

Bottom up nanotechnology for molecular and biomolecular electronics

†Serena Gagliardi, §Annamaria Gerardino, †Domenico Luciani, †Piero Morales,
‡Lucia Mosiello, †Sandra Nufri, †Bruno Rapone,

†ENEA, Unità Materiali e Nuove Tecnologie, Centro Ricerche della Casaccia
00060 S.Maria di Galeria, Roma, Italy; ‡ENEA, Unità Biotecnologie, Centro Ricerche della
Casaccia, 00060 S.Maria di Galeria, Roma, Italy; §Istituto di Fotonica e Nanotecnologie del CNR,
Via Cineto Romano 42, 00100 Roma, Italy

The integration of microelectronic circuits is quickly approaching the point where new technologies will be necessary in order to maintain the progress in performance. It is however predicted that post-CMOS technologies will have to be integrated on CMOS based circuitry in order to make the new devices accessible by the user [1]. Several solutions are being studied to overcome limitations imposed by quantum effects, by thermal fluctuations and by power dissipation. Among these, intramolecular electronics [2] and biologically controlled semiconductivity [3] might offer great advantages in terms of very low power dissipation and even, perhaps, selfassembly. However, ways must be found to interconnect these types of devices to conventional CMOS micro or nanoelectronics. This work aims at establishing possible fabrication techniques that retain the advantage of bottom up approaches while being particularly suited to parallel fabrication exploiting the great potential offered by the development of large arrays of scanning probes [4].

Assemblage of a molecular electronic device should be obtained by a method allowing precise addressing of single molecules on specific individual locations. Other ways to interconnect organic molecules to conductors, like break junctions [5], have supplied so far very valuable information on conductivity of specific molecules, but are unsuitable for nanodevice fabrication. Even if planar nanoelectrodes are fabricated by ultra high resolution lithographic processes, details of the interelectrode gap are determined by random clustering of metal atoms at the nanometric level. The electrode thickness is a further, very relevant issue for molecular electronics, as one tries to minimize tunnelling currents between the facing surfaces of the electrodes with respect to the current flowing through the semiconducting molecule. Thus, in our approach, the two fabrication issues of the molecular (organic or biological) assembly and of the metallic interconnects are both addressed by means of a combined laser-Scanning Probe bottom-up method, aiming to fabricate geometrically controlled, extremely well defined metallic junctions, to address individual molecules on their specific gaps, and to characterize both morphologically and electrically the device in real time.

Laser ablation of metals and polymers has been employed for long time for high quality coatings. An improvement of this technique consists in selection of low m/e ions by means of suitably applied electric or, even better, magnetic fields. In this way metallic clusters formed either close to the ablation source or during the flight time to the deposition substrate, can be easily removed from the ablated jet before deposition occurs. If the growth rate is low, allowing for rearrangement of the deposited atoms on the surface, extremely smooth and thin metallic layers can be obtained on insulating surfaces like silicon oxide or nitride. We report on the fabrication of 1.4 nm thick platinum layers on native silicon oxide, with a roughness almost exactly the same as that of the substrate (7 Angstrom RMS). First attempts to use this technique to narrow the gap between lithographically fabricated nanoelectrodes are also reported, showing that this technique is

well suited to obtain nanoelectrode gaps narrower than possible by other techniques. Similarly, laser ablation of suitably prepared samples yields extremely thin and uniform layers of aromatic organic molecules retaining their integrity, and even of large proteins retaining their functional properties, as demonstrated by AFM and by biological assays[6].

To develop a true bottom up fabrication technology, a further step must be investigated. Mildly focussing laser radiation on the SPM probe in a vacuum vessel in which a low pressure of the atoms or molecules of interest is present produces excitation of both tip and vapour; the nanometric features of the tip give rise, in the near field, to a high intensity scattered radiation field [7] that, under suitable conditions, produces a multiple photon excitation of the atoms or molecules of interest. If excitation reaches levels above the ionization threshold, molecular or atomic ions are generated which are subject to the polarization applied to the tip and substrate, and therefore can be conveniently directed to the substrate. On a macroscopic scale this technique has been demonstrated to be a “soft” ionization method that yields unfragmented ions of both small molecules and of fairly large aromatic molecules. The particularly relevant feature of the technique that exploits the e.m. radiation scattered by the tip, is that it is possible to produce ions only in near field of the nanometric tip apex region, thus effectively overcoming the diffraction limit. We have thus attempted to reproduce the successful multiple photon ionization method to deposit atoms and organic or biological molecules on micrometric and nanometric scales, in the near field of the SPM tip apex. In the future, localized addressing of material on the substrate will be facilitated by suitably polarized conductive structures previously fabricated on the substrate surface, such as sharply pointed nanoelectrodes. To obtain a vapour of both metal atoms and organic or biological molecules we have again exploited well established soft vaporization methods based on pulsed laser desorption of neutral material. Use of scanning probe microscopes allows real time morphological and electrical characterization.

It is also in principle possible to exploit light scattering from the nanometric tip apex to efficiently probe the deposited molecules by Raman spectroscopy, a variation of the Surface Enhanced Raman Spectroscopy method, or by excitation of molecular luminescence. A few papers have already been published demonstrating that it is possible to collect enough intensity from such nanometric regions to obtain reliable Raman spectra from films of molecules such as C₆₀. [8]. These experiments pave the way to spectroscopic studies of the molecules immobilized as active elements in future molecular electronic devices.

1. The International Technology Roadmap for Semiconductors, 2005 edition, can be downloaded at <http://public.itrs.net>
2. A. Aviram. A strategic plan for molecular electronics. *Intern. J. Quantum Chem.* 42(5) 1615 1992
3. I. Lee, J.W. Lee and E. Greenbaum. Vectorial arrays of photosynthetic reaction centers. *Phys. Rev. Lett.* 79, 3294, 1997
4. P. Vettiger, G. Cross, M. Despont, U. Drechsler U. Durig, B.Gotsmann, W. Haberle, M.A. LantzH.E. Rothuizen, R. Stutz, G.K. Binnig. The millipede- nanotechnology entering data storage. *IEEE Trans. On Nanotechnology* 1(1), 39, 2002.
5. M.A. Reed, C. Zhou, M.R. Deshpande, C.j. Muller, T.P. Burgin, L.Jones, J.M. Tour. The electrical measurement of molecular junctions. *Molecular electronics: Science and Technology. Annals of the New York Academy of Sciences* 852, 133, 1998
6. A. Gerardino, A. Notargiacomo and P. Morales. Laser assisted deposition of nanopatterned biomolecular layers. *Microelectronic Engineering* 67, 923, 2003
7. C. Girard and A. Dereux, Near-Field optics theories. *Rep. Progr. Phys.* 59, 657, 1996
8. M.S. Anderson. Locally enhanced Raman spectroscopy with an atomic force microscope. *Appl. Phys. Lett.* 76(21), 3130, 2000