Properties: The effects of the surrounding vapor on our sensing DBR were tested by reflectance measurements using a spectrophotometer arranged for experiments in the presence of gas or vapors. The samples were inserted into a glass tube through which flowed synthetic air (20.5 vol.% O2 in N2) as carrier gas. The organic vapor was introduced by bubbling synthetic air through the organic liquid and the mixing the saturated synthetic air with the carrier gas to produce the desired concentration. The measurements were carried out at room temperature.

Received: December 19, 2002  
Final version: March 24, 2003


Direction-Selective and Length-Tunable In-Plane Growth of Carbon Nanotubes**

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Carbon nanotubes (CNTs) are fascinating one-dimensional molecular structures that can be either metallic or semiconducting, depending on their diameter and helicity.[1–3] In order

Experimental

DBR Deposition: The DBR was fabricated by an ion-beam sputtering technique at room temperature. This consisted of four pairs of Teflon-like (315 nm) and Au nanoparticle/Teflon-like composite (244 nm) on a Si substrate. The Teflon-like layers were deposited by sputtering a target of Teflon with an argon ion beam (Ar+) with an energy of 850 eV and a current of 50 mA. The Au nanoparticle/Teflon-like composite layers were obtained by co-sputtering a target of Teflon and a target of Au using Ar+ ion beams. The ion-beam sputtering the

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Fig. 4. Reflectance change at a wavelength of 1.5 μm; inset shows the DBR peak shift versus the acetone molar fraction.
to create microelectronic devices comprised of CNT units, it is imperative to controllably place nanotubes in predefined orientations and configurations, and interconnect them both to each other and to other materials such as metal electrodes. Several methods have been suggested for controlled placement of CNTs onto electrode pairs, including alternating current (AC) bias-enhanced deposition\cite{6} and chemically modified adsorption.\cite{5} Direct growth of CNTs between pre-patterned electrodes by chemical vapor deposition (CVD) is a promising approach, since CVD growth is scalable and can be adapted to produce large-area CNT-electrode arrays.

While growth of vertically aligned CNTs on planar substrates by CVD has been reported extensively,\cite{6-9} obtaining nanotubes that are exclusively oriented parallel to the substrate in pre-determined orientations has been more difficult. Suspended CNTs across elevated structures have been produced recently, either by adjusting the gas flow\cite{10-12} or by applying an electrical field\cite{13,14} during CVD. However, both these approaches require pre-patternning of nanoscale catalyst particle assemblies. Also, the probability of nanotubes bridging across different catalyst islands is difficult to predict and control.

More recently, we reported a CVD-growth strategy to selectively grow unidirectionally oriented nanotubes on silica surfaces, in exclusion to silicon.\cite{15} We have combined this substrate selectivity with lithographic chiseling of SiO\textsubscript{2} layers to produce three-dimensional CNT architectures.\cite{16} Here, we adapt this methodology to exclusively grow CNT bundles in controlled directions parallel to the surface, by inhibiting CNT growth from certain SiO\textsubscript{2} pattern surfaces (e.g., the top surface) by covering them with a Au layer.\cite{17} The lengths of CNTs growing in different directions can be tuned by adjusting the Au coverage on respective SiO\textsubscript{2} pattern surfaces, the deposition time, and the SiO\textsubscript{2} pattern spacings. We utilize this strategy to fabricate arrays of low-electrical resistance nanotube-metal contact structures that could be attractive for creating nanotube-based electrical devices. The procedures used to prepare the SiO\textsubscript{2} patterns, and selectively cover certain portions with a Au layer, are described in the Experimental section and illustrated schematically in Figure 1.

We first describe the growth behavior of CNTs on pristine substrates, i.e., those that were not coated with Au before CVD. Figure 2a shows a representative scanning electronic microscopy (SEM) image of CNT architectures grown on a substrate with a row of SiO\textsubscript{2} patterns. We can see that nanotubes grow from all five surfaces of these patterns, i.e., the top surface and four sidewalls, forming a star-like structure (see inset of Fig. 2a). The CNTs in each direction are well aligned, and have the same length of ~25 μm. CNTs growing in opposite directions, towards each other between patterns cease to grow when they meet each other and form CNT–CNT interfaces (see arrow in Fig. 2b).

In contrast, CVD results on selectively Au-coated substrates show exclusive in-plane growth of aligned CNT bundles on SiO\textsubscript{2} surfaces that are not covered by Au. This is seen in Figure 2c, which shows 50 μm long CNT bridges grown from the left sidewalls of SiO\textsubscript{2} patterns whose top and right sidewall surfaces are coated with Au. The CNTs grow straight, in a direction perpendicular to the silica surface seeding them, until they arrive at the next pattern (Fig. 2d). We note that the CNT growth terminates abruptly when the nanotube tips reach the sidewall of the next pattern, which serves as a barrier to further growth. This feature is seen in Figure 2e which shows a sharp interface between CNT tips and the pattern sidewall (covered by Au) where CNT growth stops.

The process of selectively coating Au on different SiO\textsubscript{2} surfaces can be harnessed to controllably grow CNTs along any sets of in-plane directions. For example, the nanotube growth direction was reversed by coating Au on the top surface and left sidewall of each pattern (Fig. 2f), in contrast to those shown in Figure 2c. We note that the CNT length is solely controlled by deposition time in the absence of physical obstacles in the growth direction. The CNTs grown from the last pattern of the row are ~80 μm long, while those grown between patterns are only 50 μm long, identical to the inter-pattern distance. This is a useful attribute in order to simultaneously bridge patterns with different inter-pattern distances by a single CVD process, where the growth time can be chosen to allow CNTs to bridge the longest inter-pattern gaps. Figures 2c,f also show that CNTs grown on the two sidewalls of SiO\textsubscript{2} patterns (indicated by two tilted arrows in Fig. 2f) are curled and shorter compared to the straight nanotube bundles between patterns. This result suggests that a lower Au coverage—due to line-of-sight Au flux during sputter-deposition—on these SiO\textsubscript{2} surfaces leads to short nanotubes with less alignment.

In order to examine this correlation, we measured the length of CNTs grown on SiO\textsubscript{2} surfaces with different Au coverages—measured by Rutherford backscattering spectrometry (RBS)—between 0 and 1.1 x 10\textsuperscript{17} atoms cm\textsuperscript{-2}. Our results show that CNT lengths decrease monotonically with increas-
ings of carbon/catalyst flux with SiO₂, leading to a decrease in the nanotube growth rate. This results in decreased CNT lengths, with increasing Au coverage for a given deposition time. For Au coverages greater than \(~1.1 \times 10^{17}\) atoms cm\(^{-2}\), the Au layer remains continuous during CVD and masks the entire SiO₂ surface, thus completely preventing CNT growth. The CNT length dependence on the Au coverage is useful for obtaining CNTs of tunable lengths along different directions through control of Au coverage on different faces of SiO₂ patterns. This is illustrated in Fig. 3c, which shows CNTs of two different lengths growing from sidewalls that have been exposed to different Au fluxes through control of sample tilt during Au sputter deposition.

We carried out electrical resistance measurements with a two-point probe on Au coated SiO₂ patterns with and without CNT bridges to explore their use in mesoscale circuits. Figures 4a,b show a schematic sketch of the measurement geometry and plots of electrical resistance as a function of number of SiO₂ patterns, respectively. For all the three samples, the resistance increases linearly with the number of patterns. The circuit contact resistance between the probe and the Au layer on top of SiO₂ patterns (= \(2R_{\text{probe-Au}}\), obtained from the ordinate intercept of each plot, is also nearly constant at \(~200-300\ \Omega\) for all samples. However, the average resistance between two adjacent patterns, denoted by the slope of the plots, is more than a factor of two smaller for patterns bridged by CNTs (\(R_{\text{bridged}} = 54 \pm 2\ \Omega\)) compared with that of the unbridged patterns (\(R_{\text{unbridged}} = 120\ \Omega\)). This is because the resistance of the bridged sample arises from two contributions, i.e., the CNT bridges and the Au atom coverage (Fig. 3a), and no nanotube growth is observed for Au coverages above \(1.1 \times 10^{17}\) atoms cm\(^{-2}\) (nominal thickness \(~20\) nm). While the actual mechanism of this decrease in CNT lengths is yet to be identified, the salient features of the nanotube growth process can be understood as follows. The as-deposited Au layer on SiO₂ transforms into islands of sizes between a few tens and a few hundreds of nanometers upon annealing to the CVD temperature of \(~800^\circ\text{C}\) (Fig. 3b). In contrast, the as-deposited Au layers prior to annealing are continuous films, with no observable surface features at this length scale. Based on these results, we propose that the Au islands decrease the intake and interac-

\[\text{Adv. Mater. 2003, 15, No. 13, July 4} \quad \text{http://www.advmat.de} \quad \text{© 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim} \quad 1107\]
Fig. 3. a) CNT length plotted as a function of Au coverage on SiO$_2$. The nominal Au film thickness is also shown on the top axis. For all the cases, CVD conditions were identical and the reaction time was 30 min. b) SEM image of Au islands (white contrast) after annealing to 800 °C (the CVD temperature) on SiO$_2$ surface. c) CNTs grown from two side-walls of a SiO$_2$ template. Note the different CNT lengths: 40 μm (left) and 100 μm (down). The CNT lengths bear an inverse correlation with Au coverage of 0.75 x 10$^{17}$ and 0.60 x 10$^{17}$ atoms cm$^{-2}$, on the respective sidewalks, derived from the plot in Figure 3a.

Figures that combine CVD with topographical masking of patterned substrates would be attractive for controllably growing nanotube–metal architectures for future devices for electronic switching, memory storage, sensing, and actuation.

Experimental

Arrays of 50 μm × 50 μm silicon pillars were created on a Si wafer by coating and patterning a 1 μm thick photoresist followed by deep etching of 30 μm trenches using a plasmatherm tool. After stripping the resist, the wafer was heated to 1100 °C to form a 1 μm thick SiO$_2$ layer by wet oxidation. This process results in 30 μm high relief features with silica surfaces, as illustrated schematically in Figure 1a.

Au was sputtered onto SiO$_2$ substrates in a 50 mtorr Ar plasma at an anode voltage of 7 V and a current of 25 mA, leading to an average deposition rate of ~1 nm s$^{-1}$. Inside the sputter chamber, the substrates with SiO$_2$ patterns were placed in a near-vertical configuration, at a tilt angle of ~20°, with a sample–cathode distance of 30 mm (Fig. 1b). This sample placement geometry results in Au coverage on the top surface and one sidewall of each SiO$_2$ pattern that faces the Au flux, while the opposite sidewall is protected from Au coverage. Rutherford backscattering spectrometry (RBS) measurements carried out using a 2 MeV He$^+$ probe beam show that SiO$_2$ surfaces are covered with 1.1 x 10$^{18}$ atoms cm$^{-2}$ of Au (nominal thickness of ~20 nm) when exposed to the Au sputter flux for 20 s.

The Au-coated SiO$_2$ patterns were placed into a tube furnace to grow CNTs selectively on SiO$_2$ surfaces without Au coverage by a CVD process using a xylene–ferrocene mixture [18,19]. For comparison, we also loaded substrates without Au coating in the CVD furnace. A solution of 0.4 g ferrocene dissolved in 40 mL xylene was fed into the CVD furnace at the temperature of 800 °C for time intervals ranging from 5 to 30 min. This method is well-known to produce aligned CNTs, which are typically multi-walled nanotubes with diameters of ~20–50 nm [18].

Received: December 10, 2002
Final version: March 27, 2003

Effects of Annealing on the Properties of Molecular Thin Film Heterostructures**

By Sandrine Heutz,* Georgeta Salvan, Tim S. Jones, and Dietrich R. T. Zahn

Optoelectronic devices based on organic thin film materials are looking increasingly attractive because of their low cost and high versatility. However, to meet the demands of this emerging technology, ever more complex and controlled heterostructures have to be produced.1[1] An understanding of the basic properties of these complex heterostructures is crucial for optimizing device architectures and improving the resulting device performance.

Phthalocyanines (Pcs) and perylene (Pe) derivatives have been used in several types of organic thin film devices. They are particularly prominent in molecular solar cells,2[2] and devices based on these materials have resulted in some of the highest performances reported to date.3[3] Their single-layer characteristics have been investigated extensively, from epitaxial growth of very thin layers on semiconductor substrates,4[4] to unstrained growth of relatively thick layers on non-interacting substrates such as glass or indium tin oxide (ITO).5[5] H2Pc and PTCDa both form crystalline films when deposited at room temperature on glass (or ITO) and adopt the well-known herringbone structure.6[6]-[8] Their arrangement with respect to the substrate is, however, different; the molecular planes of H2Pc align perpendicular to the substrate, whereas the PTCDa molecular plane lies parallel to it.[9][10]

Post-growth annealing of single-layer H2Pc and PTCDa films has a significant effect on their properties. H2Pc films display polymorphism provided the film thickness exceeds ~50 nm, where the metastable α phase which is obtained for deposition at room temperature transforms to a more stable β structure, which consists of a more compact herringbone arrangement.[10][11]-[14] PTCDa also forms different polymorphs, α and β, but these have very similar lattice parameters.[15] It has been reported that the α and β phases coexist when films are grown at room temperature on passivated Si(100) while a progressive transition to the α polymorph takes place at higher growth temperatures.[16] We have recently established that for relatively thick (~10–150 nm) films deposited on glass substrates, only the α polymorph is obtained, independent of the growth conditions.[17]

The growth of multilayer organic thin film structures can lead to significant changes in the characteristics of the molecular film when compared to the single-layer film. It has been shown, for example, that the structural properties can be modified by the presence of an underlying ordered molecular layer.[18][19] In the case of H2Pc/PTCDa heterostructures, we have recently shown that when H2Pc is deposited on top of a PTCDa first layer, it adopts a new templated structure in which the H2Pc molecular planes are parallel to PTCDa, with an interplanar distance of 3.33 Å.[20][21] Theoretical calculations show that this structural modification is a consequence of the intermolecular interactions at the heterointerface.[22]

In this paper, we extend our work on the templated PTCDa/H2Pc heterostructures and present a study of the effects of annealing on the structural, morphological and spectroscopic properties. Since it is known that H2Pc single layers are sensitive to temperature treatment, we investigate the possible relaxation of the templated layered structure of H2Pc on top of PTCDa. We then discuss how the stability of the individual layers is modified in a double-layer heterostructure. Our studies show that the templated H2Pc structure is more stable than any of its known single-layer polymers and, furthermore, it can form a protective capping layer that prevents sublimation of PTCDa from the underlying layer.

Different in-situ annealing temperatures were applied to a PTCDa/H2Pc heterostucture which was grown at room temperature by molecular beam deposition and consists of a 190 nm thick H2Pc layer deposited on top of a 150 nm PTCDa layer. The X-ray diffraction (XRD) pattern of this heterostructure, Figure 1b, shows the main PTCDa peak at 2θ = 27.6°, which corresponds to diffraction from the (102) planes and an interplanar spacing of 3.22 Å. This peak is characteristic of single-layer PTCDa films as can be seen from the corresponding diffraction scan for a 150 nm thick PTCDa film in Figure 1a.[3] The shoulder in Figure 1b centered at 26.8° is characteristic of the planar H2Pc templated structure, with an interplanar (and intermolecular) spacing d = 3.33 Å.[20][23] No changes can be seen in the XRD patterns after annealing to 200°C.

High annealing temperatures (~325°C) are known to induce the α → β phase transition in H2Pc single layers, followed...