

NANOWIRES AS BUILDING BLOCKS OF NEW DEVICES: PRESENT STATE AND PROSPECTS

F. Hernandez-Ramirez^{1,2}, J. D. Prades², R. Rodriguez-Diaz², A. Romano-Rodriguez², J. R. Morante^{2,3}, S. Mathur⁴

¹ Electronic Nanosystems S.L., Barcelona, Spain

² EME/XARMAE/IN³UB, Dept. d'Electronica, Universitat de Barcelona, Barcelona, Spain

³ IREC, Catalonia Institute for Energy Research, Barcelona, Spain

⁴ Department of Inorganic Chemistry, University of Cologne, Cologne, Germany

ABSTRACT

Single-crystalline semiconductor nanowires have emerged as potential building blocks of new devices and circuit architectures due to their astonishing performance derived from their reduced size and well-controlled chemical and physical properties. To date, a great effort has been made in the synthesis and the electrical characterization of these nanomaterials. Nevertheless, the development of real proof-of-concepts nanodevices is still in the preliminary stages. In this contribution, the use of individual metal-oxide nanowires to obtain competitive devices and their integration in portable platforms will be reviewed. Nanowires, which are among the most promising nanomaterials, have demonstrated their suitability to fabricate gas sensors or photodetectors with high sensitivity, stable and reproducible characteristics; and they are generally considered excellent candidates to study some of the phenomena arising at the nanoscale. Finally, future work is outlined which would provide both more complex nanowire based circuit architectures as well as methods for producing these structures in a commercializable fashion.

INTRODUCTION

Monocrystalline semiconductor nanowires have unique properties derived from their high surface-to-volume ratio and well-defined atomic arrangement [1]. This facilitates their integration in many different individual nanowire-based devices such as gas sensors or photodetectors [1-4], overcoming some of the major technological drawbacks which are commonly found in their thin-film counterparts (i.e. high power consumption, lack of stability and drift problems). Nevertheless, the development of competitive devices based on nanomaterials is still in the preliminary stages, and the launch of commercial products remains a major and unsolved challenge due to the difficulties in electrically contacting nanowires and making the best use of their full potential [5]. In this paper, the ultimate advantages of using individual metal-oxide nanowires as building blocks of advanced functional devices are briefly surveyed, and the first portable prototypes based on them are shown. Finally, a discussion on current challenges for the production of commercializable nanowire based complex circuit architectures will be outlined.

ON THE ADVANTAGES OF USING NANOWIRES IN FUNCTIONAL DEVICES

The grounds of many metal-oxide devices are based on the chemico-electrical transduction reactions which take place at their surfaces [4, 6]. For this reason, increasing the surface-to-volume ratio is considered the best strategy to maximize their response towards different external stimuli such as gas molecules or impinging photons. Individual single-crystalline nanowires meet this condition, and thanks to their low mass they are excellent candidates to be integrated in a new generation of low-consumption devices [7]. Nevertheless, the controlled manipulation of individual nanowires is by no means a straightforward process, making necessary the development of well-controlled and advanced nanofabrication techniques [8]. To circumvent this technological obstacle, most of the overwhelming number of articles on metal oxide nanowires published up to now is based on the use of bundles of nanowires instead of individual ones. However, the typical drawbacks of thin-film metal-oxide devices are also found in the characterization of multiple nanowires (i.e. parasitic electrical contributions and stability problems). Figure 1.a shows a diagram

of a thin-film metal-oxide device formed by a large amount of nanoparticles put together onto a supporting substrate. Herein grain boundaries work as Schottky barriers that represent the main contribution to the overall electrical resistance [5]. The spread in both the size and the intrinsic properties of these nanoparticles complicates the interpretation of fundamental studies on the physical and chemical reactions which determine their performance, and the complexity of the inter and intragrain electrical transport is considered a major obstacle to improve present metal-oxide devices and technologies. It is noteworthy that the same conclusions are reached if multiple-nanowire devices are characterized, since the experimental set-up is similar to the former description, just as Figure 1 shows. In fact and from a theoretical point of view, there are not significant differences in using bundles of nanowires instead of conventional thin-films to fabricate functional devices with metal-oxides.

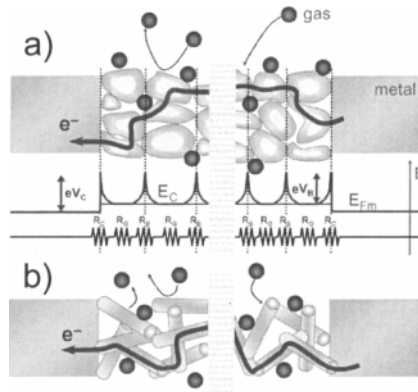


Fig. 1 Schematic diagrams of different types of conductometric gas sensors based on metal oxides. (a) Commercial thin-film sensor formed by a layer of nanoparticles. Here, electrons must go through a network of nanocrystals with different size and shape. From an energy point of view, electrons are to overcome potential barriers [(i) metal-semiconductor barriers (eV_C) and (ii) intergrain boundary barriers (eV_B)]. The overall influence of the exposure gas on the height of the barriers determines the final response of the sensor. This is equivalent to a network of resistors [(i) metal-semiconductor contacts (R_C), (ii) grain boundary interfaces (R_B) and (iii) metal-oxide grains (R_G)]. (b) Multi-nanowire sensor. The above mentioned discussion is valid here as well

On the contrary, the development of devices based on individual nanowires has many advantages. Nanowires, which are usually described as pure resistors R_{NW} (Fig.2) [9], have well-defined surfaces and exhibit good electrical and physical stability as function of time, enabling the fabrication of lasting devices. Furthermore, the complete absence of nanowire-nanowire boundaries eliminates one of the major sources of drift and aging of the devices [10]. In fact, these two problems typical of metal-oxides are usually attributed to the aforementioned grain boundary effects [10].

In short, individual nanowires, whose electrical properties and responses towards different chemico-physical stimuli can be determined by fixing their dimensions and intrinsic parameters such as the free carrier concentration n_d and mobility μ [10, 11], are considered excellent building blocks to fabricate new semiconductor devices with well-defined properties.

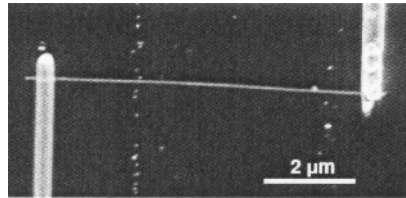


Fig. 2 SnO₂ nanowire electrically contacted with FIB nanolithography techniques.

ON THE FIRST PROTOTYPES USING INDIVIDUAL NANOWIRES

To date, the practical fabrication of complex circuit architectures based on individual nanowires remains an unattainable objective. Nevertheless, many of the theoretical potentials of nanowires have already been demonstrated in simpler devices, for instance their use as gas sensors or UV photodetectors are extensively reported elsewhere [10-14].

The outstanding responses towards both reducing (CO) and oxidizing (NO₂) gas species of individual SnO₂ nanowires confirmed most of the advantages outlined in the former section (Figure 3). Moreover, the detailed analysis of experimental data allowed the development of a theoretical model able to describe the gas sensing mechanisms in a simple way.

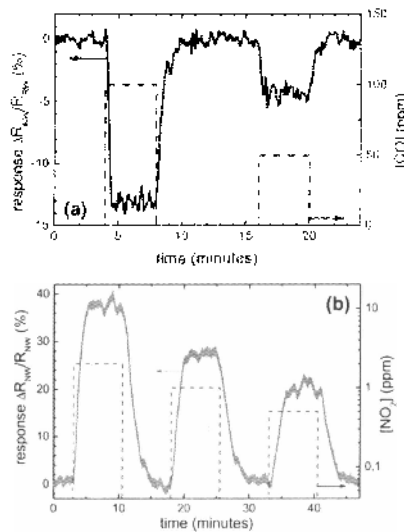


Fig. 3 (a) Response of a SnO₂ nanowire towards different CO pulses at $T = 573$ K. (b) Response of a SnO₂ nanowire towards NO₂ pulses at $T = 448$ K. In both cases, fast and reproducible behaviors are monitored, with excellent recovery of the synthetic air baseline resistance

While interaction mechanisms between gas molecules and nanowires are extremely complex; the sensing principle can be described by pure surface effects [10, 11]. To a rough approximation, adsorption of gas molecules at the nanowire modulates the width of a depleted region close to the external shell. This modifies the conduction channel through it and as a consequence R_{NW} . According to this assumption, R_{NW} under exposure to gas is given by:

$$R_{NW} = \frac{\rho L}{\pi(r-\lambda)^2} \quad (1)$$

where ρ is the nanowire resistivity, L the nanowire's length, r the nanowire's radius and λ the width of the depletion layer created by adsorbed molecules. Equation 1 lays down a connection between the nanowire's radius and the gas response: the thinner the nanowire is, the higher the gas response [10].

To meet this requirement, nanowires with radii below $r = 40$ nm are commonly used for this purpose, giving rise to technological issues derived from working at the nanoscale such as high contact resistance at the metal-nanowire interfaces [9]. Nevertheless, most of these problems are circumvented with different operating strategies reported elsewhere [9], paving the way to better gas nanosensors than their thin-film counterparts.

On the other hand and as far as the use of nanowires as photodetectors is concerned, Prades et al. demonstrated that individual SnO_2 and ZnO nanowires exhibit outstanding response towards impinging UV photons, and determined systematic fabrication strategies to enhance their responses.

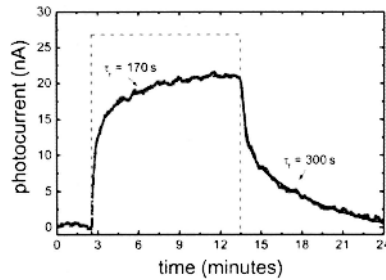


Figure 4. Dynamic behaviour of the photoresponse I_{ph} measured with one single ZnO nanowire when a UV pulse is applied (dashed line) ($\Phi_{ph} = 3.3 \cdot 10^{18} \text{ ph m}^{-2} \text{ s}^{-1}$; $\lambda = 340 \pm 10 \text{ nm}$; $V = 1 \text{ V}$).

Photodetectors based on individual n-type metal-oxide nanowires can be studied using the fundamental principles ruling light carrier generation on semiconductors [14]. Thus and according to this assumption, photocurrent I_{ph} in nanowires is given by

$$I_{ph} - I_{ph}(\alpha^{-1} W) = q \frac{W}{L} \beta \eta \tau \mu^+ V \Phi_{ph} \quad (2)$$

where three different contributions are clearly identified. The first one is related to geometric parameters of the device (W/L), the second one to the intrinsic properties of nanowires ($\beta \eta \tau \mu^+$) and the third one only depends on the working conditions ($V \Phi_{ph}$) [14]. Here, j_{ph} is the current density, α is the absorption profile of the material, W is the width of the photodetector, L is its length, q is the fundamental electrical charge, β is the fraction of photons not reflected by the surface, η is the quantum efficiency of pairs generations by one photon, τ is the carrier lifetime, μ^+ is the effective carrier mobility, V is the applied voltage and Φ_{ph} is the photon flux.

As far as the geometry of photodetectors is concerned, it is clear from Eq.2 that I_{ph} is enhanced by increasing the width (W) of the photoactive area. A convenient way to reach this objective is electrically contacting several nanowires in parallel [14]. On the other hand, distance between contacts (L) also determines the response of the photodetector (see Eq.2). L not only influences the photocaptured area ($W \cdot L$) but also determines the effective electric field E inside the nanowire due to the bias voltage V applied externally. Indeed, this second aspect dominates the overall contribution of L to the photoresponse. Therefore, it can be concluded that higher-gain photodetectors are obtained by diminishing this parameter [14]. The lower limit for L will strictly depend on the precision of the nanolithography technique we use to fabricate the electrical contacts.

In short, it can be asserted that single-nanowire prototypes are extremely useful to demonstrate the potential of nanowires. Nevertheless, the present results and responses can only be improved if complex architectures, such as multiple-nanowires contacted in parallel, are fabricated and characterized. For this reason, many research efforts are currently been devoted to reach this ambitious goal.

TOWARDS REAL DEVICES

The possibility of monitoring the electrical properties of individual nanowires with portable cost-effective and consumer-class electronics (Fig.5) was recently demonstrated [12]. These low-cost instruments, compared to lab equipments, were able to detect and quantify the response of individual nanowires towards UV light pulses and different gases with long-term stability thanks to the low current injected by the platform to the nanowire [12].

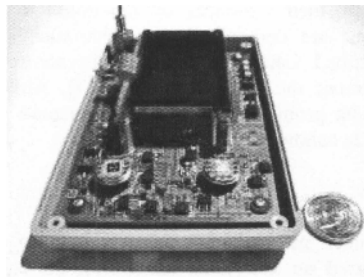


Figure 5. Low-cost electronic platform designed to characterize nanowires

It is well-known that metal oxide materials need to be heated at a specific temperature to maximize their response to a specific target [15]. Therefore, the use of a heater becomes a necessary tool to modulate the final performance of these materials. To solve this issue, both bottom-up and top-down fabrication techniques have been successfully integrated in a single process; nanowires are electrically contacted to a micro-hotplate with an integrated heater [12] (Fig.6).

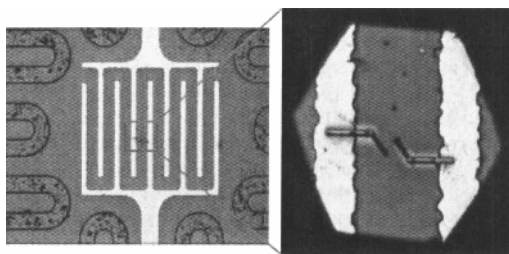


Figure 6. (right) Individual SnO_2 nanowire electrically contacted to two platinum electrodes. (left) Interdigitated platinum electrodes surrounded by a microheater. The nanowire is located in the middle (red square)

This set up allows modulating the effective temperature of the wire as function of the power dissipated at the heater in a fast and completely reproducible manner. It is noteworthy that this solution combined with a good electronic interface, which integrates the thermal control of the nanowire, is extremely useful in many sensing applications [12]. Other architectures are also being explored to solve one of the major issues of sensors: the lack of selectivity to interfering stimuli. Typical examples are photodetectors sensible to a wide range of light wavelengths or gas sensors responsive to parasitic species, such as moisture. For this reason, brand-new studies are attempting to develop electronic systems based on arrays of different individual metal oxide nanowires [16]. According to this approach, their responses are monitored in parallel, and the specific sensing characteristics of each one are determined and electronically recorded following one of the strategies previously described. Later, the data are processed by pattern recognition software to determine the composition of the external stimuli [17]. Although these studies are currently ongoing, they are the most promising solution to overcome the lack of selectivity, which is characteristic of metal oxide nanowires.

FUTURE CHALLENGES

Despite the advances in nanolithography techniques which have made possible the fabrication of devices based on individual nanowires, these techniques are only suitable for prototyping and academic purposes. To extend the use of nanowires to low cost and large scale fabrication processes, self-assembling techniques must be taken into account. In this direction, the first steps had been made to self-align one-dimensional metal-oxide nanostructures by means of dielectrophoretic techniques [18-21].

Dielectrophoresis is an attractive alternative for the positioning and alignment of nanowires thanks to its low-cost, simplicity and flexibility [18, 22]. This method is based on the well-known forces that appear when dielectrically polarized materials are in a medium in which a non uniform electric field is applied [23,24]. It has been tested for different nanomaterials like single- [25-27] and multi-walled carbon nanotubes [77, 78], polymeric [79], metal [80, 81] and semiconductor nanowires [19, 22], and of course metal oxide nanowires [18-21].

Dielectrophoresis can be applied to the fabrication of a new generation of nanodevices and it can be easily combined with other techniques like e-beam or conventional photolithography. If the right design of electrodes is used, nanowires are not only aligned but also positioned at any desired position, and thus, the time necessary to fabricate a device is significantly reduced. This advantage can be applied to the fabrication of the simplest electronic elements, like rectifying junctions [32] and transistors [26], paving the way for the development of novel electronic devices exclusively based on nanostructured semiconductor materials.

Nevertheless, before reaching this high control of self-assembly techniques, the performance of hybrid designs which combine conventional components integrated in silicon and nanowires devices must be investigated in order to achieve new microsystems with enhanced capacities [33].

CONCLUSIONS

Semiconductor nanowires have novel properties derived from their reduced dimensions and excellent crystallinity, which can be used to obtain functional devices such as gas sensors and UV photodetectors better than their bulk-counterparts. Up to now, simple prototypes based on few nanowires have been fabricated and studied. Nevertheless, complex device architectures remain unattainable objective due to the difficulties of working at the nanoscale in a controlled way. For this reason, self-assembly techniques (i.e. dielectrophoresis) or other alternatives such as electrospinning are considered excellent fabrication alternative to overcome this technological bottleneck thus enabling the development of nanowire based commercial devices in the future.

ACKNOWLEDGMENTS

This work was partially supported by the Spanish Government [projects N - MOSEN (MAT2007-66741-C02-01), and MAGASENS], the UE [project NAWACS (NAN2006-28568-E), the Human Potential Program, Access to Research Infrastructures]. JDP and RJD are indebted to the MEC for the FPU grant. Thanks are due to the European Aeronautic Defense and Space Company (EADS N.V.) for supplying the suspended micromembranes. SM thanks the University of Cologne for financial support.

REFERENCES

- ¹ M. Law, J. Goldberger and P. Yang, *Annu. Rev. Mater. Res.*, 2004, 34, 83.
- ² S. V. N. T. Kuchibhatla, A. S. Karaoti, D. Bera and S. Seal, *Progress Mater. Sci.*, 2007, 52, 699.
- ³ G. Eranna, B. C. Joshi, D. P. Runkhala and R. P. Gupta, *Critic. Rev. Sol. State Mater. Sci.*, 2004, 29, 188.
- ⁴ G. Korotcenkov, *Sens. Actuators B: Chem.*, 2005, 107, 209.
- ⁵ F. Hernandez-Ramirez, J. D. Prades, R. Jimenez-Diaz, A. Romano-Rodríguez, T. Fischer, S. Mathur, J. R. Morante, *Phys. Chem. Chem. Phys.* (submitted).
- ⁶ A. Kolmakov, D. O. Klenov, Y. Lilach, S. Stemmer and M. Moskovits, *Nano Lett.*, 2005, 5, 667.
- ⁷ J. D. Prades, R. Jimenez-Diaz, F. Hernandez-Ramirez, S. Barth, J. Pan, A. Cirera, A. Romano-Rodríguez, S. Mathur and J. R. Morante, *Appl. Phys. Lett* 93, 123110, 2008.
- ⁸ F. Hernandez-Ramirez, A. Tarancon, O. Casals, J. Rodríguez, A. Romano-Rodríguez, J. R. Morante, S. Barth, S. Mathur, T. Y. Choi, D. Poulidakos, V. Callegari and P. M. Nellen, *Nanotechnol.*, 2006, 17, 5577.
- ⁹ F. Hernandez-Ramirez, A. Tarancon, O. Casals, E. Pellicer, J. Rodríguez, A. Romano-Rodríguez, J. R. Morante, S. Barth, S. Mathur, *Phys. Rev. B* 76, 085429, 2007.
- ¹⁰ F. Hernandez-Ramirez, J. D. Prades, A. Tarancon, S. Barth, O. Casals, R. Jimenez-Diaz, E. Pellicer, J. Rodríguez, J. R. Morante, M. A. Juli, S. Mathur and A. Romano-Rodríguez, *Adv. Funct. Mater.*, 2008, 18, 2990.
- ¹¹ F. Hernández-Ramírez, A. Tarancón, O. Casals, J. Arbiol, A. Romano-Rodríguez and J. R. Morante, *Sens. Actuators B: Chem.*, 2007, 121, 3.
- ¹² F. Hernandez-Ramirez, J. D. Prades, A. Tarancon, S. Barth, O. Casals, R. Jimenez-Diaz, E. Pellicer, J. Rodríguez, M. A. Juli, A. Romano-Rodríguez, J. R. Morante, S. Mathur, A. Helwig, J. Spannhake and G. Mueller, *Nanotechnol.*, 2007, 18, 495501.
- ¹³ J. D. Prades, F. Hernandez-Ramirez, R. Jimenez-Diaz, M. Manzanares, T. Andreu, A. Cirera, A. Romano-Rodríguez and J. R. Morante, *Nanotechnol.*, 2007, 19, 465501002E.
- ¹⁴ J. D. Prades, R. Jimenez-Diaz, F. Hernandez-Ramirez, L. Fernandez-Romero, T. Andreu, A. Cirera, A. Romano-Rodríguez, A. Cornet, J. R. Morante, S. Barth and S. Mathur, *J. Phys. Chem. C*, 2008, 112, 14639.

- ¹³ N. Barsan, D. Koziej, and U. Weimar. *Sensors and Actuators B* 121, 18 (2007).
- ¹⁶ V. V. Sysoev, B. K. Burton, K. Wepsiec, S. Dmitriev, and A. Kolmakov. *Nano Lett.* 6, 8, 1584 (2006).
- ¹⁷ V. V. Sysoev, J. Goschnick, T. Schneider, E. Strelcov, and A. Kolmakov. *Nano Lett.* 7, 10, 3182 (2007).
- ¹⁸ S.-Y. Lee, A. Umar, D.-I. Suh, J.-E. Park, Y.-B. Hahn, J.-Y. Ahn, S.-K. Lee. *Physica E*, 40, 866 (2008).
- ¹⁹ H. W. Seo, C.-S. Han, S. O. Hwang and J. Park. *Nanotechnology* 17, 3388 (2006).
- ²⁰ S. Kumar, S. Rajaraman, R. A. Gerhardt, Z. L. Wang, P. J. Hesketh. *Electrochimica Acta*, 51, 943 (2005).
- ²¹ J. Suehiro, N. Nakagawa, S. Hidaka, M. Ueda, K. Imasaka, M. Higashihata, T. Okada, M. Hara. *Nanotechnology*, 17, 2567 (2006).
- ²² X. Duan, Y. Huang, Y. Cui, J. Wang and C. M. Lieber. *Nature* 409, 66 (2001).
- ²³ H. A. Pohl. *J. Appl. Phys.* 22 869 (1951).
- ²⁴ H. A. Pohl. *Dielectrophoresis*. Cambridge University Press, London, (1978).
- ²⁵ M. Lucci, R. Regoliosi, A. Reale, A. Di Carlo, S. Orlanducci, E. Tamburri, M.L. Terranova, P., Lugli, C. Di Natale, A. D'Amico, R. Paolesse. *Sensors and Actuators B* 111, 181 (2005).
- ²⁶ P. Stokes and S. I Khondaker. *Nanotechnology* 19, 175202 (2008).
- ²⁷ H. W. Seo, C.-S. Han, W. S. Jang, J. Park. *Current Applied Physics* 6, 216 (2006).
- ²⁸ S. Tung, H. Rokadia, W. J. Li. *Sensors and Actuators A* 133, 431 (2007).
- ²⁹ Y. Dan, Y. Cao, T. E. Mallouk, A. T. Johnson, S. Evoy. *Sensors and Actuators B* 125, 55 (2007).
- ³⁰ P. A. Smith, C. D. Nordquist, T. N. Jackson, T. S. Mayer, B. R. Martin, J. Mbindyo, and T. E. Mallouk. *Appl. Phys. Lett.* 77, 1399 (2000).
- ³¹ J. J. Boote and S. D. Evans, *Nanotechnology* 16, 1500 (2005).
- ³² Y. Lee, T.-H. Kim, D.-I. Suh, J.-E. Park, J.-H. Kim, C.-J. Youn, B.-K. Ahn, S.-K. Lee. *Physica E*, 36, 194 (2007).
- ³³ Evoy, N. DiLello, V. Deshpande, A. Narayanan, H. Liu, M. Riegelman, B.R. Martin, B. Hailer, J.-C. Bradley, W. Weiss, T.S. Mayer, Y. Gogotsi, H.H. Bau, T.E. Mallouk, S. Raman. *Microelectronic Engineering*, 75, 31 (2004).