SELF-ASSEMBLY


Double-ended aryl dithiols [alpha, alpha'-xylyldithiol (XYL) and 4,4'-biphenyldithiol] formed self-assembled monolayers (SAMs) on gold(111) substrates and were used to tether nanometer-sized gold clusters deposited from a cluster beam. An ultrahigh-vacuum scanning tunneling microscope was used to image these nanostructures and to measure their current-voltage characteristics as a function of the separation between the probe tip and the metal cluster. At room temperature, when the tip was positioned over a cluster bonded to the XYL SAM, the current-voltage data showed "Coulomb staircase" behavior. These data are in good agreement with semiclassical predictions for correlated single-electron tunneling and permit estimation of the electrical resistance of a single XYL molecule (approximately 18 &plusmn; 12 megohms).


We use the technique of ionically self-assembled monolayers (ISAMs) to produce photovoltaic devices of well-controlled thickness and composition. The ISAM nanostructure fabrication method simply involves the alternate dipping of a charged substrate into aqueous cationic and anionic solutions at room temperature. We have employed several approaches to combine the tetrahydrotriphenium precursor of PPV with fullerenes and other organic materials. We apply modulation spectroscopy for the electro-optical characterization of the ISAM-devices. Analyzing the thickness dependence of the recorded photocurrent action spectra allows us to identify the photoactive region within the devices. The modulation frequency dependence of the photocurrent can be assigned to the influence of trapped charges taking part in the photovoltaic process. By utilizing the ability to control both thickness and composition of the organic layer at a nanometer level of precision, the composition and concentration of these defects has been systematically varied. (24 References).


Self-assembled systems such as micelles and liquid crystals are currently of interest as templates for the controlled formation of nanoscale structures. Knowledge of the mesophase structure, structural evolution, and interparticle interaction is of great importance in understanding the behavior of such systems especially for applications such as nanoreactors. Here, we compare the use of cyclic voltammetry, chronomperometry, and the rotating disk electrode (RDE) for the determination of micellar hydrodynamic radii and show that only the steady-state RDE yields values directly comparable with nonelectrochemical techniques. The RDE is applied for the determination of cetyltrimethylammonium chloride micellar structure and observing micellar structural evolution as well as evaluating the usual intermicellar interactions. The results clearly show (a) the collapse of the micellar shear plane toward the hard-sphere surface with increasing electrolyte concentration, (b) the electrolyte-dependent spherical expansion of the micellar hard-spheres due to increasing aggregation (N) number, (c) the structural transition from spherical to rodlike micelles, and (d) micellar elongation. As well as structural evolution, the evolutionary changes in interaction processes are also observed, i.e. the transition from Coulombic interactions to excluded volume interaction. This paper describes in detail the voltammetric measurement of these processes and explicates the necessary experimental conditions for successful observation of micellar structural evolution.


A molecule containing a nitroamine redox center (2'-amino-4-ethynylphenyl-4'-ethynylphenyl-5'-nitro-1'-benzenethiol) was used in the active self-assembled monolayer in an electronic device. Current-voltage measurements of the device exhibited negative differential resistance and an on-off peak-to-valley ratio in excess of 1000:1.


We present and characterize a new J-aggregate-type nanostructure formed by self-assembling of 3,3'-diethylthiadicarbocyanine iodide molecules in a solution. We measure picosecond kinetics of fluorescence from the lowest exciton band, lying in the far-red wavelength range around 810-830 nm. At temperatures 4-300 K we observe a non-exponential fluorescence decay and show that this is a result of exciton-exciton annihilation in a small exciton domain regime. We also measure the temperature dependence of single-exciton radiative lifetime and give a consistent description of it in terms of a self-trapping of exciton in a discrete one-dimensional chain. (38 References).


Interaction of high-power laser light with materials often causes irreversible damage of the near-surface region. It is shown that copper single-crystal surfaces can be patterned by laser light. Irradiation with green light produced adatoms and vacancies, which self-organized into nanoscale pyramids. This restructuring can be removed by annealing. In contrast to green light, infrared laser irradiation at equivalent absorbed energy density did not produce any structural change. This, for metallic systems, unforeseen spectral difference in laser light action points to a concerted process as the source for structural modification, which involves long-lived primary excitation of localized d-electrons through interband transition together with phonon excitation.


The spontaneous formation of organized nanocrystals in semiconductors has been observed during heteroepitaxial growth and chemical synthesis. The ability to fabricate size-controlled silicon nanocrystals encapsulated by insulating SiO2 would be of significant interest to the microelectronics industry. But reproducible manufacture of such crystals is hampered by the amorphous nature of SiO2 and the differing thermal expansion coefficients of the two materials. Previous attempts to fabricate Si nanocrystals failed to achieve control over their shape and crystallographic orientation, the latter property being important in systems such as Si quantum dots. Here we report the self-organization of Si nanocrystals larger than 80 A into brick-shaped crystallites oriented along the (111) crystallographic direction. The nanocrystals are formed by the solid-phase crystallization of nanometre-thick layers of amorphous Si confined between SiO2 layers. The shape and orientation of the crystallites results in relatively narrow photoluminescence, whereas isotropic particles produce qualitatively different, broad light emission. Our results should aid the development of maskless, reproducible Si nanofabrication techniques.


Relaxor ferroelectrics are one of the important classes of self-assembled nanostructure composite materials. Interesting features associated with the nanoregions give rise to the most interesting device related characteristics and unusual properties in these materials. Besides, they possess the largest property coefficients by themselves or when modified with lead titanate (PT). In this report, a detailed temperature dependent study has been carried out on (1-x)PZN-xPT relaxors with compositions x=0.05 and 0.085 using polarized Raman scattering under optical and E-field variables and inferred the structure-property relations in order to obtain information to characterize the material for matching the application criteria. In addition, phase transitions associated with the relaxors have also been investigated to understand the polarization mechanism(s) for the unpoled and poled specimens Pb(Zn/sub 1/3/Nb/sub 2/3/)O/sub 3/-PbTiO/sub 3/. (24 References).


Self-organized semiconducting structures can be generated by including conjugated chains in block copolymers, it is reported here. Thin films of rod-coil copolymers containing a conjugated and a non-conjugated segment show nanoribbons of the conjugated material, indicating that this approach may open the door to an easy method for nanofabrication. (20 References).


CdS-mercaptoacetic (CdS/M) clusters were synthesized by using mercaptoacetic acid as the stabilizing agent in the aqueous solution. From the transmission electron microscopy (TEM) image and the electron diffraction (ED) pattern, a two-dimensional nearly ordered CdS/M cluster array is observed and the CdS/M cluster is found to be constructed of small CdS/M nanocrystals. The model of self-assembly of the CdS/M clusters with internal structure is presented. The absorption spectrum of the CdS/M nanocrystal solution reveals a maximum at 372 nm and the corresponding photoluminescence (PL) spectrum shows a strong peak at 556 nm at room temperature. The PL spectra of various concentrations of CdS/M reveal the passivation effect of mercaptoacetic acid. (7 References).


Structural information on complex biological RNA molecules can be exploited to design tectoRNAs or artificial modular RNA units that can self-assemble through tertiary interactions thereby forming nanoscale RNA objects. The selective interactions of hairpin tetraloops with their receptors can be used to mediate tectoRNA assembly. Here we report on the modulation of the specificity and the strength of tectoRNA assembly (in the nanomolar to micromolar range) by variation of the length of the RNA subunits, the nature of their interacting motifs and the degree of flexibility of linker regions incorporated into the molecules. The association is also dependent on the
Advances in techniques for the nanoscale manipulation of matter are important for the realization of molecule-based miniature devices with new or advanced functions. A particularly promising approach involves the construction of hybrid organic-molecule/silicon devices. But challenges remain—both in the formation of nanostructures that will constitute the active parts of future devices, and in the construction of commensurately small connecting wires. Atom-by-atom crafting of structures with scanning tunnelling microscopes, although essential to fundamental advances, is too slow for any practical fabrication process; self-assembly approaches may permit rapid fabrication, but lack the ability to control growth location and shape. Furthermore, molecular diffusion on silicon is greatly inhibited, thereby presenting a problem for self-assembly techniques. Here we report an approach for fabricating nanoscale organic structures on silicon surfaces, employing minimal intervention by the tip of a scanning tunnelling microscope and a spontaneous self-directed chemical growth process. We demonstrate growth of straight molecular styrene lines—each composed of many organic molecules—and the crystalline silicon substrate determines both the orientation of the lines and the molecular spacing within these lines. This process should, in principle, allow parallel fabrication of identical complex functional structures.


Self-assembly (‘building’) approaches can provide well-controlled structures and assemblies at the nanometer scale, but typically do not provide the specific structures or functionalities required for robust nanoelectronic circuits. One approach to realize high-density nanoelectronic circuits is to combine self-assembly techniques with more conventional semiconductor device and circuit approaches (‘chiseling’) in order to provide suitable functionality and arbitrary circuit functions. An interesting challenge is to find approaches where these techniques can be combined to realize suitable device structures. This paper describes recent work which combines self-assembly techniques involving metal nanoclusters and conjugated organic molecules with semiconductor interface and device structures to form structures of interest for nanoelectronics. One key requirement for this approach is the availability of a chemically stable semiconductor surface layer, which can provide a low-resistance interface between the metallic nanostructure and the semiconductor device layers following room-temperature, ex situ processing. As an illustration of the structures which can be realized, we describe a nanometer-scale ohmic contact to n-type GaAs which utilizes low-temperature-grown GaAs as the chemically stable interface layer. Contact structures have been realized using both isolated (sparse) clusters and using close-packed arrays of clusters on the surface. The low-resistance contacts between the nanoclusters and the semiconductor device layers indicates that relatively low surface barriers and high doping densities have been achieved in these ex situ structures. The general conduction model for this contact structure is described in terms of the interface electrical properties and the contributions from the various components are discussed. (24 References).


We have grown chains of crystalline-Si nanospheres: the crystalline-Si nanospheres of about 10 nm in diameter are supported in amorphous silica and carbon at a nearly equal spacing by a self-organized process. The self-organized phenomenon was attributed to the periodic instability of catalyst on the top of growing wire and oxidation during the growth of nanowires. (11 References).


A family of nanoscale-sized supramolecular cage compounds with a polyhedral framework is prepared by self-assembly from tritopic building blocks and rectangular corner units via noncovalent coordination interactions. These highly symmetrical cage compounds are described as face-directed, self-assembled truncated tetrahedra with T(d) symmetry.


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Single electron tunneling devices were made by combining standard electron beam lithography and the self-assembly of chemically synthesized gold clusters. These clusters, with diameters from 2 to 5 nm, were captured in a 5-10 nm gap between two gold electrodes. The gold particles as well as the electrodes were covered with self-assembled monolayers (SAM) of organic molecules which served as tunnel barriers. Operating devices show a suppressed current due to the Coulomb blockade of tunneling at room temperature. When cooled to 4.2 K, a Coulomb staircase was observed. By applying a voltage to an oxidized aluminum gate beneath the electrodes and the trapped gold cluster the current voltage characteristics were modulated. Anomalous effects are observed such as constant current plateaus whose positions are gate-voltage dependent. An electrodeposition method for gold has been used to fabricate gaps between electrodes smaller than 2 nm. A self-assembled monolayer was used successfully on the electrodes in order to prevent the gold atoms from migrating on the surface between the electrodes and thereby short-circuiting the junction. The conductance of such a tunnel junction has been measured and compared to the theory with good agreement. From this comparison the capacitance of the junction was estimated, and we could use that value to calculate a rough estimation of the distance between the electrodes. (15 References).


It is shown that in the low-temperature (0.37 kelvin) environment of superfluid helium droplets, long-range dipole-dipole forces acting between two polar molecules can result in the self-assembly of noncovalently bonded linear chains. At this temperature the effective range of these forces is on the nanometer scale, making them important in the growth of nanoscale structures. In particular, the self-assembly of exclusively linear hydrogen cyanide chains is observed, even when the folded structures are energetically favored. This suggests a design strategy for the growth of new nanoscale oligomers composed of monomers with defined dipole (or higher order) moment directions.


DNA is a promising construction material for the supramolecular 'bottom-up' engineering of artificial nanostructured devices. The use of DNA for the selective positioning of macromolecular components, the fabrication of nanostructured DNA scaffolds, as well as the DNA-templated synthesis of nanometer-sized and mesoscopic complexes, consisting of inorganic and bioorganic compounds, are exciting areas of current research.


We describe a new type of self-organized nanostructure for Au, Ag and Cu thin foils irradiated with high-energy electrons at around 100 K. The nanostructure appears on the electron exit surface and consists of aligned grooves which developed parallel to the surface, and nanoholes and hillocks which grew parallel to the electron beam. The groove pattern depends on the irradiation direction, the surface orientation, and the kind of metal. After about 1000 s of irradiation, penetration of the foil by grooves and holes occurs, finally leading to the formation of nanoslits or nanoparticles. These structures are probably the smallest ones generated so far on each metal surface. It is suggested that some irradiation-induced effects are closely related to the generation of nanostructures. (11 References).


BACKGROUND: Multiple-stranded DNA assemblies, encoded by sequence, have been constructed in an effort to self-assemble nanodevices of defined molecular architecture. Double-helical DNA has been probed also as a molecular medium for charge transport. Conductivity studies suggest that DNA displays semiconductor properties, whereas biochemical studies have shown that oxidative damage to B-DNA at the 5'-G of a 5'-GG-3' doublet can occur by charge transport through DNA up to 20 nm from a photo-excited metallointercalator. The possible application of DNA assemblies, in particular double crossover (DX) molecules, in electrical nanodevices prompted the design of a DNA DX assembly with oxidatively sensitive guanine moieties and a tethered rhodium photo-oxidant strategically placed to probe charge transport. RESULTS: DX assemblies support long-range charge transport selectively down the base stack bearing the intercalated photo-oxidant. Despite tight packing, no electron transfer (ET) crossover to the adjacent base stack is observed. Moreover, the base stack of a DX assembly is well-coupled and less susceptible than duplex DNA to stacking perturbations. Introducing a double mismatch along the path for charge transport entirely disrupts long-range ET in duplex DNA, but only marginally decreases it in the analogous stack within DX molecules. CONCLUSIONS: The path for charge transport in a DX DNA assembly is determined directly by base stacking. As a result, the two closely packed stacks within this
assembly are electronically insulated from one another. Therefore, DX DNA assemblies may serve as robust, insulated conduits for charge transport in nanoscale devices.


Self-assembled polyhedral structures are common in biology. The coats of many viruses, for example, have a structure based on icosahedral symmetry. The preparation of synthetic polyhedral molecular assemblies represents a challenging problem, but supramolecular chemistry has now advanced to the point where the task may be addressed. Macromolecular and supramolecular entities of predefined geometric shape and with well-defined internal environments are potentially important for inclusion phenomena, molecular recognition and catalysis. Here we report the use of self-assembly of molecular units driven by coordination to transition-metal ions to prepare a cuboctahedron from 20 tridentate and bidentate subunits in a single step. The cuboctahedron is an archimedean semiregular polyhedron that combines square and triangular faces. Our self-assembled polyhedral capsules, characterized by NMR and electrospray mass spectrometry, are around 5 nanometres in diameter.


Enamel formation is a powerful model for the study of biomineralization. A key feature common to all biomineralizing systems is their dependency upon the biosynthesis of an extracellular organic matrix that is competent to direct the formation of the subsequent mineral phase. The major organic component of forming mouse enamel is the 180-amino-acid amelogenin protein (M180), whose ability to undergo self-assembly is believed to contribute to biomineralization of vertebrate enamel. Two recently defined domains (A and B) within amelogenin appear essential for this self-assembly. The significance of these two domains has been demonstrated previously by the yeast two-hybrid system, atomic force microscopy, and dynamic light scattering. Transgenic animals were used to test the hypothesis that the self-assembly domains identified with in vitro model systems also operate in vivo. Transgenic animals bearing either a domain-A-deleted or domain-B-deleted amelogenin transgene expressed the altered amelogenin exclusively in ameloblasts. This altered amelogenin participates in the formation an organic enamel extracellular matrix and, in turn, this matrix is defective in its ability to direct enamel mineralization. At the nanoscale level, the forming matrix adjacent to the secretory face of the ameloblast shows alteration in the size of the amelogenin nanospheres for either transgenic animal line. At the mesoscale level of enamel structural hierarchy, 6-week-old enamel exhibits defects in enamel rod organization due to perturbed organization of the precursor organic matrix. These studies reflect the critical dependency of amelogenin self-assembly in forming a competent enamel organic matrix and that alterations to the matrix are reflected as defects in the structural organization of enamel. Copyright 2000 Academic Press.


The self-organized growth nanometer quantum dots are spontaneous quantum dot structures formed by Stranki-Krastanov growth mode. In general, the formed nanometer quantum dots are lattice mismatched systems with substrate material, and they have certain size, shape and density. This paper introduces ultimate principles of self-organized growth of nanometer quantum dots, self-organized growth mechanism of various quantum dots, and their photoluminescence properties. (18 References).


By using scanning tunneling microscopy and reflection high-energy electron diffraction it is demonstrated that self-organized ordered Si structures develop during submonolayer Si deposition on vicinal GaAs(001) surfaces, provided the preferred adsorption sites in the trenches of the (2*4) reconstruction are filled with Ga. The evolution of different reconstructions with increasing Si coverages is accompanied by step bunching and de-bunching processes. This unexpected behavior is explained by the interaction between reconstructions and steps from a thermodynamic equilibrium view. For particular coverages the complex process leads to a separation of different surface phases and Si coverages on terraces and in step regions. (27 References).


A stress-driven formation of self-assembled InGaAs islands has been studied by the growth on GaAs(100) substrates with sub-micron platinum stripe pattern. Islands or quantum dots preferentially nucleate at the boundary of metal patterns. In addition, a quantum dot-free region near the boundary of the metal pattern is found. Those results are attributed to the stress between metal stripe and GaAs surface, which produces a laterally stressed region around the metal stripe. Adatoms on this region preferentially migrate toward the edge of metal stripes with maximum stress. This result may show a possible way for the interconnection between
randomly distributed self-assembled quantum dots and metal stripes. (19 References).


The effects of a supporting proteinaceous surface-layer (S-layer) from Bacillus coagulans E38-66 on a 1,2-diphytanoyl-sn-glycero-3-phosphatidylcholine (DPhPC) bilayer were investigated. Comparative voltage clamp studies on plain and S-layer supported DPhPC bilayers revealed no significant difference in the capacitance. The conductance of the composite membrane decreased slightly upon recrystallization of the S-layer. Thus, the attached S-layer lattice did not interpenetrate or rupture the DPhPC bilayer. The self-assembly of a pore-forming protein into the S-layer supported lipid bilayer was examined. Staphylococcal alpha-hemolysin formed lytic pores when added to the lipid-exposed side. The assembly was slow compared to unsupported membranes, perhaps due to an altered fluidity of the lipid bilayer. No assembly could be detected upon adding alpha-hemolysin monomers to the S-layer-faced side of the composite membrane. Therefore, the intrinsic molecular sieving properties of the S-layer lattice do not allow passage of alpha-hemolysin monomers through the S-layer pores to the lipid bilayer. In comparison to plain lipid bilayers, the S-layer supported lipid membrane had a decreased tendency to rupture in the presence of alpha-hemolysin.


We present the optical and the structural properties of self-assembled InAs/GaAs quantum dot (QD) structures grown on GaAs(100) and (311)A substrates using molecular beam epitaxy. The photoluminescence (PL) measurements as a function of the temperature and the excitation power density were performed in a closed-cycle refrigerator in the temperature range from 17 to 280 K. The redshifts of the luminescence emissions from the QDs and the quantum wells (QW) followed the Varshni equation. The temperature behaviors of the luminescence for the (100) and the (311)A samples indicated a change in the shapes and thermal quenching activation energies of the QDs. (19 References).


S-layers are produced by the self assembly of proteinaceous subunits on the surfaces of prokaryotes, so that planar, monomolecular-thick crystalline lattices are formed. Some archael and eubacterial S-layer proteins are glycosylated. These lattices typically have center-to-center spacings of less than 25 nm, which makes them attractive for biomimetic or nanotechnological applications.


Systematic study of molecular beam epitaxy-grown self-assembled In(Ga)As/GaAs, InAlAs/AlGaAs/GaAs, and InAs/InAlAs/InP quantum dots (QDs) is demonstrated. By adjusting growth conditions, surprising alignment, preferential elongation, and pronounced sequential coalescence of dots under the specific condition are realized. Room-temperature (RT) continuous-wave (CW) lasing at the wavelength of 960 nm with output power of 1 W is achieved from vertical coupled InAs/GaAs QDs ensemble. The RT threshold current density is 218 A/cm/sup 2/. An RT CW output power of 0.53 W ensures at least 3000 h lasing (only drops 0.83 db). This is one of the best results ever reported. (11 References).