NANOSCIENCE

Atomic jewelry

A handful of gold and silver particles can form intriguing nanometric jewels

Igor Zolnerkevic

A historic moment for Brazilian science occurred on December 17, 2001. That week's issue of the world's premier physics journal, *Physical Review Letters* (*PRL*), featured for the first time on its cover a study conducted entirely by Brazilian researchers. The computer simulation described in the featured article by Edison Zacarias da Silva of the University of Campinas (Unicamp) and Adalberto Fazzio and Antônio José Roque da Silva, both of the University of São Paulo (USP), revealed for the first time how a mass of 300 gold atoms stretched by the tips can expand and form a wire, which breaks only after it thins to form a linear chain of just five atoms.

This theoretical study was inspired by the results of experiments conducted in electron microscopes that at the time were under the management of the Brazilian Synchrotron Light Laboratory (LNLS), now part of the National Nanotechnology Laboratory (LNNano) in the city of Campinas, Brazil. The experiments were conceived by the creative Argentine physicist Daniel Ugarte. When he arrived in Brazil in 1993 to work at LNLS, Ugarte, who is now a professor at Unicamp, formed a team whose research to this day is generating articles in *PRL* and other high-impact journals. After observing the gold nanowires—a feat that other experimental groups

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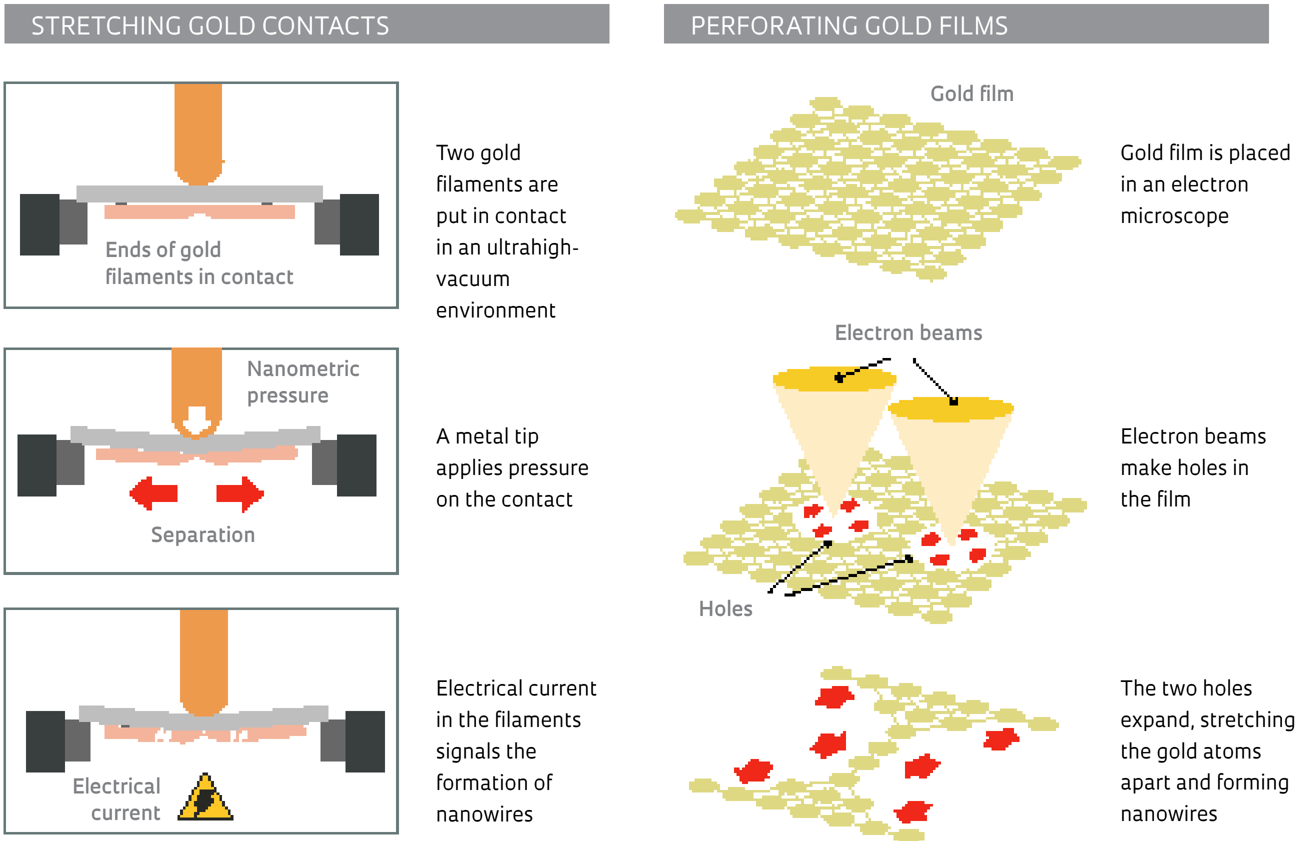
A recipe for gold wires



INFOGRAPHIC TIAGO CIRILLO, SOURCE: USP/UNICAMP/LNLS SIMULATION ZACARIAS DA SILVA, ROQUE DA SILVA AND ADALBERTO FAZZIO

had already accomplished—Ugarte's team spent the past decade discovering and explaining the formation of completely unprecedented structures a few nanometers (millionths of a millimeter) in size, made of atomic chains of noble metals. They are the smallest metal alloys ever constructed and the smallest silver nanotube possible in nature.

Understanding these metal nanostructures is becoming increasingly important as miniaturization of the microchips in electronic devices comes ever closer to atomic scale. It is quite likely that transistors in the next few years will be made of a single molecule. And to connect a series of these molecules in a microchip, engineers will need strong nanometric wires that conduct electricity well.

NANOCRAFTSMANSHIP

Ugarte began to study copper, gold, silver, and platinum nanowires in 1996 with Varlei Rodrigues, who at the time was a master's degree candidate and is now a professor and colleague of Ugarte at Unicamp. Rodrigues built an instrument that could create nanowires and measure their electrical properties, using the so-called mechanically controlled break junction experiment. The biggest challenge in doing so was to create an ultrahigh-vacuum chamber, an extremely clean, airless compartment where they could analyze the purest possible samples of their materials.

In the equipment developed by Rodrigues, the tapered ends of two metal filaments approximately one-tenth of a millimeter thick are placed in contact with one another. In the ultrahigh-vacuum environment, the two ends are joined by the attractive force between their atoms. Then the researchers gently force contact between them. It is at that moment that the nanowires form, like melted cheese between two slices of pizza being separated, hanging between the ends of the filaments. The instrument does not allow for viewing the nanowires, which can be seen only through electron microscopes. In order to detect their presence, the researchers monitor the passage of an electrical current through the filaments. Unlike a macroscopic wire, electrical current in a nanowire does not drop off gently and linearly as its diameter is reduced. Instead, the electrical current remains constant in certain size bands and drops off in several abrupt jumps. Each type of nanowire has a different pattern of jumps, which functions as a digital impression.

The ability to see nanowires has been possible only since 1998, when Ugarte began coordinating the assembly at LNLS of what would, in ten years' time, become Brazil's most complete electron microscope laboratory. Used by hundreds of researchers throughout Brazil, its six instruments—with magnifications of over a million—were financed by FAPESP at a cost of R$8 million. Ugarte oversaw the special design of the building and the rooms that house the microscopes, built with R$6 million in funding from the Brazilian Innovation Agency (Finep). The rooms provide maximum isolation for the delicate instruments to protect them from mechanical vibrations, temperature changes and electromagnetic fields.

"Roughly speaking, a transmission electron microscope works like an overhead projector," explains Jefferson Bettini, a researcher at LNNano. Rather than light from a lamp, it is an electron beam focused by magnetic lenses that passes through a sheet of material and interacts with it. The beam resulting from the interaction is then projected by other lenses and recorded by a video camera. It sounds easy to use, but in fact a student may take two or three years to master the instrument and obtain relevant images. "Microscopy is not about pressing buttons," Ugarte says. "It's you in the driver's seat."

To create the nanowires in the electron microscope, Ugarte used the machine's electron beam. At its tightest focus, the beam is capable of producing holes in thin sheet metal surfaces only a few dozen atoms thick. After perforating the sheet until it looked like Swiss cheese, the physicist quickly adjusted the electron beam to explore its surface. On narrow tips at the edge between two holes very close together, the metal stretches spontaneously in a matter of seconds until it forms the nanowires.

Ugarte and Rodrigues discovered that, depending on their orientation in relation to the way in which the atoms are organized in the metal, the nanowires may break suddenly or little by little, elongating until they form linear chains of atoms. Using a simple geometric model, they were also the first to successfully relate the atomic structures of the nanowires seen under the microscope to their digital impressions of electrical conductance. The findings were published in *PRL* in 2000.

THEORY IN PRACTICE

There was no simple theoretical model, however, that could explain how the gold wires formed with the thickness of only one atom until Zacarias da Silva, Fazzio and José Roque, inspired by Ugarte, decided to conduct an extremely detailed simulation based on precise solutions from quantum mechanics equations. The simulation featured on the cover of *PRL* was finally able to show step by step the arrangements that a group of gold atoms assumes under stress, lengthening until they form a line of five atoms before breaking.

The trio of physicists also discovered that, at the ends of that row of atoms, the gold atoms form a very stable structure, which they referred to as a French hat, owing to its resemblance to the soldier's hats that children make out of newspapers. In later studies conducted by Fazzio and his team, the Simulation Applied to Atomic Materials and Properties group (Sampa) at USP, the new structure was used in computer simulations to construct the ends by connecting a transistor made of a single molecule with a gold surface. The discovery also motivated Fazzio and his team to develop techniques that realistically simulate the passage of electrons through organic molecules, metal nanowires, nanotubes, nanoribbons and carbon surfaces, which yielded several publications, *PRL* among them.

At the same time, Ugarte's group began a partnership that continues today with the team headed by theoretical physicist Douglas Galvão at Unicamp. "We meet with students, his and mine, and we discuss what is possible to measure and calculate," Ugarte says. "It's an extremely fruitful collaboration," adds Galvão. In addition to doing some calculations similar to those done by Fazzio's team that simulate a few hundred atoms at most, Galvão, along with Fernando Sato, Pablo Coura and Sócrates Dantas, all from the Federal University of Juiz de Fora, developed a more approximate method that nevertheless makes it possible to simulate thousands of atoms and thus compare the results of the calculations directly with the experimental measurements.

The first challenge faced together by Ugarte's and Galvão's groups was to attempt to explain the extremely long distances between the gold atoms in the atomic chains. While in any piece of gold the nuclei of the atoms are 0.3 nanometer apart, Ugarte observed distances of up to 0.5 nanometer between the gold atoms in the chains. The proposed explanation in a 2002 article in *PRL* by Ugarte, Rodrigues, Galvão and

A nanowire forms and breaks


A
B
C
D
E
F

The simulation published in Physical Review Letters in 2001 revealed step by step (A to F) the bonds and positions of the gold atoms during the formation and breaking of a nanowire.

Sérgio Legoas of the Federal University of Roraima was that carbon atoms, with much less electrical charge than gold and therefore invisible to the electron microscope, had slipped into the atomic chains and lodged among the gold atoms. Fazzio and his collaborators, however, rejected the explanation in another article published the following year in *PRL*, arguing that the impurity between the gold atoms was not carbon, but rather hydrogen atoms.

The debate remains lively, with both groups publishing articles and comments, many of them in *PRL*, on defense of their theories. Ugarte comments that the discussion "is very aggressive, but that's the way we work in science: we disagree and we don't take offense from it." For his part, Fazzio celebrates the fruits of what he calls "healthy dissention." For example, studying the effect of various types of impurities in nanowires, Fazzio's group showed in another article published in *PRL* in 2006 that inserting oxygen atoms made the gold atomic chains stronger—an effect later confirmed in experiments by other researchers.

Now, Fazzio and his team hope to settle the matter once and for all by developing even more detailed simulation methods that take into account quantum effects of the movement of atomic nuclei and thermal fluctuations—methods that will be applicable in many other studies. From the standpoint of the contention between the two groups, however, the still-preliminary results of these calculations do not seem encouraging. "Perhaps Ugarte is right," Fazzio admits.

ALLOYS AND TUBES

Another question that Galvão and Ugarte attempted to answer, this time with undeniable success, was how nanowires are formed, not from a pure element but from a metal alloy. The simulations performed by Galvão's theoretical team to study the formation of atomic chains of alloys with varying composition of gold and silver revealed a strange behavior. No matter how much silver the alloy contained, stretching the nanowires expelled the silver atoms, causing the atomic chains to contain only gold. Only when the concentration of silver exceeded 80% did atomic chains of mixed gold and silver result.

At first, Ugarte thought it would be impossible to verify the results from these simulations, because gold and silver atoms are practically indistinguishable in the black and white images from the electron microscope. But his colleague Bettini spent a year refining the instrument's data processing and detection systems, until he obtained sufficient sensitivity to distinguish between the gray tones of the two type of atoms, and captured the first images of the smallest metal alloys yet observed. The results were published in 2006 in the prestigious journal *Nature Nanotechnology*. The journal's editors named the study one of the most important of the year. Around that same time, the researchers were able to observe gold-copper nanoalloys.

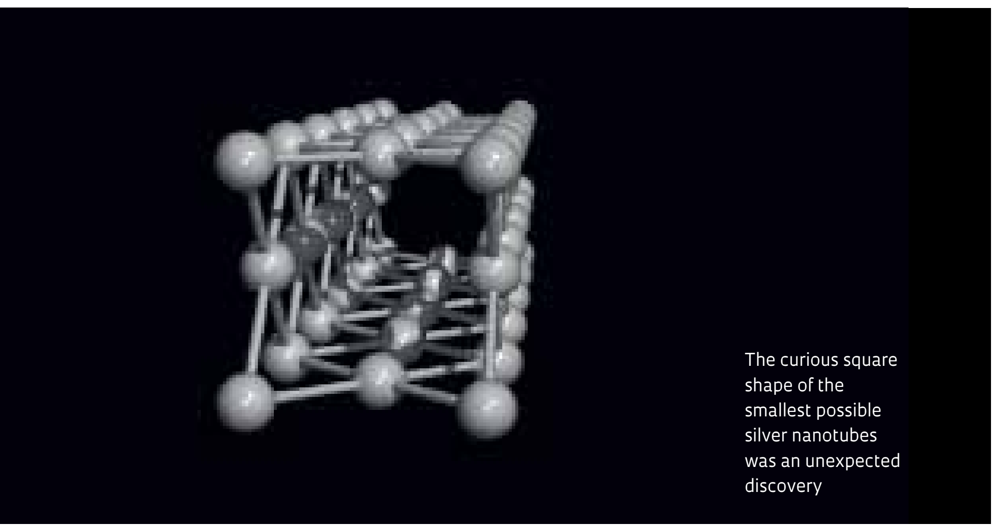
In 2005, Maureen Lagos, a new student from Peru, accepted another challenge: using liquid nitrogen to redo at -150°C Ugarte and Rodrigues' experiments that had been conducted at ambient temperature. The researchers hoped that, when cooled to that extreme temperature, the atoms would arrange themselves in different ways and create nanowires with altogether new properties.

Lagos spent two years modifying the equipment created by Rodrigues to measure the electrical conductance of the cooled nanowires. Then she adapted the method for creating and observing nanowires in the electron microscope for low temperatures. Due to vibrations from microscope parts caused by the cooling process, the experiment demanded that Lagos spend four days shuttered in a dark room until she obtained the stability needed for her measurements. It took years of work to obtain a few dozen films a few seconds long in which the nanowires can be clearly seen.

The debate continues, with both groups publishing articles and comments in defense of their theories

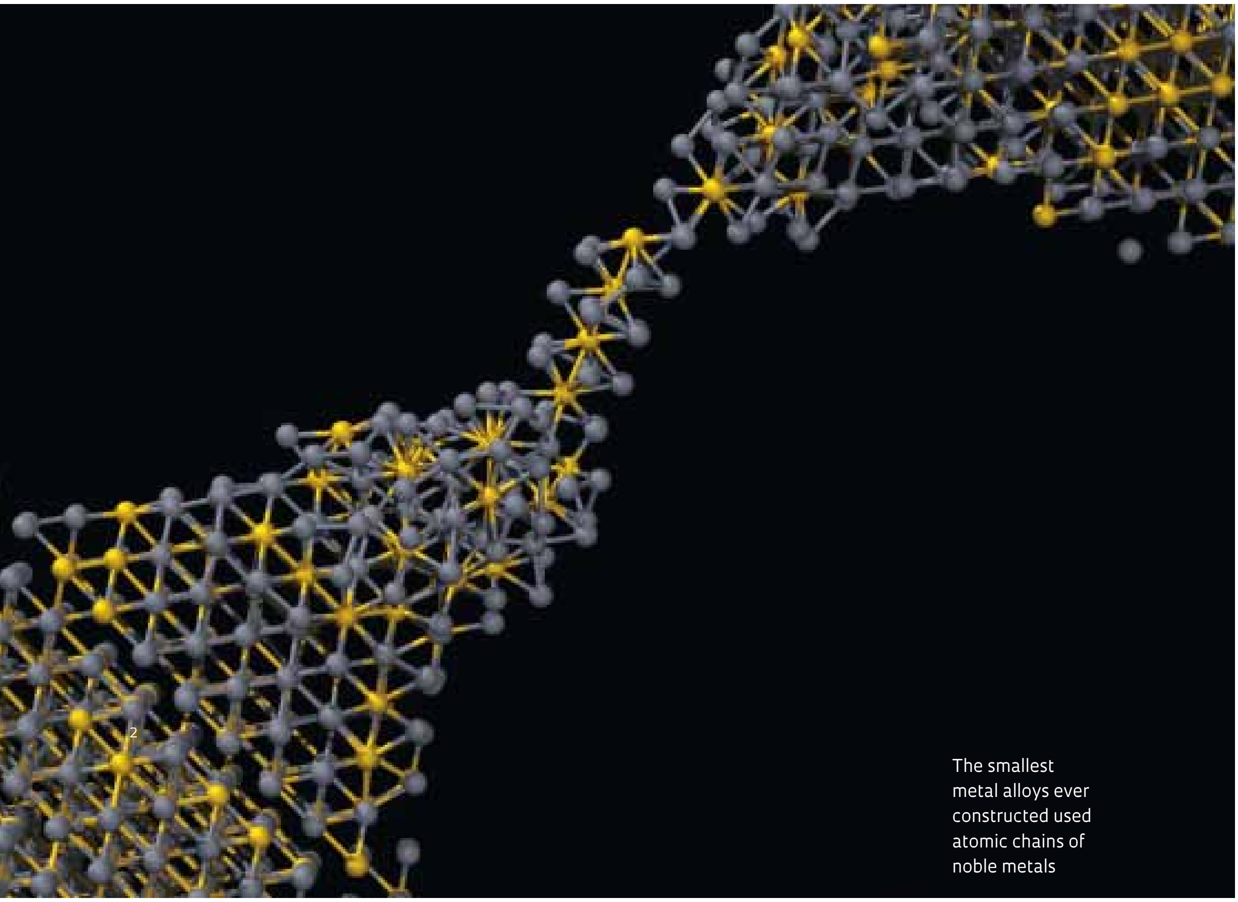
The most spectacular of the nanowires observed was a hollow tube with a square cross-section made of silver atoms. The structure appears and then disappears in a matter of seconds during the elongation of a rod a few atoms thick, shortly before it tapers into an atomic chain and breaks. Galvão explains that it is the smallest three-dimensional structure that silver can form. "It had not even been theoretically speculated that this nanotube could exist", he said. "It was truly an unexpected discovery."

Although the emergence of the curious structure looks obvious in the videos taken by Lagos, it was not at all easy for the researchers to determine its true nature. Only after much thought and many computational simulations did they confirm that the tube they saw in



The curious square shape of the smallest possible silver nanotubes was an unexpected discovery

PHOTOS FERNANDO SATO



The smallest metal alloys ever constructed used atomic chains of noble metals

PROJECTS

1. Center for High-Resolution Electron Microscopy – nº 1996/04241-5 (1998-2002)
2. Conductance quantization in metallic nanostructures – nº 1996/12546-0 (1997-2000)
3. Synthesis and characterization of nanostructured materials – nº 1997/04236-4 (1997-1999)
4. Analytical transmission electron microscope for spectroscopic nanocharacterization of materials – nº 2002/04151-9 (2004-2009)
5. Computational simulation of nanostructured materials – nº 2001/13008-2 (2002-2006)
6. Simulation and modeling of complex nanostructures and materials – nº 2005/59581-6 (2006-2010)
7. Electronic, magnetic and transport properties in nanostructures – nº 2010/16202-3 (2011-2011)

GRANT MECHANISMS
1-4. Research assistance – Regular
5-7. Thematic project

COORDINATORS
1-4. Daniel Mário Ugarte – Brazilian Synchrotron Light Laboratory
5-7. Adalberto Fazzio – Physics Institute of USP

INVESTMENT
1. R$2,621,484.09
2. R$113,921.64
3. R$69,251.70
4. R$5,039,090.12
5. R$924,102.48
6. R$607,550.62
7. R$1,324,211.88

profile in the images was actually hollow and consisted of a series of squares made of four atoms of silver. By comparing their calculations with the images, they also explained how the squares of silver can move by rotating, contracting or expanding the nanotube. “Being able to see and understand this was wonderful,” Ugarte says. The discovery was published in *Nature Nanotechnology* in 2009, and details of the nanotube dynamics model implemented by Pedro Autreto produced an article in *PRL* in 2011.

Also published in *PRL* in 2011 was the researchers’ explanation for the principal conclusion of Lagos’ Ph.D. dissertation, considered among the best of 2010 and awarded the Air Marshal Casimiro Montenegro Filho Award conferred by the Brazilian Secretariat for Strategic Affairs. Lagos observed that, when cooled to -150 °C, nanowires do not become as brittle as might be imagined. Quite the contrary, wires that would break abruptly at ambient temperature remain more flexible and can be elongated to form atomic chains. The secret of this plasticity is that the atoms in the nanowires move more slowly at low temperatures. Therefore, they cannot rearrange themselves abruptly, which would cause the wire to break. Rather, planes of atoms move within the wire, creating ladders on the surface. It is these surface defects that enable the wire to elongate further without breaking. The researchers’ calculations showed how the size and shape of these defective surfaces control the deformation of the nanowires.

As of now, Galvão, Rodrigues and Ugarte plan to concentrate on studying the influence of these defects on the mechanical properties of materials by investigating the relationship between the nanometric and macroscopic worlds. “Metal fatigue and fracture are phenomena that are not yet fully understood, and they are linked to the propagation of these defects on the nanometer scale,” Galvão explains. The new research may be helpful in developing new and stronger materials that could be used, for example, in airplane fuselages. ■

SCIENTIFIC ARTICLES

1. SILVA, Z. da et al. How do Gold Nanowires Break? **Physical Review Letters**. v. 87, p. 25610, 2001.

2. LAGOS, M. J. et al. Observation of the smallest metal nanotube with a square cross-section. **Nature Nanotechnology**. v. 4, p. 149-52, 2009.

FROM OUR ARCHIVES

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Issue No. 115 – September 2005

The impurities of gold
Issue No. 85 – March 2003

Challenges for the future
Issue No. 74 – April 2002

Atoms of gold enter the circuit
Issue No. 72 – February 2002