Thin oxide films for development of model materials for semiconductors, sensors and batteries

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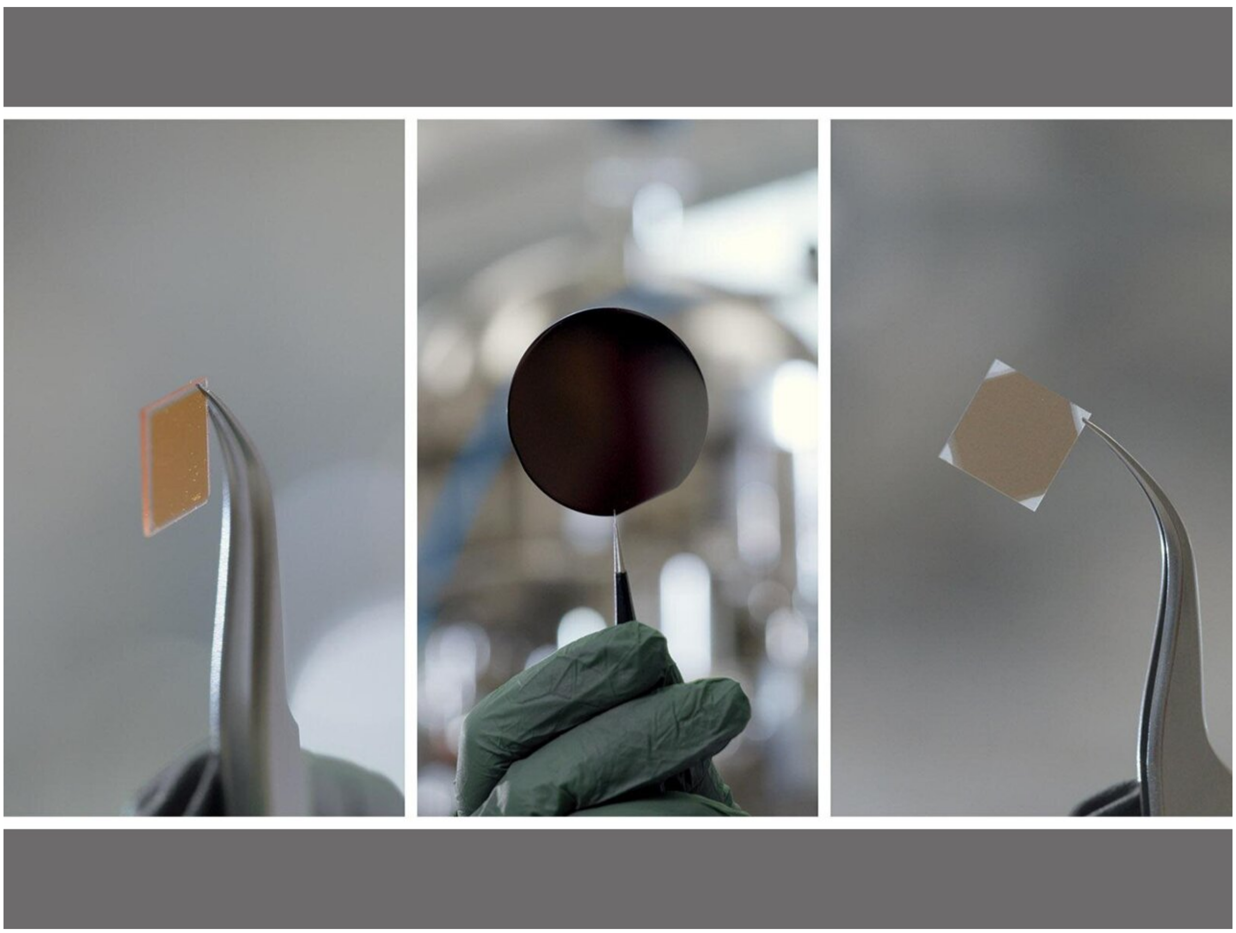

The thin oxide films grown in the Energy Sciences Center allows researchers to study complex processes in controlled systems. Credit: Eddie Pablo, Pacific Northwest National Laboratory

One of the first sights greeting visitors to Pacific Northwest National Laboratory's (PNNL's) Energy Sciences Center are windows into busy lab spaces. Filled with equipment and researchers going about their work, the film growth lab looks out onto the lobby. It houses a team that creates extremely thin and precise films of different materials.

On any given day, researchers including Yingge Du and Tiffany Kaspar might be growing materials for next-generation batteries, photocatalysts, electronic devices, or nuclear reactors. "Our work focuses on understanding thin oxide films at an atomic level," said Du. "This knowledge allows us to learn why materials behave in certain ways, which we can use to make new materials with specific properties. For example, placing a few atoms of oxygen below the surface of a semiconductor, such as silicon, changes how electrons move within the complex oxide deposited on top."

Thin oxide films are used in applications as diverse as the semiconductor chips that power electronics to fuel cells that help store energy. These specialty materials improve our lives in many ways. But making them can be a tricky business.

Founded by PNNL Lab Fellow Scott Chambers, the thin film team uses precise growth techniques to deposit selected elements on top of a target crystal, atom by atom. This level of control allows them to develop model systems that simplify complex realities, enabling the researchers to understand fundamental material properties. The team has discovered unexpected sources of conductivity in oxides, shown how interfaces can control material behavior, and used structural control to create materials that were previously unstable.

They also develop films that have specific, and useful, properties. Their approaches range from modifying the materials to change how they interact with electricity to tuning the material surfaces to generate renewable fuels more efficiently. The team manages a broad range of projects that focus on these functional materials. Their expertise in controlling films allows them to create new films for use in energy conversion reactions, including converting water to hydrogen and oxygen , and energy storage devices, with work exploring how the movement of ions affects battery materials.

"Our research encompasses so many different aspects of oxide materials," said Kaspar. "We can explore atom-scale properties one day and create films for a specific application the next day. It's exciting to work so broadly with these materials."

The PNNL lab contains special equipment, customized to give the researchers exquisite control over their films. The team worked directly with manufacturers to modify their instruments, specifically targeting oxide films. The focused modifications allow the researchers to produce complex and meticulously created materials, which they then carefully study using other instruments and techniques available in the Energy Sciences Center and Department of Energy user facilities.

"The PNNL team is a world-class group in oxide thin film growth," said Kelsey Stoerzinger, a collaborator, Assistant Professor of Chemical Engineering at Oregon State University, and PNNL joint appointee. "Their impressive attention to detail, coupled with innate scientific curiosity, has resulted in numerous fruitful collaborations between our groups. We are always excited to work together by measuring the electrochemical performance of such high-quality films."

Understanding lithium movement for better batteries

Many of the lab-grown films include multiple layers of different oxide materials. The areas where the different materials touch, known as interfaces, are some of the most important parts of devices like batteries.

In the batteries that power modern electronics, the interface between moving lithium atoms and stationary electrodes is a critical place where new structures form and existing materials break down. This can lead to poor battery performance and eventually stop them from working.

In real devices, the interfaces between different battery components change during charging and discharging. This can lead to the formation of new materials during atom movement. Developing model systems to study these materials and processes has been challenging.

A recent study by the film growth lab team found that a multi-step growth process can introduce lithium into different oxide materials. By growing a different metal oxide atop a lithium-based film, the researchers produced new oxides with lithium and the second metal. Understanding how these new oxides form could help researchers learn how materials inside a battery change over time.

"We know that lithium can move through materials," said Du, who has taken on increasing responsibility for the film growth lab and leads this project. "But our results really show how lithium migration can lead to the formation of new oxides. These new oxides are promising model systems for studying how lithium moves in solid materials, fundamental work for developing next-generation solid-state batteries."

The study primarily focused on the incorporation of lithium into titanium and tungsten oxides, but the team plans to expand their work. In particular, iron and molybdenum oxides have exciting potential applications for energy storage devices.

Understanding oxygen mixing

Tiffany Kaspar focuses on understanding how atoms move in materials, including when those materials are under the extreme conditions found in nuclear reactors. Kaspar is a member of the Fundamental Understanding of Transport Under Reactor Extremes (FUTURE) Energy Frontier Research Center.

For most materials, the surface plays a critical role in determining how they interact with the world. It can have an outsized impact on the overall behavior of a material, making it essential to study. Their thinness and precise control make PNNL's thin oxide films ideal for modeling the surfaces of materials.

Kaspar and her collaborators study how oxygen moves during the growth of chromium and iron oxide surface layers. For many materials, the addition of oxygen and formation of oxides is part of how they break down. This is known as corrosion and is the process that forms rust on steel. Oxidation is a particularly challenging problem at extreme conditions, under which the environment causes materials to degrade faster. Understanding how oxygen moves through materials can help researchers develop improved, degradation-resistant alloys.

To study oxygen in materials, the team first grew a standard iron or chromium oxide film. Then they switched the oxygen source to add specifically labeled and trackable oxygen atoms. The two layers of distinct oxygen atoms allowed the team to study oxygen movement. If the oxygen atoms remained stuck in their original positions, the final film would have two distinct layers—this is the conventional understanding of film growth. That is not what the team saw. Using 3D mapping, they found that oxygen from the upper and lower layers mixed in the material during film growth.

The researchers were able to identify how this happens at an atomic level. They found a mechanism by which newly added surface atoms "pull up" atoms from the layer below. The atoms then undergo a ring-like rotation that circulates atoms within the material. This means that what happens at the surface of the material does not stay at the surface.

The mixing mechanism identified in Kaspar's work may apply to more than just depositing thin films and may be active during material degradation. Changes that happen at the surface have deeper effects, altering the material several layers down. Using Kaspar's precise, labeled thin films, the team is exploring how radiation affects atom movement, and they have additional plans to study the combined effects of radiation and corrosion.

"It's exciting to see what comes next for the team," said Chambers, who continues to carry out research on the properties of complex oxide/semiconductor heterostructures for advanced electronics applications. "It is deeply gratifying to see younger team members I've mentored for years, like Yingge and Tiffany, taking on increasing leadership. The program is in good hands."

Provided by Pacific Northwest National Laboratory