

# Printed diodes operating at mobile phone frequencies

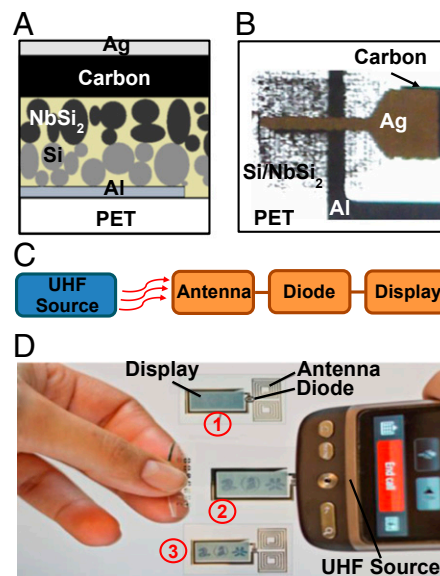
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Printing electronics is a revolutionary approach for fabricating mechanically flexible, low-cost, lightweight, roll-to-roll manufacturable, and large-area optoelectronic devices (1–3). This disruptive technology relies on unconventional electronic materials (semiconductors, dielectrics, conductors, passives) that can be formulated into inks and then printed into specific patterns using processes borrowed from the graphic arts industry (4, 5). Electronic and photonic building blocks, such as transistors, diodes, circuits, light emitters, light harvesters, batteries, and sensors will soon be fabricated and combined to enable applications, such as flexible active/passive displays, plastic radio frequency identification tags (RFID), wireless devices, disposable diagnostic devices, and rollable solar cells, to cite a few (6, 7), which is forecast as a multibillion-dollar market. The goal of printed electronics is not to replace the conventional inorganic-based electronic industry but to offer opportunities for new products and reduce production costs for given devices (Table 1). The main obstacle to the realization of this technology is on the materials side and, above all, the semiconductor (charge-transporting

material), because semiconductors printed in ambient and at low temperature typically exhibit poor charge-transport characteristics. Furthermore, it is challenging to use newspaper printing presses for processing thin functional materials spaced by a few micrometers. Despite the above-mentioned issues, in PNAS Sani et al. (8) demonstrate the first all-printed diode rectifier powered by a mobile phone, thus operating at ultra-high frequencies (UHF), and enabling direct communication between a printed electrochromic display (e-label) and a mobile phone operating at the Global System for Mobile Communications (GSM) band.

The diode is an electronic building block performing several functions, including that of extracting energy from an electromagnetic field to provide DC power to electronic devices without batteries (9). This device can be fabricated with different architectures, such as a vertical diode and a diode thin-film transistor structure, and organic semiconductors have been used for this application (10, 11). Rectifiers based on organic or hybrid semiconductors with both diode architectures and operating at radio-frequencies (RF) (e.g., 13.56 MHz, which is the current standard



**Fig. 1.** (A) Cross-section of the diode rectifier used by Sani et al. (8). (B) Optical image of the printed diode with the materials components highlighted. (C) Schematic representation of the wireless system powering the e-label display. (D) Picture of the complete antenna-diode-display device and a mobile phone as an RF source. The picture also shows the display switching from the off state (1), to partial (2), and full-on state (3) upon making a phone call.

carrier frequency for low-cost passive RFID tags) have been demonstrated (12, 13). Although RF is suitable for several applications, tags or other wireless devices operating far away from the electromagnetic source require operation speeds in the UHF range for antenna miniaturization (14). Compared with the diode rectifier, the other device components are less demanding in terms of high-frequency performance. For example, the transistors used for data modulation—although operating at the same incoming frequency of the base carrier—can function at considerably higher voltages than the rectifying device and can use the full period of the carrier wave. The remaining circuit elements can operate at much lower frequencies because the data clock is

**Table 1. Conventional versus printed electronics**

Comparison	Conventional electronics	Printed electronics
Advantage or disadvantage	High performance Small area/feature size High cost/unit area High capital investment Long production run Durable Rigid Vapor deposition High temperatures Glass/Si substrates Subtractive Photolithography Selected markets	Low performance Large area/feature size Low cost/unit area Low capital investment Short production run Disposable Flexible Solution deposition Low temperature Plastic substrates Additive Printing Everywhere
Materials	Semiconductor, conductor, dielectric, passive, substrate	
Devices/applications	Transistors, diodes, antennas, resistors, capacitors, inductors, conductive traces, circuits, memories, sensors, displays, batteries, photovoltaics	

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considerably slower (at most a few 100 KHz) than the carrier frequency. Several studies have addressed the goal of extending the operational bandwidth of diodes and rectifiers to the UHF range using either organic, inorganic, or hybrid semiconductors. Thus, realizing fully printed RF/UHF rectifying devices is considered the bottleneck for mass utilization of wireless label/tag technologies into the supply chain. Because the diode operational frequency scales with the performance of the diode charge-transporting layer, enabling semiconductors exhibiting high carrier mobilities and materials combinations yielding ideal diode characteristics at UHF is a major research goal in this field.

Sani et al. (8) report a unique materials combination to print high-performing diodes. After testing different conditions, the best devices in terms of yields, rectification ratio, current output, and cut-off frequencies consist of using as the conducting layer a combination of silicon (Si) and niobium silicite ( $\text{NbSi}_2$ ) microparticles ( $\mu\text{Ps}$ ) with an organic binder (cross-linked SU-8) (Fig. 1 A and B). The fabrication process begins with patterned Al electrodes on polyethylene-terphthalate (PET) substrates on which SU-8 and then Si- $\mu\text{P}$  are deposited by screen printing. To achieve a good contact with the bottom electrode, the Si- $\mu\text{Ps}$  are pressed and the film UV-cured. The same sequence is repeated for the  $\text{NbSi}_2/\text{SU-8}$  layer and the device is completed by screen-printing carbon and finally Ag top conducting layer. When excluding devices with low current or poor rectification ratio, statistical analysis indicates that 77% of these printed devices have a cut-off frequency  $>1$  GHz ( $\sim 1.6$  GHz for 33%) and an average rectification factor of 100 at 1 V. Note that state-of-the-art printed organic diodes operate at

$<10$  MHz (15) or at 13.5 MHz for more complex architectures (16), whereas printed inorganic systems may exhibit even greater performance (17–19). Impressively, Sani et al. (8) show that these devices are quite stable after 2 y from fabrication

## Sani et al. report a unique materials combination to print high-performing diodes.

or upon operation at 1.6 GHz for more than 1 h ( $>10^{12}$  cycles). Next, the authors tested the capabilities of the best diodes by fabricating an antenna-diode-electrochromic display circuit (e-label), which was powered by a mobile phone operating within the GSM band (maximum power = 2 W, frequencies 0.9 and 1.8 GHz). Despite the unmatched frequencies and the power loss because of wireless signal transfer, in optimal devices the display turns on within 10 s.

As with every pioneering study, the work by Sani et al. (8) raises new questions and opportunities for optimization. Obviously, the printed diode and the overall circuit yields must be improved for commercial impact. Thus, it would be instructive to see if, using more controlled Si/ $\text{NbSi}_2$  microparticle size distribution, the device yields improve and whether the use of other semiconductor micro- or nanostructures may provide a better entry. Another advance would come by simplifying the printing process, as in these experiments the conducting layer requires four screen-printing plus two pressing plus two photo-curing steps. Probably, it would also be beneficial if these nanoparticles could be formulated with SU-8 and then printed. Finally, it would be exciting to achieve integration with more sophisticated printed circuits, enabling data storage and processing. Nevertheless, the door is now open for new and exciting opportunities.

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