Research Center for Molecular-Scale Nanoscience

IX-C Nano-science and Nano-Technology toward Molecular Scale Electronics

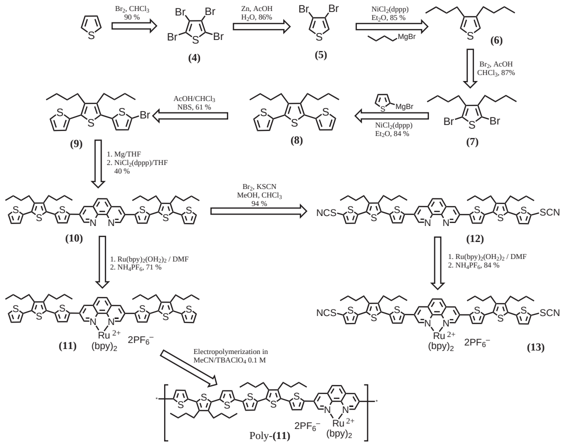
Studies on electric properties of organic and in-organic nano structures are challenging field in material science. Those of aggregates, crystals, or polymers which are made from a large number of molecules or atoms have been already established. In contrast, electronics of nano scale materials which are constructed from small number or single molecules are the forefront of science and technology, and have been revealed gradually to show their diverse phenomena such as quantum conductance, the Kondo effect, the Coulomb blockade, and resonance tunneling. In order to promote this field further, we are studying preparation or fabrication of new organic and in-organic nano materials, and developing new methods to measure their physical properties.

IX-C-1 Bridging Nano-Gap Electrodes by *In Situ* Electropolymerization of a Bis-Terthiophenylphenanthroline Ruthenium Complex

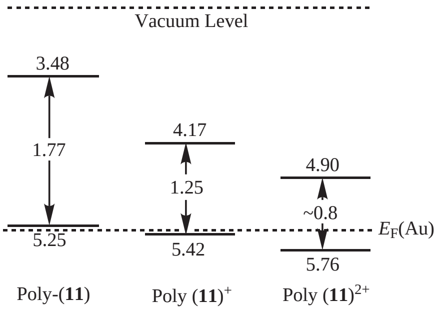
ARAKI, Koiti[1,3]; ENDO, Hiroaki[1,2]; MASUDA, Gou[2]; OGAWA, Takuji[1]
([1]IMS, JST; [3]Ehime Univ.; [3]Univ. São Paulo)

[*Chem. Eur. J.* **10**, 3331–3340 (2004)]

A novel 3,8-bis-terthiophenyl-(1,10-phenanthroline) coordinated to [Ru(bpy)$_2$] was synthesized and characterized by electrochemical and spectroscopic techniques, and shown to be a suitable starting material for the electrodeposition of functionalized molecular wires in between nano-gap electrodes, generating stable molecular nano-devices. Temperature dependent non-linear *I-V* curves were obtained in the 80 to 300 K range. The material can be deposited on ITO also, forming compact electrochromic films at surface concentrations lower than about 1 × 10^{-8} mol·cm^2, but a more loosely bond fibrous form is preferentially deposited at higher surface concentrations.



Scheme 1.



Scheme 2.

IX-C-2 Multi Curve Fitting Analysis of Temperature Dependent *I-V* Curves of Poly-Hexathiophenephenanthroline Bridged Nano-Gap Electrodes

ARAKI, Koiti[1,3]; ENDO, Hiroaki[1,2]; TANAKA, Hirofumi[1]; OGAWA, Takuji[1]
([1]IMS, JST; [2]Ehime Univ.; [3]Univ. São Paulo)

[*Jpn. J. Appl. Phys.* **43**, L634–L636 (2004)]

Stable junctions were obtained by preparing poly-hexathienylphenanthroline coordinated wires to [Ru(bpy)$_2$] complexes directly in the Au electrode nano-gaps by electropolymerization. Reproducible non-linear and strongly temperature dependent curves, similar to that found for π-conjugated dithiols and diisocyanides self-assembled inside nano-holes, were obtained rather than a tunneling behavior commonly found in alkane-thiol self-assembled monolayers. This is the first time that such a consistent series of data are collected for a polymer and interpreted based on a multi curve fitting method using a linear combination of tunneling, Frankel-Pool and hopping mechanism, suggesting that various independent conduction pathways may be present.

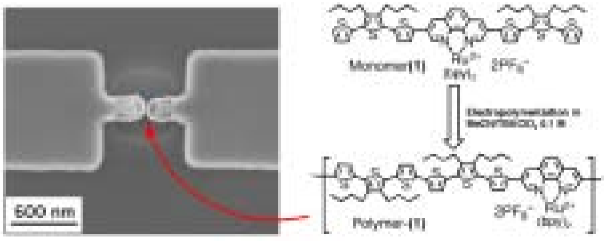


Figure 1.

IX-C-3 Position-Selected Molecular Ruler

TANAKA, Hirofumi; ANDERSON, Mary E.[1]; HORN, Mark W.[1]; WEISS, Paul S.[1]
([1]Pennsylvania State Univ.)

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The molecular ruler method allows the precise control of the gap between a parent gold structure and a deposited daughter structure using a conveniently grown self-assembled molecular multilayer as a lithographic mask. However, we cannot choose a position where the gap should be placed, since the ruler attaches to all exposed gold surfaces. In this work, a convenient method of selecting the position of nano-gaps by further patterning the molecular multilayer using low-energy electron beam irradiation and piranha etchant is described.

The development of a convenient technique to fabricate precise nanostructures in large quantity is required for many types of application, such as electric devices, micromachines and biological equipment, since the "top-down" approach like electron lithography will reach its physical limit soon. Accordingly, it is urgently required to develop "bottom-up" techniques such as molecular self-assembly in order to achieve this goal.

Recently, many researchers have tried to create nano-gaps between electrodes to measure the electronic property of a single molecule or several molecules. For example, shadow evaporation, the break junction method and e-beam lithography have been investigated for this purpose. One of the most convenient approaches coupling the top-down and bottom-up approaches was developed as the molecular ruler method. This is based on the use of compact self-assembled molecular multilayers grown on a parent gold structure as a convenient photoresist. Gap width is precisely controlled by the length of the molecular ruler and the number of monolayers deposited on the top of parent structures, for example, prepared by conventional lithography techniques. One of the advantages of this method is that both sides of the gap are vertically parallel and the desired gap sides can be formed precisely. Another advantage is the position of the gap can be controlled. Multilayers are grown by the successive sequential deposition of monolayers of α,ω-mercaptoalkanoic acid ($HS(CH_2)_xCOOH$) and Cu^{2+} ions, until desired thickness is achieved.

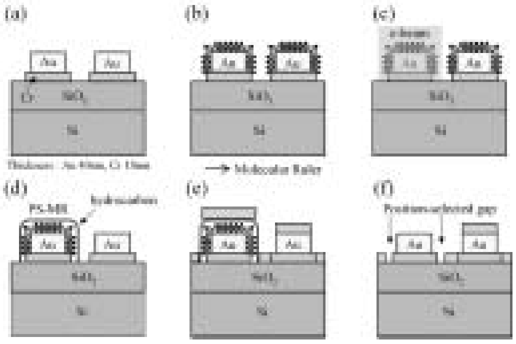

Figure 1.

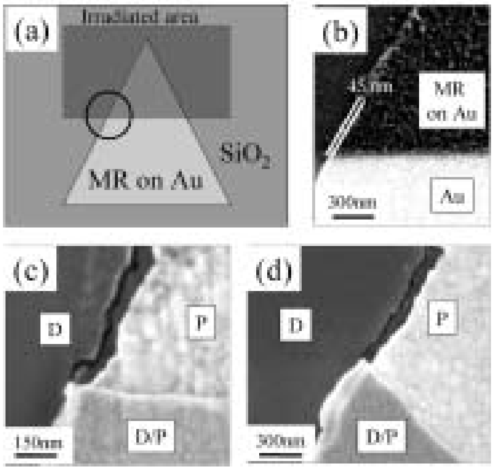

Figure 2.

IX-C-4 Advances in Nanolithography Using Molecular Rulers

ANDERSON, Mary E.[1]; TAN, L. P.[1]; TANAKA, Hirofumi[2]; MIHOK, M.[1]; LEE, H.[1]; HORN, Mark W.[1]; WEISS, Paul S.[1]
([1]Pennsylvania State Univ.; [2]IMS and Pennsylvania State Univ.)

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The combination of conventional lithographic techniques with chemical self-assembly allows for the creation of nanostructures whose spacing and edge resolution reach nanometer-scale precision. The controlled placement and thickness of self-assembled multilayers composed of alternating layers of α,ϖ-mercaptoalkanoic acids and coordinated metal ions form precise molecular ruler resists that enable the production of tailored and lithographically defined metal patterns. Initial structures created by conventional techniques are referred to as parents and subsequent structures generated by the molecular ruler process are identified as daughters. We report the further creation of subsequent generation structures ~granddaughters! that have sub-100 nm dimensions. The granddaughter structures are created by forming molecular rulers on parent and daughter structures, and can be isolated by removing sacrificial parent and/or daughter structures. This process has also been utilized in combination with parent structures created by the process of nanosphere lithography to produce arrays of metal features with 10 nm spacings. Since our original report, we have improved the throughput and reproducibility of the molecular ruler process by automating its iterative nature and by utilizing appropriate chemical lift-off solutions.

IX-C-5 Reactive Ligand-Protected Nano-Particles

ARAKI, Koiti[1,3]; MIZUGUCHI, Eisuke[1,2]; TANAKA, Hirofumi[1]; OGAWA, Takuji[1]
([1]IMS, JST; [2]Ehime Univ.; [3]Univ. São Paulo)

Gold nano-particles exhibit interesting bonding and electronic properties and have been proposed for many applications such as in photoelectrochemical devices, drug delivery systems and sensors. Such applications exploit the molecule-like electronic properties and the particle like behavior of such materials, behaving as highly dispersed solids possessing an exceedingly high functionalizable surface area. In fact, a very significant number of atoms constituting small nano-particles are in the surface and can bond species containing coordinating groups such as thiols, disulphides, phosphines, ammines, *etc*. This means that almost any molecular species can be anchored in the surface imparting their physico-chemical properties to them or leading to the appearance of new properties. On the other hand electronic properties such as light absorption, excited state and electron-transfer characteristics can be controlled by changing the size and the nature of the surface anchored species.

As pointed out above, the preparation of nanoparticles with narrow size distribution is a very important issue and some methods have being developed. For example, Brust et al developed a general method for the preparation of thiol-protected gold-nanoparticles with a narrow size distribution, based on the reduction of $AuCl_4^-$ in toluene with an aqueous $NaBH_4$ solution. The toluene solution also contains protecting species such as *n*-dodecanethiol, essential for the stabilization of the metal clusters, and tetraoctylammonium bromide (phase transfer agent). Teranishi *et al.* have shown that *n*-dodecanethiol protected Au-nanoparticles with very narrow size distribution can be obtained by controlled thermal treatment of previously prepared solid samples.

Another main issue for the widespread use of gold-nanoparticles is the sluggishness of the functionalization reactions, which in the case of *n*-dodecanethiol protected material generally can take more than a couple of days. To overcome such drawback more weakly binding protecting groups such as triphenylphosphine, amines and *terc*-dodecanethiol have being proposed. However, in the first case only very small (~1–2 nm diameter) nanoparticles can be obtained and the reactivity are not so much higher in any case. For this reason, even very unstable gold-nanoparticle solutions, obtained in the absence of coordinating organic protecting groups, have been employed. This starting material is quite unstable and should be used soon after its preparation, making almost impossible its proper characterization before use. This is a main issue since can compromise their applications. We disclosed a method for the preparation of highly reactive ligand-protected nanoparticles.