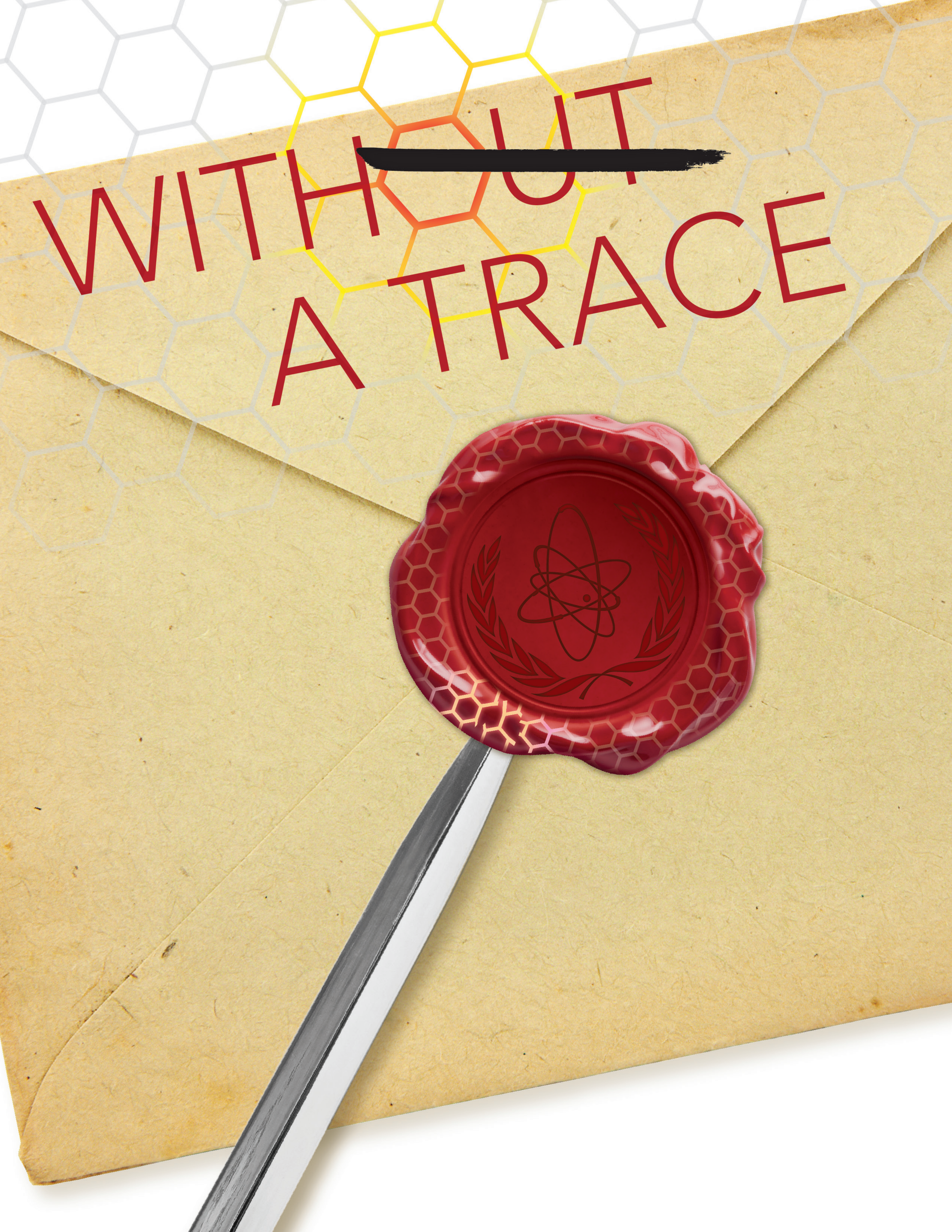
# WITHOUT A TRACE



A WAX SEAL ON CORRESPONDENCE among royalty in the 16th century had a very specific purpose. It did not lock the envelope—anyone could surely get in and reveal the confidential contents. However, the security breach would be known. The unique stamp imprinted in the wax would be permanently damaged and the receiver of the message would be the wiser. The practice of safeguarding parcels continues today as tamper-evident seals are added to a variety of consumer products for this very reason: to let people know if someone has tried to get in. For instance, a simple plastic wrap tears if a medicine bottle is opened, and a vacuum makes the lid pop upon opening a jar of spaghetti sauce.

When it comes to special nuclear material, however, the stakes are much higher, and plastic wrap won't suffice. Anyone who would tamper with this kind of cargo would likely have a sophisticated method in hopes of evading detection. And although tamper-evident materials have come a long way since the sealing wax of the 16th century, there is still room for improvement. Paving the way for a new era of verification technologies, a team at the Los Alamos Engineering Institute is developing a novel tamper-evident seal that is both remotely readable and self-authenticating.

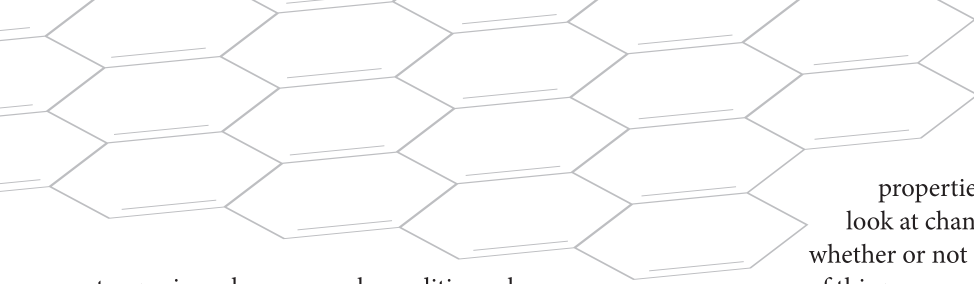
**SOME PACKAGES ARE SO VALUABLE THAT THEY REQUIRE A WAY TO UNEQUIVOCALLY REVEAL IF ANYONE HAS TRIED TO GET IN.**

## Continuity of knowledge

In 1957, the International Atomic Energy Agency (IAEA) was created to ensure the peaceful use of nuclear technology after President Eisenhower's "Atoms for Peace" speech to the United Nations General Assembly. As part of its safeguards mandate under the Nuclear Nonproliferation Treaty, the IAEA regularly conducts inspections of nuclear sites worldwide. This includes monitoring facilities for enriching uranium and fabricating fuel for nuclear reactors to verify that nuclear material hasn't been diverted from peaceful activities.

The IAEA uses seals to maintain continuity of knowledge on nuclear material in storage, or in transit between facilities, and even on monitoring equipment, such as surveillance cameras. The seals play an important role in reducing the inspectors' efforts spent on materials not currently in use, freeing up precious time for the IAEA to pursue other tasks. By verifying a seal on the outside of a storage container (typically applied at the interface where normal access occurs), the inspectors can quickly inventory the material by counting it as a single item—without having to remeasure the individual contents.

Ideally, a tamper-evident seal must fulfill certain requirements. First, it must be robust against the common mechanisms someone might use to defeat it. For instance, if the seal is stuck onto a drum with an adhesive, an adversary might use steam or solvents to lift it, or even simple mechanical action to pry it off. However, if the seal has characteristics that make such techniques obvious, the adversary's actions would be known. For instance, the seal material could have properties that make it break into pieces rather than deform elastically as a single object, so that it crumbles when an attempt is made to remove it. Conversely, the seal must also be robust against environmental changes (such as elevated humidity or high radiation fields) so that it doesn't give a false positive for



Single pristine graphene sheet

tampering whenever such conditions change. Tamper-evident seals should be authentic—devices the IAEA inspectors can recognize as their own—and they should be difficult to counterfeit. Finally, seals must be inexpensive and efficiently monitored, since the IAEA typically deploys more than 30,000 of them per year.

Currently, seals are created via many sophisticated methods. Some have barcodes or labels that change upon tampering, while others use etchings or crimping patterns that require manual

**THE MATERIAL IS THE CIRCUIT, THAT'S THE KEY.**

examination to verify. Unfortunately, many of the seals currently in use require a lot of the inspectors' time for verification.

Karen Miller is a scientist in the Nuclear Engineering and Nonproliferation Division at Los Alamos who works on technology development for nuclear safeguards. A few years ago, she was participating as a mentor in the Advanced Studies Institute at the Los Alamos Engineering Institute, and she had an idea for streamlining the inspectors' verification process.

"I was excited to learn of the high detection sensitivity the Institute scientists were able to achieve using certain materials and advanced sensing for structural-health monitoring," Miller says. "I realized that what I was seeing could be useful for tamper-evident seals." Miller posed a challenge to the multidisciplinary group of doctoral students and postdoctoral researchers she was mentoring: she asked them to develop a novel tamper-evident technology.

The team first developed a solution that was based on a cable consisting of multiple elements with different resistance properties. The concept developed by the students was to look at changes in the resistance of the cable to determine whether or not tampering had occurred. At the completion of this program, David Mascareñas, one of the scientists at the Engineering Institute, began to think more deeply about the challenge of tamper-evident seals. As a result, he and postdoctoral researcher Alessandro Cattaneo decided to combine two scientific hot topics: a material called graphene and a signal-processing scheme called compressive sensing.

## Strong, yet sensitive

Graphene is a one-atom-thick hexagonal sheet of carbon—basically a single layer of graphite from a pencil. Isolation of single-layer graphene was realized in 2004, earning its discoverers a Nobel Prize in 2010, and has since been the center of a great deal of excitement due to its strength, flexibility, and ability to efficiently conduct electricity. During this time, much work has been done to produce graphene, or graphene-like materials, in more efficient ways.

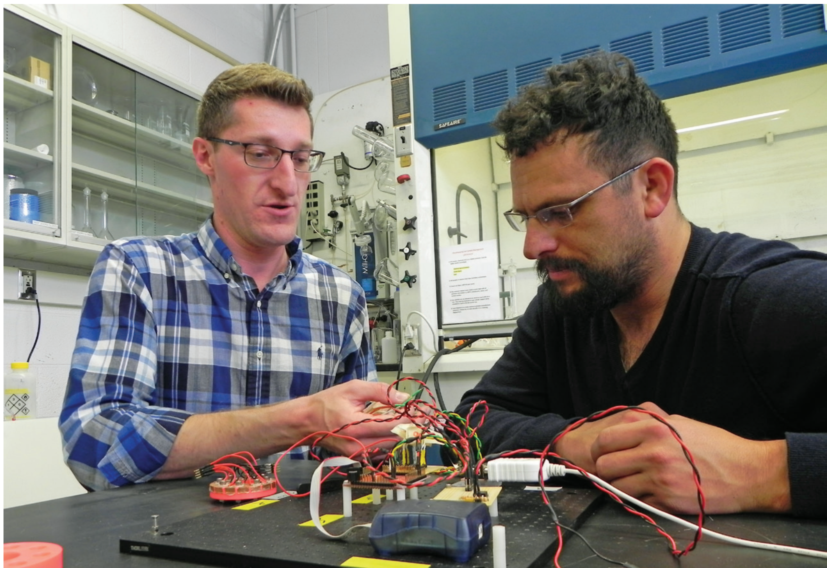
The first production of graphene was made by repeatedly pulling sheets of graphene off of graphite using sticky tape. Scientists have since been able to exfoliate graphite by adding acid and high temperatures to oxidize and break up the layers. Then, this graphite oxide (GO) solution can be vacuum filtered, creating a thin, paper-like film that can be selectively reduced via temperature or laser engraving to remove the oxygen atoms, resulting in reduced graphene oxide (rGO) on the top few layers of the GO film. The GO-reduction process leaves holes in the honeycomb-shaped lattice of carbon atoms, making the resulting graphene less conductive but maintaining most of the desired graphene characteristics in a more efficient production process.

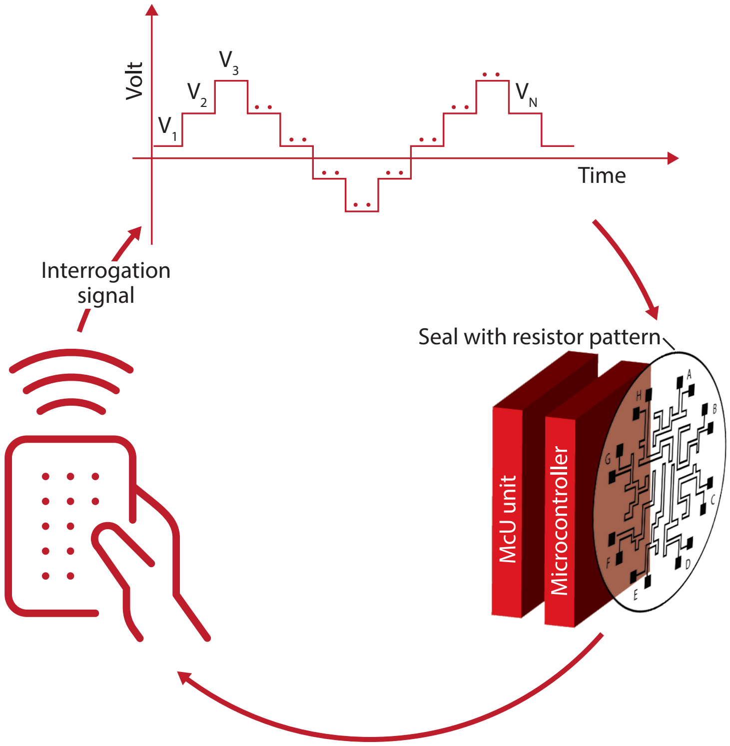
Mascareñas and Cattaneo hypothesized that the paper-like mixture of GO and rGO could be used as a tamper-evident seal with an integrated electrical fingerprint—a unique signature created by printing or embedding a circuit on the film. The paper-like material can be bent and manipulated to

The International Atomic Energy Agency deploys approximately 30,000 tamper-evident seals per year to barrels and other containers of special nuclear material. The seals are used to help ensure that none of the material is diverted from peaceful activities.

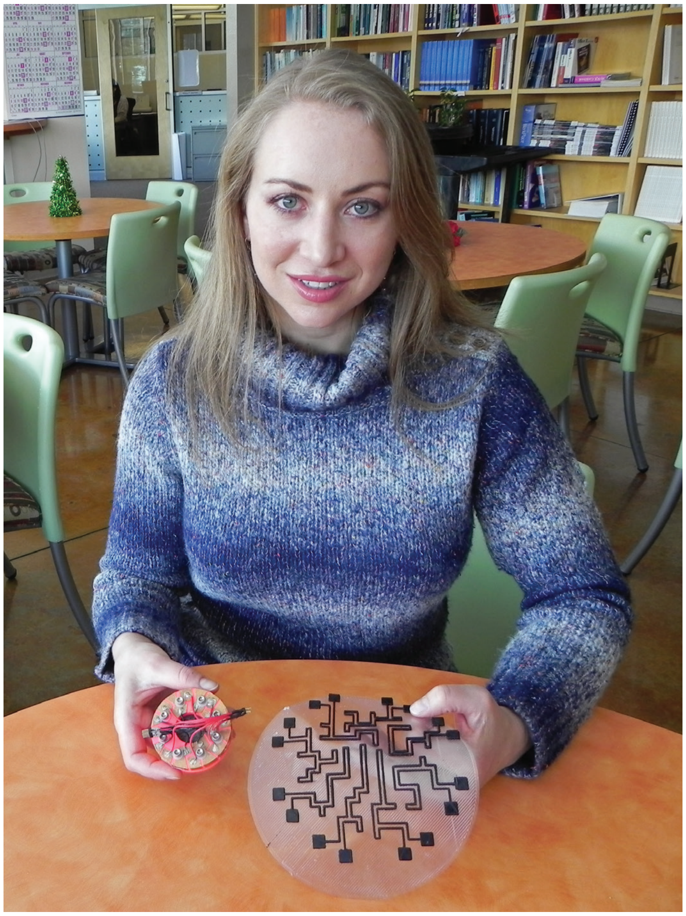
*CREDIT: International Atomic Energy Agency*


Alessandro Cattaneo (left) and David Mascareñas adjust the electronics connected to their prototype tamper-evident seal. Once optimized, they will be able to miniaturize the micro-controller unit so that it can be easily hidden behind the seal.






How the seal works: First, a remote reader sends an interrogation signal of voltage samples ($V_1$, $V_2$, $V_3 \ldots V_n$) through the rGO resistors in a random sequence (D, C, A, A, F...). This process is repeated many times using different random resistor sequences. The output that is sent back to the reader is a series of compressed samples in a linear combination of the initial interrogation signal—a sparse data set used to verify that the whole resistor circuit is intact.



In her right hand, Alexandria Marchi holds the first prototype of the team's tamper-evident seal. Encased in a protective container (orange ring), the rGO and GO film is visible as a dark circle in the middle. In her other hand, she holds a 3D-printed version using an off-the-shelf conductive material printed on a polyurethane sheet, making the whole seal much thinner and more flexible. Ultimately, she plans to integrate graphene-based materials into polymers to make the seal 3D-printable.

use as a seal, but once in place, its delicate lattice of carbon atoms is easily disrupted to indicate foul play.

"The material *is* the circuit," Mascareñas says. "That's the key."

To make the seal, Mascareñas and Cattaneo pulled together a team of materials science and engineering experts, including colleagues at the Los Alamos Center for Integrated Nanotechnologies. Using a laser, team members engraved onto the GO paper seal an rGO-based pattern of eight resistors, each of which is characterized by a unique resistance value. Knowing that the conductivity of graphene is highly sensitive to humidity, temperature, and breakage, they felt any tampering would damage the circuit pattern. But they still needed a way to detect the change.

## Critical minimum

Since coming to Los Alamos, Cattaneo has worked closely with Mascareñas on advanced sensing. In particular, he has become an expert in a relatively new method of signal processing called compressive sensing (CS), which has proven to be a key aspect of the team's tamper-evident seal.

Widely used since 2004, CS relies on the idea that high-resolution data actually contain a lot of redundant information. Take the example of a high-resolution photo. When the image is compressed, the redundant information is thrown out—posing the question: why not *only* collect the most important data in the first place?

Adapting this concept to the tamper-evident seal, CS is used to both encrypt and decrypt a sparse interrogation signal used to authenticate the seal and verify its integrity. To achieve this, the seal is equipped with a microcontroller that routes the interrogation signal through a series of resistors in the seal in a random sequence known only to the receiver. By repeating this operation multiple times using different random sequences, a set of compressed samples is collected—a random linear combination of the interrogation signal's values after their amplitudes have been modified by the rGO resistors. A modification in the circuit structure of the seal caused by a tampering attack will irreversibly compromise the encryption and decryption mechanism, thus enabling tampering detection. Integrating these electronics into the seal provides a low-power verification scheme that is both self-authenticating and adaptable to small environmental changes.

This data can be gathered remotely—so if an inspector walks into a warehouse with 1000 containers, the signal can be sent out to the seals without requiring the inspector to walk up

Reduced graphene oxide

to each individual container. Extra security layers can be added by enabling the inspector's reader to change both the interrogation signal and the switching sequence used to route the signal through the resistors. Ultimately, using the CS technique, the reader can recreate the circuit architecture, confirming the integrity of the seal.

The Engineering Institute team tested its seal against a number of tampering scenarios, performing 100 simulations on each scenario. Their initial results were promising—the error rates were within reason, and the seal proved to be robust against small perturbations in the environment that could otherwise cause false positives.

"The seal is designed to provide irreversible evidence that someone has tried to contact the item or location," Cattaneo says.

### Can you print that?

Now that they have a successful first prototype, members of the team are focusing on seals that can be made faster, more cheaply, and with greater stability. (Simulations showed that if the material stability were improved, false positives could be eliminated entirely.) Seaborg Institute Postdoctoral Fellow Alexandria Marchi joined the team in 2014 and began to look for a way to speed up the manufacturing process of the GO-rGO film.

"Right now, the material takes time to make—about three weeks," Marchi says. "In order to make these seals on a larger scale, we need them to be made in minutes."

Marchi decided to try printing the seal using a standard commercial inkjet printer. First, she experimented with adding different polymers to the GO material in order to increase its stability, facilitate the breakdown of the layers, and control viscosity and particle size to make the material flow easily through a printer. Then, to further adapt the process for printing, she added a solvent. But Marchi still wasn't satisfied with the result and has turned to 3D printing as a possible solution.

Using a 3D printer, Marchi could eliminate the need for the GO paper and laser engraving the circuit by building the seal with a graphene-embedded, 3D-printable filament. Her first attempt resulted in a seemingly more robust seal, which was created in a fraction of the time (see photo on page 25). After that will be a round of tests to evaluate its performance.

One challenge Marchi anticipates is how to attach the seal to a container. An ideal solution would be to integrate the adhesive properties into the seal material itself. Or better yet, if the 3D-printing process is optimized, Marchi suggests that an entire container could be printed using a modified graphene-based printable material.

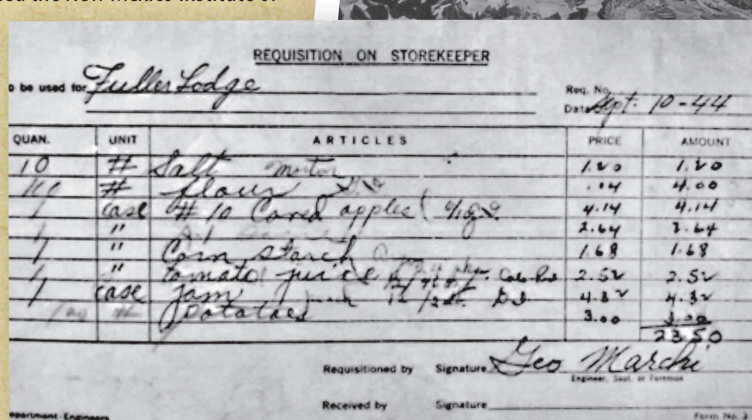
"We could make the whole container into a sensor," Marchi says. This way, any attempt to access the container—not just at the standard opening—would be known. Surely that would be the best tamper-evident seal of all. LDRD

*—Rebecca McDonald*

# A Manhattan Story

The rich history of Los Alamos and its role in the Manhattan Project has long been inspiration for books, movies, and a television series. But for some in Los Alamos, it is a very personal history, as their families have lived and worked here for generations. Alexandria Marchi, a postdoctoral researcher working on tamper-evident seals, has one of those personal histories; for four generations, her family has been a part of Los Alamos. Marchi's great-grandfather, George B. Marchi Sr. (photo at right), was the chef at Los Alamos's Fuller Lodge from 1943–1960. (A surviving requisition order of his reminds us that a case of tomato juice cost only $2.52 in 1944.) Her grandfather, George Marchi Jr., was the Lab's Chemical Warehouse Group Leader, and her grandmother, Rita, was a Lab typist.

Alexandria Marchi's father spent his early years growing up in Los Alamos, but she grew up in Albuquerque. Her path back to Los Alamos began with an undergraduate cooperative-education position in the Lab's Gas Transfer Systems Group while she attended the New Mexico Institute of Mining and Technology. After receiving her Ph.D. in biomedical engineering from Duke University, she decided to return to Los Alamos in the Engineering Institute, where she currently holds a Seaborg Institute Postdoctoral Fellowship. In addition to her work on tamper-evident seals, Marchi is investigating high-accuracy density measurements and fluid compatibility of plutonium. She is currently working with her alma mater (New Mexico Tech) to encourage more students to enhance their education through student jobs at the Lab. Marchi hasn't forgotten her roots and believes strongly in "educating students here in New Mexico and keeping them here."



REQUISITION ON STOREKEEPER

To be used for Fuller Lodge

Req. No.

Date Sept. 10-44

| QUAN. | UNIT | ARTICLES | PRICE | AMOUNT |
|---|---|---|---|---|
| 10 | # | Salt | 1.20 | 1.20 |
| [illegible] | # | Flour | .04 | 4.00 |
| 1 | case | #10 Canned apples | 4.14 | 4.14 |
| 1 | " | [illegible] | 2.64 | 2.64 |
| 1 | " | Corn starch | 1.68 | 1.68 |
| 1 | " | tomato juice | 2.52 | 2.52 |
| 1 | case | Jam | 4.32 | 4.32 |
| [illegible] | # | Potatoes | 3.00 | 3.00 |
| | | | | 23.50 |

Requisitioned by Signature Geo Marchi (Engineer, Supt. or Foreman)

Received by Signature

Department Engineers

Form No. 3