SEMICONDUCTORS

Nitride perovskite becomes polar

An oxygen-free polar perovskite offers several advantages over perovskite oxides

By **Xia Hong**[1,2]

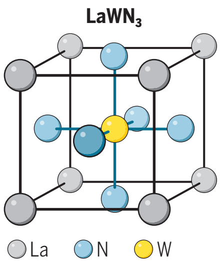
There is a strong drive behind the quest for thin-film materials that are oxygen-free and polar. Oxygen hinders the integration of ferroelectric oxides with semiconductors, which affects efforts to develop nonvolatile memory—that is, a memory that can sustain its information without power. Ideally, one would use single-crystalline perovskite films to construct these devices so that the polarization can be maximized. However, when depositing crystalline polar perovskite oxides onto silicon or germanium, a nonpolar oxide buffer layer (*1*) or a native oxide layer (*2*) can be present at the interface, compromising device performance. A nitrogen-based perovskite may overcome this limitation (*3*). On page 1488 of this issue, Talley *et al.* (*4*) report the synthesis of lanthanum tungsten nitride ($LaWN_3$) thin films, which marks the first demonstration of polar nitride perovskite. This may lead to oxygen-free integration of functional perovskite on a semiconductor platform.

Perovskites, defined by their ABX_3 composition and structure, are one of the most abundant naturally occurring crystal structures on Earth. Despite the simplicity of their pseudocubic structure, perovskite materials form a versatile playground for fundamental exploration and technological development. For example, in perovskite oxides (ABO_3), the B-site cation is surrounded by the oxygen octahedron, which not only defines the crystal structure but also facilitates electron hopping and magnetic exchange. This enables the fine-tuning of the energy scales of various material phenomena, such as charge correlation, electron-phonon coupling, and spin ordering, all by manipulating the crystal structure. The competition between these energy scales has produced a diverse roster of functional materials that spans the entire electronic spectrum, ranging from superconductors to insulators and from dielectrics to ferroelectrics and even multiferroic materials.

Perovskite oxides whose structures are not inversely symmetric tend to exhibit piezoelectricity (generation of polarization in response to applied mechanical stress). Ferroelectrics form a subset of the polar piezoelectric oxides that possess a spontaneous polarization or ordered electric dipole moments, which can be switched by an electric field. Tailoring the ordering of these dipole moments at the nanoscale can lead to a plethora of technologically relevant quantum phenomena, such as a polar vortex state with applications in piezoelectronics (*5*), a negative capacitance effect for low-power logic applications (*6*), and topologically protected domain walls for nonvolatile memories (*7*). Besides oxides, another class of perovskite with polar characteristics is the hybrid halide perovskite, which has drawn enormous research interest as a promising photovoltaic material. It has been suggested that being polar is one of the critical factors that lead to its high power-conversion efficiency (*8*, *9*).

Despite numerous theoretical efforts to study perovskite nitrides (*10*–*13*), there have only been a few successful experimental demonstrations of oxygen-free nitride perovskites—and mostly in non–single-crystalline, powder forms (*14*). Among the many possible cation combinations, $LaWN_3$ has been predicted to be thermodynamically stable (*10*). Talley *et al.* synthesized polycrystalline $LaWN_3$ films on fused silica and p-type silicon substrates and confirmed the crystal structure with x-ray scattering and electron microscopy. Characterizations by means of spectroscopy techniques further showed that these films are free of oxygen content.

Research opportunities for polar nitride perovskites



PROPERTY	APPLICATIONS
Piezoelectricity	• Thin-film bulk acoustic resonator • Mechanical energy harvester
Pyroelectricity	• Thermoelectric energy device • Thermosensor
Ferroelectricity	• Nonvolatile memory • Neuromporphic system-on-chip • Negative capacitance transistor • Photovoltaic device

Perhaps the most interesting finding of the $LaWN_3$ film is that it is polar. Talley *et al.* narrowed down the possible crystal structure to either noncentrosymmetric rhombohedral or centrosymmetric tetragonal. Further characterization by using piezo-response force microscopy revealed a large piezoelectric coefficient (d_{33}) of about 40 pm/V. This confirmed that the material is indeed polar as a noncentrosymmetric rhombohedral structure, which agrees with the theoretical prediction (*11*). Compared with the piezoelectric oxide and nitride reference samples, the d_{33} value of $LaWN_3$ is considerably higher than that of $LiNbO_3$ and $Al_{0.92}Sc_{0.08}N$ and only smaller than that of $PbZr_{0.52}Ti_{0.48}O_3$, whose composition is close to the structural phase boundary. This makes the polar $LaWN_3$ highly competitive for applications such as mechanical energy harvesters.

Theoretically, $LaWN_3$ has been predicted to be ferroelectric, with a large remnant polarization of about 61 μC/cm² and a small energy barrier of about 110 meV for switching the polarization (*11*). If this is true, these properties can be used to develop nonvolatile memory applications with high efficiency and low operation power. Although the global measurements of the switching characteristics of polarization made by Talley *et al.* did not yield conclusive results, they observed hysteresis behavior in the piezo-response force microscopy measurements, which may have originated from ferroelectric switching. At this stage, the existence of ferroelectricity in $LaWN_3$ remains inconclusive.

The demonstration of oxygen-free nitride perovskite with competitive piezoelectric response paves the way for integrating the rich functionalities of polar perovskites with the mainstream semiconductor industry (see the figure). In addition to thin-film bulk acoustic resonators, a range of innovative applications may be possible, including mechanical energy harvesters (*3*), sensors (*3*), thermoelectronics (*12*), nonvolatile memories (*7*), neuromorphic devices (*15*), negative capacitance transistors (*6*), and photovoltaic devices (*3*). Because many of these device con-

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GRAPHIC: A. MASTIN AND C.SMITH/*SCIENCE* cepts operate on ferroelectric polarization switching, there are also materials challenges to be tackled. Confirming ferroelectricity in $LaWN_3$ calls for the synthesis of polycrystalline films with large grain size or even single-crystalline films—or identifying strategies for band gap engineering. It is also of strong interest to discover polar nitride perovskites with an intrinsically large band gap and to explore other theoretically predicted properties, such as magnetic order (*10*), distinctive spin textures (*13*), and topological phenomena (*12*). Future progress in this field thus relies on the collective efforts of computationally driven materials search, materials synthesis, property characterization, and device implementation. As an emerging field, it is conceivable that the discovery of functional nitride perovskites provides a promising material platform for fundamental exploration as well as the development of innovative device applications. ■

"The demonstration of oxygen-free nitride perovskite with competitive piezoelectric response paves the way for integrating the rich functionalities of polar perovskites with the mainstream semiconductor industry."

REFERENCES AND NOTES

1. A. Lin *et al.*, *Appl. Phys. Lett.* **78**, 2034 (2001).
2. R. M. Moghadam *et al.*, *Nano Lett.* **17**, 6248 (2017).
3. T. Mikolajick *et al.*, *J. Appl. Phys.* **129**, 100901 (2021).
4. K. R. Talley, C. L. Perkins, D. R. Diercks, G. L. Brennecka, A. Zakutayev, *Science* **374**, 1488 (2021).
5. A. K. Yadav *et al.*, *Nature* **530**, 198 (2016).
6. P. Zubko *et al.*, *Nature* **534**, 524 (2016).
7. J. Ma *et al.*, *Nat. Nanotechnol.* **13**, 947 (2018).
8. J. M. Frost *et al.*, *Nano Lett.* **14**, 2584 (2014).
9. H. Zhu, K. Miyata, Y. Fu, J. Wang, P. P. Joshi, D. Niesner, K. W. Williams, S. Jin, X.-Y. Zhu, *Science* **353**, 1409 (2016).
10. R. Sarmiento-Pérez, T. F. T. Cerqueira, S. Körbel, S. Botti, M. A. L. Marques, *Chem. Mater.* **27**, 5957 (2015).
11. Y.-W. Fang *et al.*, *Phys. Rev. B* **95**, 014111 (2017).
12. M.-C. Jung, K.-W. Lee, W. E. Pickett, *Phys. Rev. B* **97**, 121104 (2018).
13. H. J. Zhao *et al.*, *Phys. Rev. B* **102**, 041203 (2020).
14. S. D. Kloß, M. L. Weidemann, J. P. Attfield, *Angew. Chem. Int. Ed.* **60**, 22260 (2021).
15. S. Oh, H. Hwang, I. K. Yoo, *APL Materials* **7**, 091109 (2019).

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CANCER IMMUNOLOGY

An atlas of intratumoral T cells

Intratumoral T cell composition is relevant for disease outcome across tumor types

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The T cells that are present in human tumors display a diversity of cell states. Because not all T cells have an equal capacity to contribute to antitumor responses, understanding this diversity is critical to define their role in natural tumor control and cancer immunotherapy. On page 1462 of this issue, Zheng *et al.* (*1*) describe a "T cell atlas" that contains transcriptional profiles of T cells across 21 cancer types, addressing aspects such as recurring T cell states, cell differentiation trajectories, and prognostic value. Although there are many ways to slice these data, aspects of particular interest are the pan-cancer identification of T cell subsets that may play an active role in tumor control and the observation that the relative abundance of T cells with distinct states has prognostic value that transcends tumor type, which takes a step toward immune type–based patient stratification.

The capacity of T cells to recognize and eliminate tumor cells forms the mechanistic basis for the activity of immune checkpoint–blocking therapies that have revolutionized cancer care. There is compelling evidence that the contribution of individual T cells to tumor control varies strongly and appears to be associated with their cell state. Specifically, analysis of T cell infiltrates in human tumors has demonstrated that only a small fraction of T cells at such sites is tumor reactive (*2*). In some tumor types, the expression of hallmarks of dysfunction (or exhaustion), including expression of inhibitory receptors such as programmed cell death 1 (PD-1), can be used to distinguish tumor-reactive T cells from neighboring "bystander" cells (*3*, *4*). Additionally, within the tumor-reactive T cell compartment, T cells differ in their capacity to convey antitumor effects. Studies in mouse models have, for example, shown that cells with an early dysfunctional cell state, characterized by the expression of transcription factor 7 (*TCF7*) and longer-term renewal potential, are particularly important for durable responses to immune checkpoint therapy (*5*, *6*).

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A central question that is addressed by Zheng *et al.* is how the properties of the T cell pool with presumed tumor-reactivity compare across cancer types. $CD8^+$ T cells that are enriched at the tumor and that show clonal expansion, as inferred from T cell receptor (TCR) sequencing, are predominantly observed in the cell pool with a (terminal) exhaustion (T_{ex}) phenotype, which is consistent with chronic antigen exposure driving T cell dysfunction. The same T cell states showed enhanced gene expression signatures associated with both cell division and TCR signaling, which might suggest that tumor-reactive T cells in many human cancers are actively responding to tumor cells even in the absence of therapy. Similarly, use of the latter criteria on the $CD4^+$ T cell compartment identified a regulatory T cell (T_{reg} cell) population that expresses tumor necrosis factor (TNF) receptor superfamily member 9 (*TNFRSF9*), which encodes the activation marker 4-1BB, as most highly enriched for potential tumor reactivity. This demonstrates that both cytotoxic and suppressive tumor-reactive T cell populations may potentially be identified across cancer types according to their transcriptional characteristics, holding promise for both diagnostic and therapeutic applications.

Continuous antigen exposure forms a major driver of T cell dysfunction, but the varied presence of antigen as well as additional cell-bound and soluble factors, such as immune checkpoint ligands and transforming growth factor–β (TGF-β), at the tumor site provide ample opportunity for potential diversification in this process. On the basis of their pan-cancer dataset, Zheng *et al.* propose a model in which two distinct differentiation paths lead to a state of terminal dysfunction, an observation that extends recent work in non–small cell lung cancer (NSCLC) (*7*). Both T_{ex} cell differentiation paths, characterized by the presence of either a granzyme K ($GZMK^+$) or zinc finger protein 683 ($ZNF683^+$) intermediate $CD8^+$ T cell state, were shown to coexist in a substantial part of tumors. This may be explained by intratumoral heterogeneity in the signals that drive dysfunction but could also reflect the developmental origin of these T cell populations outside of the tumor—for example, because of differential imprinting of naïve T cells during priming, a matter that deserves further attention. The preferential connection

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