The memory of the future

Very thin layers of ferroelectric film may replace ferromagnetic films in computers

Yuri Vasconcelos

Ferroelectric film, made up of very thin layers of semiconductor material, may be used to manufacture memory for computers and an infinite number of electronic devices, offering advantages over ferromagnetic films currently employed by the semiconductor industry to produce chips. The storage capacity of this new material, created halfway through the past decade by the Multidisciplinary Center for Development of Ceramic Materials (CMDMC), is up to 250 times greater than that of conventional memory. Its durability is also immensely superior: around 300 years, compared with five years for today's chips.

This innovation could greatly benefit consumers and may set the computer and electronics industry on a new course both nationally and internationally, according to the researchers involved. The work was done by two groups of researchers, one of which was coordinated by Professor José Arana Varela, of the Interdisciplinary Laboratory of Electrochemistry and Ceramics (Liec) of São Paulo State University (Unesp), in the city of Araraquara, and the other by Professor Elson Longo, of the laboratory also named Liec, at the Federal University of São Carlos (UFSCar). Varela is the current director-president of FAPESP and Longo, retired from UFSCar, works at the Unesp Liec.

Developing ferroelectric film relies on a new, relatively simple and inexpensive method of chemical deposition using a household microwave oven. It is produced from an organic solution obtained from citric acid, present in fruits such as lemons and oranges. This solution is used to prepare a solid compound with a polymeric chemical structure, similar to that of plastic, whose ingredients are barium, lead and titanium. The compound is placed in a simple oven, at a temperature of up to 300°C to remove undesirable organic elements such as carbon. The material is crystallized in a microwave oven to obtain a thin film of barium titanate and lead.

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"We had to overcome a number of technical problems to develop the ferroelectric film. When we started the work 30 years ago, this was a new area of research, because everyone was using magnetic memory. At the time, using a chemical method to make memory was considered the frontier of knowledge," says Longo. "When we decided to begin researching this new material, we had no expertise in the area. It took us two years to make the first high quality thin films that were reproducible," he adds. According to Longo, a key aspect to the venture's success was the multidisciplinary nature of the team, comprised of physicists, chemists and engineers.

Collaboration with scientists from other Brazilian states and abroad was also important in terms of overcoming obstacles that arose during the course of the work. "We wanted to work with groups that had expertise in areas other than ours," Longo recalls. The group's research began after a trip by Varela to the United States where he came in contact with the new technology. "Upon his return, we realized that we had to develop thin films and focus on the areas of memory, sensors and catalysts," says Longo.

HOW TO DO IT

Manufacturing chips with ferroelectric memory, however, requires an ultra-clean environment and professionals able to do thin film deposition. Film is defined here as any thin film that separates two phases of a system, or that forms its own interface from this separation. It is formed out of two liquids, as in the case of what happens between water and oil, between a liquid and a vapor, or on the surface of solids. Research in the area of solid thin films – with a thickness of less than a micrometer (one millionth of a meter) – has evolved significantly because of the advantages offered by this material, primarily in the miniaturization of electronic equipment.

"Large industrial groups from the United States, Europe and Asia are investing millions of dollars to obtain ferroelectric thin films, because they are compatible and easily integrated with the current technology for producing integrated circuits which uses silicon and gallium arsenide chips," says Longo. In 2010, researchers at Cornell University in the United States were able to create a film of europium titanate that was both ferromagnetic and ferroelectric. This was considered quite a feat, since there are almost no materials in nature that simultaneously possess ferroelectric properties (those electrically polarized and without current conduction) and ferromagnetic properties (those with a permanent magnetic field).

Europium titanate, when sliced into nanometric layers, stretched and positioned on a dysprosium compound – a chemical element of the lanthanides group, as is europium – exhibits ferromagnetic and ferroelectric properties superior to those currently known.

To Jacobus Willibrordus Swart – a professor at the School of Electrical and Computer Engineering of the State University of Campinas (Unicamp) and coordinator of the National Institute of Science and Technology for Micro and Nanoelectronic Systems (INCT/Namitec), financed by the federal government and FAPESP – chances are good that there will be a market for ferromagnetic memory, but it will take some time. "It may sound strange, but the microelectronics and semiconductor industries are very conservative. They are only open to new materials when there is an urgent need and a justified demand," he says.

"Ferromagnetic memory has proven technical advantages. But for it to have a future, it needs to prove its commercial viability," says Swart. According to Swart, exchanging the material in use – in this case magnetic memory – for a new one involves technological adjustments, new learning processes and the risk of decreased productivity in chip manufacturing.

OPTIMIZED ENERGY

Among the advantages of using ferroelectric films in the preparation of electronic devices, compared to ferromagnetic ceramics used for memory, are their smaller size, low weight, fast reading and writing speed and low-voltage operation. "It is now possible to store 1 megabyte (MB) of information on a 1-square-centimeter semiconductor chip. The new memory will enable storage of 250 MB in the same amount of space," says Longo. In addition, ferroelectric materials enable the construction of electronic memory that requires only a minimum of energy to operate. "Information storage capacity is tied to the arrangement of the atoms," says Longo.

Each memory cell consists of a single access transistor connected to a ferroelectric capacitor, a device that stores energy in an electric field. The transistor acts as a switch, enabling the control circuit to read or write the 0 and 1 signals of the binary system to be stored in the capacitor. The principle is the same as that used by the magnetic semiconductors employed in common credit cards and travel tickets. "The difference is that magnetic cards need to come in contact with a reader to convey the information, whereas ferroelectric cards can be read from six meters away," Longo explains. Reading is done by radiofrequency. The chip, about 2 square millimeters in area, is not visible. Embedded in cards or mobile phones, for example, it has a system to protect against hackers.

Four years ago, the possibility of building a plant to produce ferroelectric semiconductors in São Carlos was thought to be an investment that would have amounted to R$1billion. Initially, the ferroelectric random access memory, or FeRAM, also known as a non-volatile memory – since once the power is turned off, the information continues to be stored – would be produced with technology developed by the American firm Symetrix. It was established 20 years ago in the United States by Carlos Paz de Araújo, a Brazilian professor of electrical engineering at the University of Colorado. Based on initial understandings, the Multidisciplinary Center for Development of Ceramic Materials (CMDMC), one of the FAPESP Research, Innovation and Dissemination Centers (RIDC), would be an active participant in the development of the new ferroelectric memory and materials.

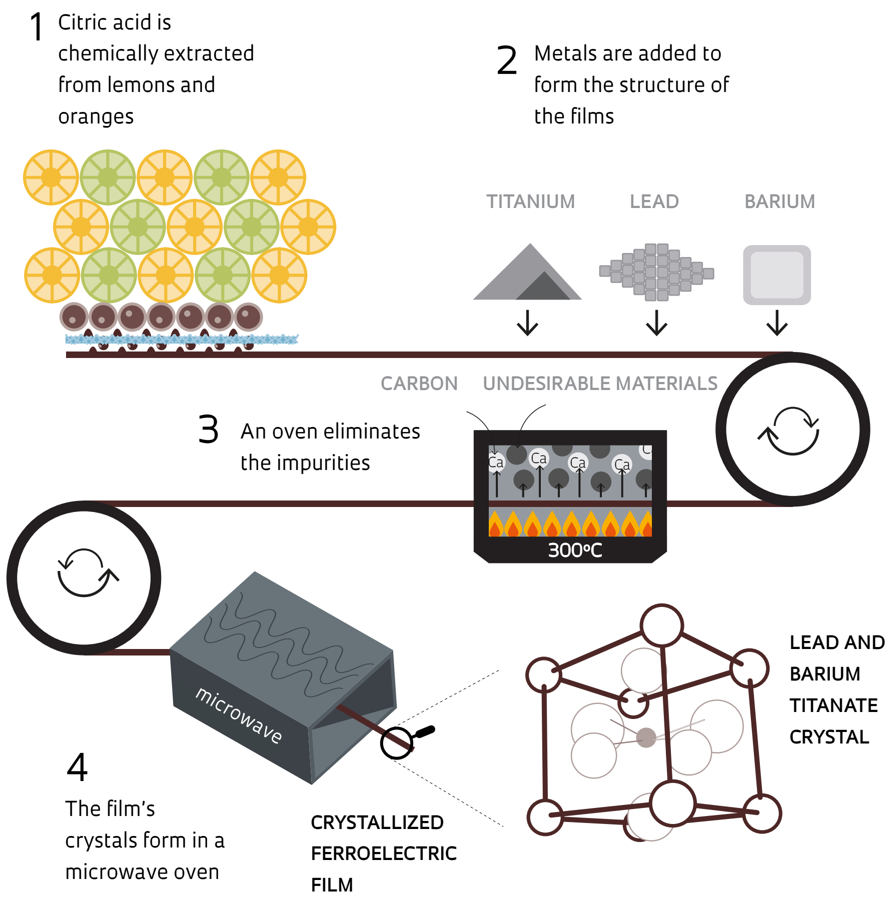
"Unfortunately, the negotiations went nowhere, and Symetrix decided to build its plant in China. It was a shame, because, besides the plant itself, we estimated that 300 to 400 new companies in the production chain would have been built in the region," says Elson Longo. According to him, the success of the business ran into the problem of obtaining funding for construction of the unit in São Carlos. "Symetrix began discussions with a private Brazilian investor, contacted by us, but the negotiations did not bear fruit. Building a semiconductor industry is complex and involves various interests, which were not considered," says Longo. The technology developed by Araújo and his team was licensed by Panasonic in Japan, where it is used in Metro cards, trains and driver's licenses.

IN THE SUPERMARKET

Ferroelectric memory can also be used as a component in automobile manufacturing and in supermarkets. In the automotive industry, it may be part of a collision avoidance system, a technology patented by Symetrix, "This memory can be used when installing a vehicle security system with sensors in the infrared range that will act as night vi-

The juice that became film

The raw material for crystallized ferroelectric films comes from lemons and oranges



sion cameras to detect the presence of people, animals or stopped cars, within a range of 100 to 200 meters in front of the vehicle," Longo explains. In supermarkets, the use of ferroelectric memory instead of bar codes will enable integrated product control. Information such as the product's expiration date, manufacturer's name, price, stock and quantity purchased will be placed in a device the size of a pin tip. "It is not just a bar code, but an intelligent memory," says Longo.

"Each label with an embedded chip may cost less than R$0.02," Varela points out. Consumers who go shopping will know in advance how much they have spent after passing just three or four meters away from a panel. If the consumer agrees to complete the purchase, before going out the door, a charge will be made to the debit or credit card carried in his or her pocket. "While a magnetic card (either a credit or debit card) lasts four to five years, the ferroelectric one, whose reading and writing works electrically (information is recorded in the ferroelectric memory) can be used up to a trillion times, which amounts to an average useful life of 300 years," says Varela. One reason for the shorter useful life of magnetic cards is their need to make direct contact with the reader.

The Unesp group in the city of Araraquara recently synthesized another promising material with ferroelectric properties: bismuth ferrite, an alloy of bismuth, iron and oxygen. It could be an alternative to conventional memory, because of its low energy consumption. "The weak point is its high leakage of current, which reduces its applicability. We are working to reduce the high leakage of current," says Longo. According to him, until now the principal application of the new material, synthesized by the Russians and the Americans, has been the development of sensors.

The research that led to thin films of barium titanate and lead is part of a 30-year global race to overcome one problem in microelectronics: the size of the memory cell. Every year this component is being reduced in order to increase the number of devices and provide greater capacity for computer storage and data processing. The scientists associated with the group that gave rise to the CMDMC began to study ferroelectric materials in 1992. The knowledge originating from these studies resulted in the publication of 208 scientific articles in Brazilian and international journals. Since 2000, when this RIDC was created, 18 doctorates and 22 master's degrees in ferroelectric materials have been awarded.

Other potential applications include automobiles and bar codes

The innovations produced by teams led by Professors Longo and Varela, who together coordinated three FAPESP thematic projects – *Development of ferroelectric ceramics and films through microstructure control*, *Synthesis and characterization of ferroelectric thin films and ceramics*, and *Influence of texturizing and crystalline defects on the ferroelectric properties of thin films and ceramics* – may, in the future, reduce Brazil's historic dependence on importing semiconductor devices, which reached US$4.9 billion in 2011, according to data from the Brazilian Electrical and Electronics Industry Association (Abinee) – an amount 10% higher than the previous year.

The worldwide semiconductor market is a billion dollar market and, according to the Semiconductor Industry Association, totaled US$ 299.5 billion in 2011, a historical record. For a number of years, the Brazilian government has been unsuccessful in its attempts to attract a multinational semiconductor industry to the country. The CEITEC plant opened in Porto Alegre in 2010. This state enterprise, linked to the Ministry of Science and Technology, has been designated as the embryo of the Brazilian semiconductor plant. ■

INFOGRAPHIC TIAGO CIRILO SOURCE: JOSÉ ARANA VARELA/UNESP, ELSON LONGO/UFSCAR

PROJECTS

1. *Development of Ferroelectric Ceramics and Films through Microstructure Control* – No. 1998/14324-0 (2000-2012)
2. *Synthesis and Characterization of Ferroelectric Thin Films and Ceramics* – No. 2000/01991-0 (2000-2005)
3. *Influence of Texturizing and Crystalline Defects on the Ferroelectric Properties of Thin Films and Ceramics* – No. 2004/14932-3 (2005-2009)

GRANT MECHANISMS
1. Research, Innovation and Dissemination Centers (RIDC)
2. and 3. Research Assistance – Thematic Project

COORDINATORS
1. Elson Longo – Multidisciplinary Center for Development of Ceramic Materials, Federal University of São Carlos
2. and 3. José Arana Varela – Interdisciplinary Laboratory of Electrochemistry and Ceramics, Unesp

INVESTMENT
1. R$21,025,671.96 per year for the entire Multidisciplinary Center for Development of Ceramic Materials (CMDMC)
2. R$1,319,395.06
3. R$704,506.70

SCIENTIFIC ARTICLES

1. COSTA, C. E. F. et al. Influence of strontium concentration on the structural, morphological, and electrical properties of lead zirconate titanate thin films. Applied Physics A: **Materials Science & Processing**. v. 79, n. 3, p. 593-97, 2004.
2. SIMÕES, A. Z. et al. Electromechanical properties of calcium bismuth titanate films: A potential candidate for lead-free thin-film piezoelectrics. **Applied Physics Letters**, v. 88, p. 72916-19, 2006.

FROM OUR ARCHIVES

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Issue No. 153 – November 2008

Heavy investments
Issue No. 144 – February 2008

Magnetic and sensitive
Issue No. 175 – September 2010

Conductor in the oven
Issue No. 97 – March 2004

Safe to grow
Issue No. 72 – February 2002

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Issue No. 52 – April 2000