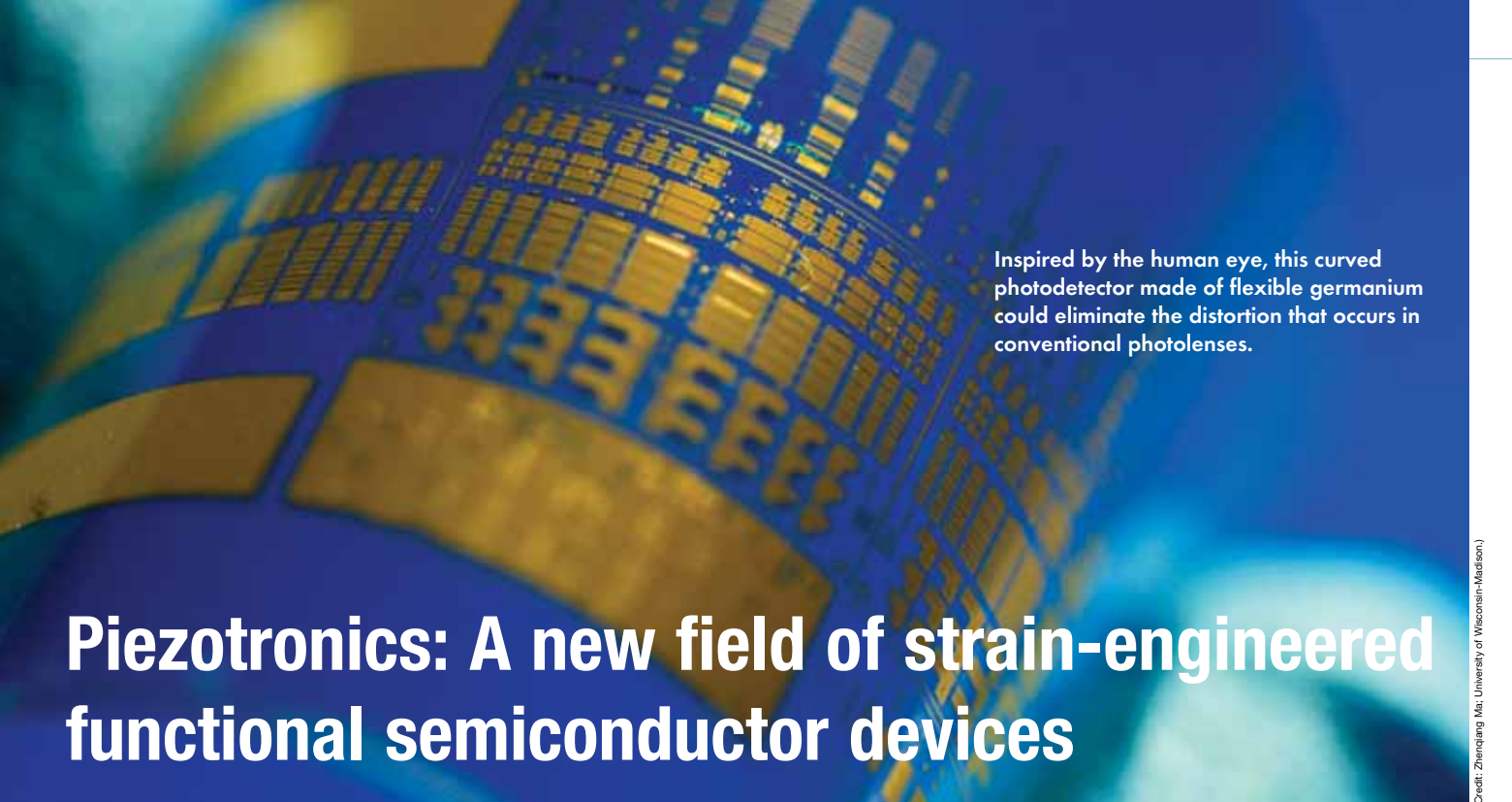




Inspired by the human eye, this curved photodetector made of flexible germanium could eliminate the distortion that occurs in conventional photolenses.

Piezotronics: A new field of strain-engineered functional semiconductor devices

By Xudong Wang

Coupling piezoelectric polarization with semiconductor properties results in devices with novel functionalities.

Piezoelectric materials are the key functional component in many devices, such as sensors, actuators, ultrasonic transducers, sonar systems, and energy scavengers. These applications take advantage of the direct or reverse piezoelectric effects caused by simultaneous shifts in positive and negative charge centers within the primitive unit cell in response to mechanical deformation. Ideal piezoelectric materials also are perfectly dielectric. However, most piezoelectric materials are wide bandgap semiconductors that have a finite amount of free charges. The polar field resulting from the direct piezoelectric effect naturally interacts with charged species present in the solid in a Coulombic manner, and, thus, influences charge carrier distribution throughout the solid. This interaction also exists in many widely used semiconductors that are piezoelectric, such as ZnO, GaN, and CdS. Nevertheless, this polar field–charge interaction effect long has been overlooked by piezoelectric and semiconductor researchers until the recent emergence of the field known as *piezotronics*.¹

Piezotronics is a new field that deals with the coupling of piezoelectric polarization (P_{pz}) with semiconductor properties to design new devices with novel functionalities and enhanced capabilities (Fig. 1). The general principle of piezotronics lies on the P_{pz} -induced internal and external free charge redistribution that can tune the local interfacial band structure and, thus, provide a mechanism to engineer the charge transport properties without altering the interface structure or chemistry.^{2–4} In a heterojunction, the effect of the energy state discontinuity is profound, with electronic transport properties that are exquisitely sensitive to the magnitude of the discontinuity. It then follows axiomatically that the electronic properties of the heterojunction system can be tailored by precise modification of the interfacial energetics. To that end, P_{pz} could have a significant influence on the heterostructure's electronic properties.

In 2006, the piezotronic phenomenon was first demonstrated in a P_{pz} -gated ZnO nanowire (NW) transistor.⁵ The great promise of the piezotronic principle has been explored since then in a variety of semiconductor systems as a means for gating transistors, switching diodes, augmenting the quantum efficiency of light-emitting diodes (LEDs), improving photovoltaic (PV) performance, and optimizing catalytic ability.⁶ This emerging field has quickly attracted researchers worldwide from a wide range of disciplines, including materials science, physics, chemistry, electrical engineering, and mechanical engineering. This article outlines the basic principles, current research progress, and promising future of the new, interdisciplinary research field of piezotronics.

Minding the gap—Semiconductor band engineering

In a heterojunction structure involving a piezoelectric semiconductor material, the appearance of piezoelectric polarization will lead to a considerable change of free charge distribution in the piezoelectric material and its adjacent semiconductor or metal contacts.³ For example, in the p - n junction shown in Fig. 2(a), the original interfacial band structure results from charge redistribution caused by Fermi-level mismatch. Because one of the junction materials is piezoelectric, straining creates immobile piezoelectric charge (σ_{pz}) at the piezo-material surface. The free charge concentrations in both junction-forming materials are finite. Therefore, free charges with an opposite sign to σ_{pz} (that is, screening charge) are attracted to the interface internally from the piezo-material ($\sigma_{s,in}$) and externally from the contacting material ($\sigma_{s,ex}$) (the bottom picture of Fig. 2(a)). The sum of $\sigma_{s,in}$ and $\sigma_{s,ex}$ is typically equal or very close to σ_{pz} , and the relative ratio between $\sigma_{s,in}$ and $\sigma_{s,ex}$ is determined by the material's carrier concentrations and density of states. The net charge gain at the interface ($\sigma_{pz} - \sigma_{s,in}$) at the piezo-material side, and $\sigma_{s,ex}$ at the non-piezo side) creates additional potential profile at the interface (top curves of Fig. 2(b)).

Figure 2(b) illustrates the effect of P_{pz} on the p - n junction. The original band structure is shown by blue dashed lines, and the band structure modulated by P_{pz} is sketched in red solid lines. The left and right diagrams, respectively, illustrate situations of positive and negative σ_{pz} at the interface. Superimposing the P_{pz} -induced potential profile onto the original semiconductor band structures resolves the shifted band structure. The greatest band shifting exists at the interface, whereas the band structure remains unchanged far from the interface. With this modification, the built-in potentials and depletion regions in both materials change. Figure 2(b) demonstrates a situation where the σ_{pz} is so large that it completely inverts the band tilting direction at the n -type piezo-semiconductor side (for positive σ_{pz} , left picture)

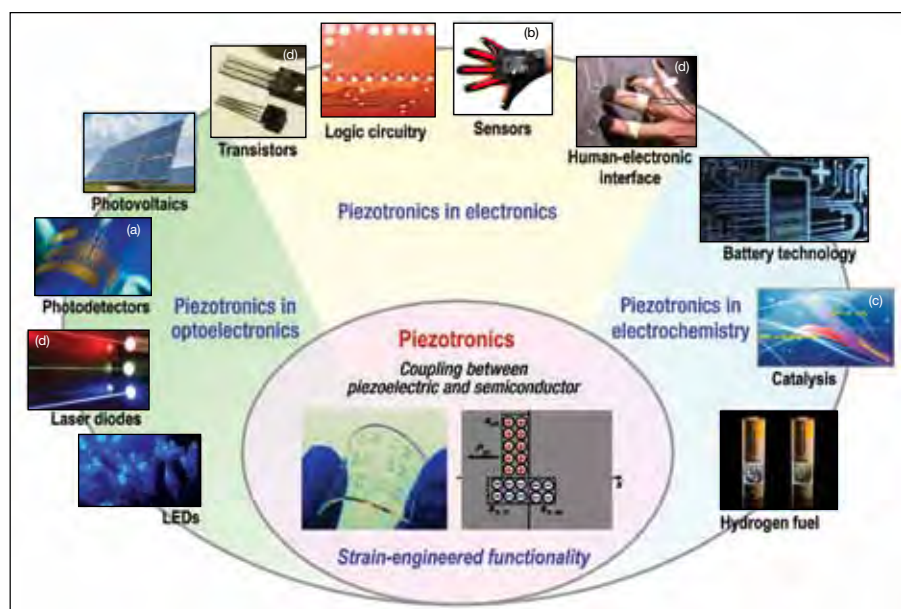


Figure 1. The new field of piezotronics couples the piezoelectric and semiconducting properties of materials to engineer strain-induced functionality into a wide range of new and familiar materials.

or the p -type non-piezo-semiconductor side (for negative σ_{pz} , right picture).

Metal–semiconductor (MS) heterojunctions are another large category of solid-state devices. Here, the screening length in metal is negligible compared with the semiconductor. Therefore, the P_{pz} -induced band shifting occurs only on the semiconductor side. Figure 2(c) illustrates a MS Schottky junction. Positive σ_{pz} at the MS interface reduces the Schottky barrier height. If σ_{pz} is large enough, the Schottky barrier can become ohmic (left picture in Fig.

2(c)). When negative σ_{pz} appears at the MS interface, the barrier height is more pronounced and creates a Schottky diode with higher threshold voltage.

The existence of P_{pz} is a steady-state effect as long as the strain is held, although the screening charges prevent external detection of a piezopotential.⁴ Therefore, applying strain to a piezo-semiconductor constantly influences the band structure as described, and it offers an effective strategy to modulate the performance of practical heterojunction-based devices.

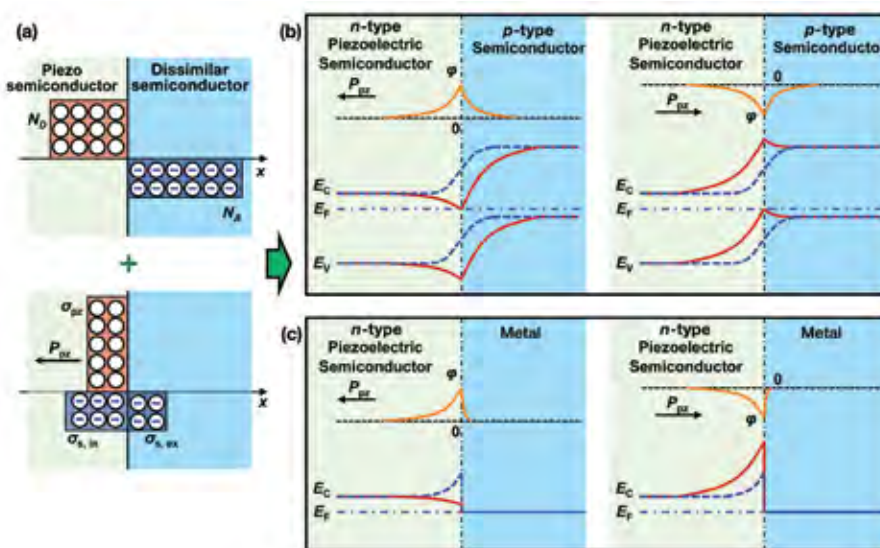


Figure 2. (a) Schematic charge distribution at semiconductor hetero-interface (top) and P_{pz} -induced charge redistribution (bottom). (b) and (c) Band structure change as a result of the combination of intrinsic and P_{pz} -induced charge distributions when the piezo-material is (b) n -type semiconductor and the other material is p -type semiconductor or (c) metal.

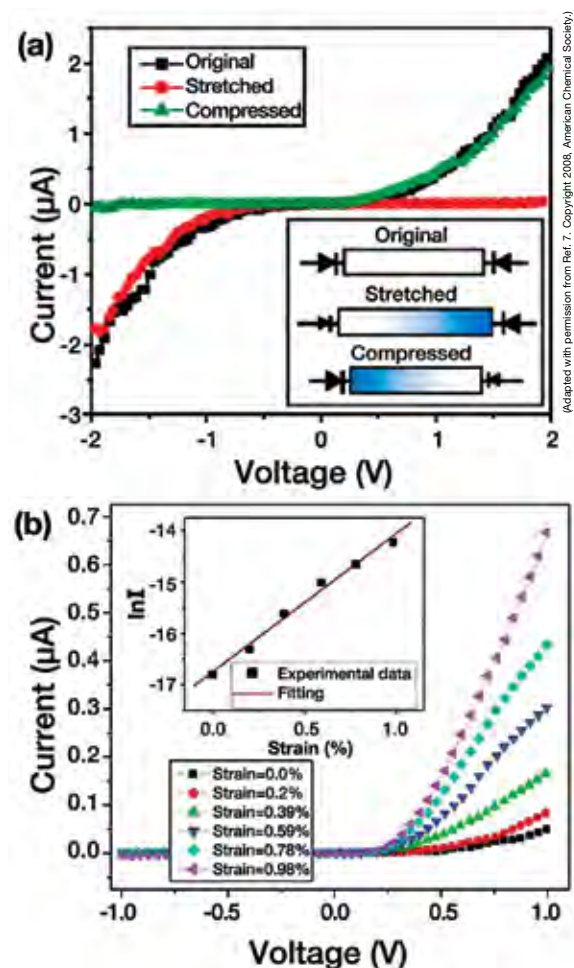


Figure 3. (a) *I*-*V* characteristics of a Ag-ZnO-Ag system under zero, compressive, and tensile strains. (b) Strain-sensing performance of the Ag-ZnO piezotronic device.

New transistor and sensor devices—Memory switches and artificial skin

The most direct application of the P_{pz} -band structure relationship presented in Fig. 2 is its modulation of charge transport through the piezoelectric material, that is, a piezotronic transistor. In a piezotronic transistor, the piezoelectric potential induced by strain replaces the conventional gate voltage. This configuration requires only two electrical terminals (electrodes) and is much simpler than regular electrically gated transistors. This is a great advantage for system miniaturization and 3D integration, for example, incorporating vertical NW arrays that can be individually addressed and controlled.

The first piezotronic transistor based on a single crystal ZnO microwire (MW) was demonstrated in 2006.⁵

Through in-situ bending and *I*-*V* characterization in a scanning electron microscope chamber, a monotonic reduction of source-drain current was observed when the deflection generated a piezopotential along the MW's side wall. This work marked the first discovery of the piezotronic effect and quickly led to further research that involved more comprehensive characterization and obtained deeper understanding of the piezotronic phenomenon. For example, using a ZnO NW, Zhou et al. demonstrated a strain-induced *I*-*V* characteristic change in a Ag-ZnO-Ag system consisting of back-to-back Schottky barriers (Fig. 3(a)).⁷ This system can be represented by the MS model shown in Fig. 2(c), where both electrodes share the same magnitude but opposite sign of potential change at the interface. This produces asymmetrical *I*-*V* curves, which makes it possible to use the M_1 - S - M_2 structure as a memory switch.

Intuitively, strain sensors are a direct application of the strain-regulated conductivity change. Different from the piezoresistivity, which is a bulk property and typically follows a linear relationship with strain, the piezotronic effect controls the interface barrier height, and, thus, the current change follows an exponential relationship with strain (Fig 3(b)). As a result, a piezotronic strain sensor offers a much enhanced gauge factor (the ratio between current change and strain amplitude). The highest reported gauge factor from a piezotronic ZnO NW was about 1250.⁸ This value significantly exceeds the gauge factors of commercial semiconductor strain sensors (~100–200) and the highest gauge factor reported for carbon nanotubes (~1000).

Because of their high sensitivity and simple configuration, NW piezotronic strain sensors represent an ideal solution for artificial skin and human–electronic interfaces. Most recently, Wu et al. developed a large-area flexible piezotronic sensor sheet using individually addressed vertical ZnO NW-bundle arrays.⁹ When subjected to external force or pressure, P_{pz} was generated at the ZnO–metal contact interface and modulated the barrier height. Thus, the sensitivity was improved by a factor of at least 30 compared with resistive devices. The sensor array provided shape-adaptive force–pressure imaging with a very high resolution of 8,464 pixel/cm², which is more than an order of magnitude higher than mechanoreceptors in the skin of human fingertips (~240 /cm²). This transparent and flexible force–pressure sensor sheet is able to mimic the sense of human skin and offers a novel platform for interfacing human body and electronics.

Similar to regular transistors, piezotronic transistors also can be used for logic circuits, where the on–off states are switched by strain-induced P_{pz} . Wu et al. demonstrated that multiple ZnO NW–Ag Schottky junctions that were integrated and operated by straining could perform universal logic operations, including NAND, NOR, and XOR.¹⁰ Such mechanically operated logic units offer a new function component for advanced nanoelectromechanical systems.

Working with light—Piezophototronics and piezotronic-enhanced photovoltaics

Piezophototronics involves modulation of optoelectronic phenomena by engineering the band structure using the piezotronic effect. The basic principle also follows the diagram shown in Fig. 2, where the amplitude of band shifting at a heterojunction is controlled by strain to manipulate charge recombination (for light-emitting devices) or separation (for photovoltaic devices) at the junction.

Yang et al. reported a dramatic improvement in the emission intensity of an *n*-ZnO MW/*p*-GaN-based LED

by straining the ZnO MW component (Fig. 4).¹¹ This is the case of p - n junction modulation described in Fig. 2(b). In this configuration, P_{pz} -induced interfacial charge redistribution forms a potential dip at the ZnO–GaN interface, which traps electrons or holes and facilitates their recombination. Similar to LEDs, in the case of a GaN–InGaN quantum well laser, the quantum well profile can be rectified by P_{pz} at the well's interface.¹² Whether there is a negative or positive effect on the quantum efficiency results depends on the polarity of this potential.

A similar effect also exists in PV devices, whose performance relies on effective electron–hole separation at a semiconductor heterojunction. The built-in field at the heterojunction provides a critical driving force for charge separation and, thus, dictates open-circuit voltage and short-circuit current. When a PV structure involves a piezoelectric semiconductor, the presence of P_{pz} may lead to a considerable change of free carrier distributions in the piezoelectric material and its adjacent semiconductor or metal contacts and, thus, influences the device performance.

One example has been demonstrated based on a n -ZnO/ p -PbS quantum dot (QD) heterostructure, where the built-in field in the depleted PbS layer ($\phi_{bi,PbS}$) is essential to charge extraction from the QD layer.¹³ Additional driving force could be expected when interfacial charge redistribution is induced by P_{pz} from strained ZnO. Figure 5(a) shows that, when positive P_{pz} appears at the ZnO–PbS interface, conduction and valence bands of PbS are bent further downward, producing a sharper, extended built-in field, which is preferable for sweeping excitons apart. In this scenario, the driving force for extracting electrons from the PbS QD assemblage is augmented to $(\phi_{bi,PbS} + \Delta\phi_{pz,PbS})$, and the width of the depletion region in PbS under zero external bias expands accordingly. This enlarged depletion region in the PbS QD layer is necessary for enhanced charge extraction. Meanwhile, the positive P_{pz} also may yield a shorter depletion region ($\delta_{pz,ZnO}$) and shallower band bending on the ZnO

side. Figure 5(b) schematically illustrates the overall change of depletion region at the ZnO–PbS interface. Therefore, positive P_{pz} at the ZnO–PbS interface is a favorable condition for charge extraction.

The P_{pz} -engineered PV performance was tested on flexible QD solar cells (QDSCs) fabricated using p -type PbS QDs and an n -type textured, (0001) orientation ZnO thin film. Appreciable change in current density (J_{ph}) occurred under various strains (Fig. 5(c)). A linear relationship was identified from the plot of J_{sc} versus strain (blue squares in Fig. 5(d)), where J_{sc} exhibited a 0.02 $\mu\text{A}/\text{cm}^2$ (or 1.1%) increase per 0.01% strain drop. Under zero strain, the efficiency of the QDSC was $\sim 3.1\%$ (red circles in Fig. 5(d)). Approximately 4.0% efficiency was obtained at a compressive strain of -0.25% , corresponding to a $\sim 30\%$ improvement. The efficiency also exhibited an approximately linear relationship with strain within the testing range ($-0.25\% - 0.15\%$), where a 1.2% efficiency enhancement per 0.01% strain drop was identified.

More significant band shifting in the piezoelectric material would be observed if the external contact material, for example, a polymer, had a very low carrier density. Depending on its electrical permittivity, the screening length of a polymer can be fairly large and the P_{pz} -induced electric field can be sensed far away from the interface in the polymer. This situation was first demonstrated in a polymer solar cell, where ZnO MWs served as electron conductors and poly(3-hexylthiophene) (P3HT) was the photon absorber.¹⁴ By straining the ZnO MW under photoillumination, the cell's open-circuit voltage increased when positive P_{pz} appeared at the ZnO–P3HT interface and lowered the conduction band of ZnO. A similar effect also has been observed from a ferroelectric poly(vinylidene fluoride) (PVDF)–

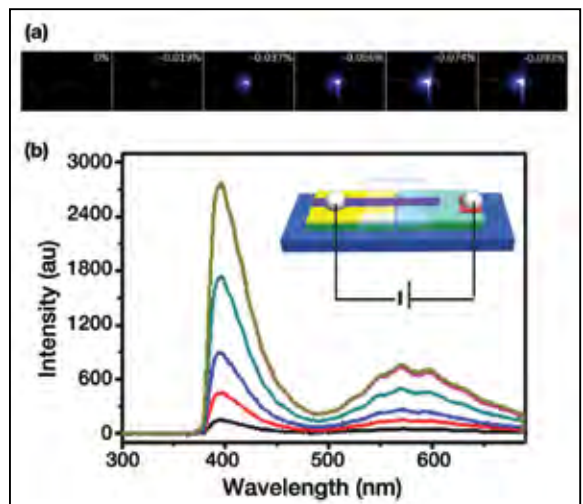


Figure 4. (a.) Optical images showing the strain-dependent emission intensity from a n -ZnO/ p -GaN LED. (b) Electroluminescence spectra of the LED subject to various strains at a bias of 9 V.

P3HT heterostructure, where the permanent polarization from PVDF enhances the PV performance.¹⁵ So far, all the experimental evidence indicates that the piezotronic effect holds great promise for improving the performance of PV devices by enhancing the effectiveness of charge extraction and modulating the open-circuit voltage.

Piezocatalysis—Straining to split water

In addition to modulating regular semiconductor functions, coupling piezopotential with electrochemical processes creates a new effect, denoted as piezocatalysis. Because the strain state and electronic state of these materials are strongly coupled, piezocatalysis could be prominent in piezoelectric materials. Piezocatalysis is the product of an intimate interaction between the native electronic state of the piezoelectric material, the chemistry of the surrounding medium, and a strain-induced piezoelectric potential.

Mechanically deforming a piezoelectric material induces a peruse electric field that augments the energetics of free and bound charges throughout the material. The thermodynamic feasibility and kinetics of electrochemical processes occurring at the surface of the piezoelectric material is sensitive to the electrochemical potential difference between charges on the piezoelectric's surface and in the surrounding medium. Thus, piezoelectric potential, which can affect dra-

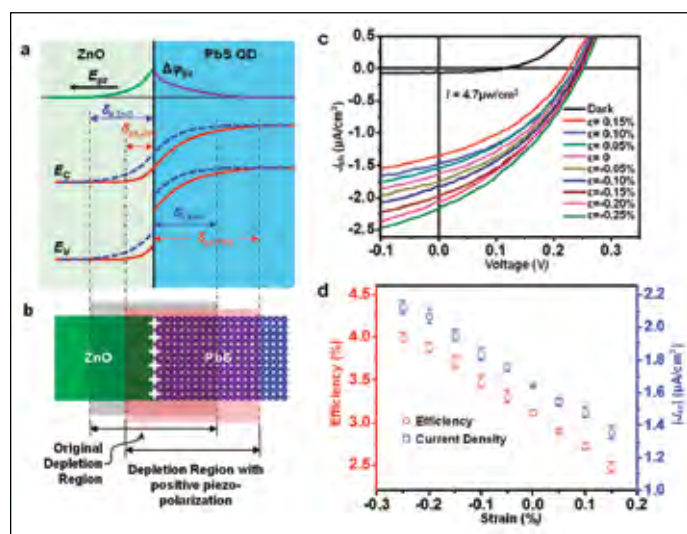


Figure 5. (a) The tailoring of the quantum dot solar cells (QDSC) band diagram when a positive P_{pz} appears at the ZnO–PbS interface. (b) Schematic illustration of corresponding change of the depletion regions in ZnO–PbS QD assembly. (c) J–V characteristics of a ZnO–PbS QDSC when the cell was subjected to various strains. (d) Plot of QDSC efficiency (red circles) and J_{sc} (blue squares) as a function of strain.

matically the difference between these electrochemical potentials, is a new means of modulating the material's electrochemical activity via its strain state.

Recently, we demonstrated a piezocatalysis process in a strained ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 \cdot 32\text{PbTiO}_3$ (PMN-PT) beam in a deionized water system. We observed that hydrogen evolution from the water depended strongly on the material's piezoelectric potential.¹⁶ The experiments measured hydrogen gas evolution as a function of time during mechanical oscillation of the PMN-PT cantilever in deionized water at select frequencies (Fig. 6(a)). The hydrogen concentration increased at a rate of ~ 0.22 ppb/s at 10 Hz oscillation. At 20 Hz oscillation, the hydrogen-gas concentration increased at a rate of ~ 0.68 ppb/s, demonstrating that more strain cycles could result in a higher hydrogen output per unit time.

The electrical-to-chemical energy conversion efficiency (piezocatalytic efficiency) was estimated by comparing the total surface charge generated on the strained piezoelectric material to the amount of hydrogen-gas produced. The efficiency per oscillation was less than 0.7% even under the favorable condition of high piezoelectric poten-

tial. However, it could be improved to 2%–2.4% given sufficient time for piezocatalyzed electrochemical reactions to proceed.

The water reduction–oxidation system serves as a good example to illustrate the fundamental principle of piezocatalysis. Figure 6(b) demonstrates a means by which piezopotential is sufficient to create a favorable energetic landscape for generating Faradic currents on opposing gold electrode surfaces, promoting the reduction of protons in solution (evolving hydrogen-gas) and the oxidation of water.

In the limit where the piezoelectric material is a perfect dielectric, the appearance of piezopotential induces a linear shift of the Fermi level. Accordingly, the electron energy levels of both electrodes shift by an equal and opposite amount and the difference is the observed piezoelectric voltage output (solid red lines in Fig. 6(b)). This electronic perturbation induced by the mechanical deformation modifies the electrons' energy in the gold electrodes and moves it away from equilibrium. The electrochemical potential differences between the electrode and solution are a driving force for electron transfer across the electrode–solution interface and thus induce electrochemical reactions. This process is similar to that which occurs in an electrolysis system, where an applied bias disrupts the Fermi-level equilibrium across the interface resulting in a driving force for electrochemical reactions. Therefore, when the potential on the negative electrode exceeds the proton reduction potential (right Au electrode in Fig. 6(b)), electrons of sufficient

energy transfer from the electrode to protons on or near the surface, producing hydrogen. Similarly, when unoccupied electron energy levels of the electrode are made sufficiently positive in potential so as to exist below the water oxidation potential (left Au electrode in Fig. 6(b)), electrons transfer from water molecules to the electrode, producing oxygen.

Such piezoelectric-potential-driven electrochemical reactions create Faradic currents in the electrolyte and deplete piezoelectric-induced surface charge. Therefore, the piezoelectric potential drops accordingly, and eventually the reactions cease when the electron energy levels are no longer energetically favorable for net charge transfer (dashed red lines in Fig. 6(b)).

In addition to piezocatalyzed water splitting, numerous recent studies have confirmed the broader correlation between electrochemical activity and P_{pz} . For example, a study conducted using ferroelectric PVDF demonstrated that in-situ piezopotential can influence lithium-ion battery charging behavior.¹⁷ Also, electrochemical deposition can be selectively activated by the ferroelectric domain polarization.¹⁸ Thus, the novel coupling effect between P_{pz} and electrochemical processes emboldens a new and promising strategy for mechanically tailoring interface energetics and chemistry.

Conclusion

Piezotronics is an exciting new interdisciplinary field bridging between piezoelectrics and semiconductors. Promising proof-of-principle devices and systems are revolutionizing our understanding and practice of strain-regulated semiconductor functions. So far, the piezotronic effect has been used to

- Create local potential wells for enhanced LED quantum efficiency;
- Improve performance in GaN–InGaN quantum well lasers;
- Form electromechanical memory diodes;
- Increase open-circuit voltage and photocurrent extraction in PV and PEC devices; and
- Activate or facilitate electrochemical reactions.

Considering that P_{pz} depends directly

upon the linear piezoelectric coefficient and the strain tensor, a more pronounced piezotronic effect can be obtained by using

- Materials that are capable of sustaining large strains without failure and
- Making use of certain piezoelectric materials that have pronounced piezoelectric coefficients and attractive semiconductor functionality.

The first case results in a more rugged piezoelectric component capable of enduring substantial strain. A design where peripheral, robust, strained piezoelectric films sandwich an active semiconductor heterojunction located within a neutral strain axis is a conceivable architecture for enhancing piezotronic performance.

A key challenge facing the second case is the low conductivity of the piezoelectric materials in conjunction with their pronounced piezoelectric coefficients. In devices whose functionality depends on the transport of charge carriers, this impediment cannot be overstated. A peripheral approach, where the piezoelectric material itself does not take part in the active heterojunction, may alleviate the problem. Alternatively, GaN and many other III–V wurtzite materials are the core semiconductor components in solar cells, lasers, LEDs, and PEC cells. These materials also exhibit appreciable piezoelectric effect, and thus make good candidates for using the piezotronic effect to regulate their functionalities.

In general, piezotronics brings new knowledge to classic semiconductor theories, where semiconductor band theory and the behaviors of electrons and holes are interpreted with additional contributions from P_{pz} . Piezotronics also introduces a new concept to the classic piezoelectric electromechanical coupling effect by addressing the contributions from free-charges, junction materials, surface and interface properties, and external illumination. New science obtained from the coupling between crystal structure, mechanical strain and electronic properties opens a new route toward designing, operating, and enhancing electronic, optoelectronic, photovoltaic, and even catalytic materials and systems.

Piezotronics will find a significant role in the operational principles of flexible devices, MEMs, sensors, human-CMOS interfacing, and energy conversion and storage systems.

Acknowledgements

The author thanks Zhong Lin Wang at Georgia Institute of Technology for his pioneering work on piezotronics, as well as J. Shi and M. Starr for their contributions to the work in this article. The author gratefully acknowledges the financial support of DARPA under Grant No. N66001-11-1-4139 and the National Science Foundation under Grant No. CMMI-1148919.

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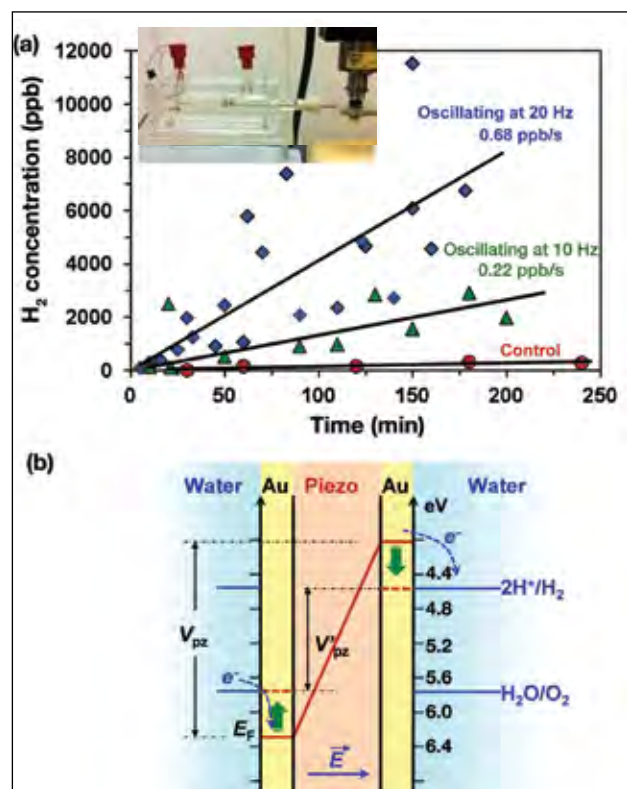


Figure 6. (a) H₂ concentrations measured as a function of oscillating time of the piezoelectric beam in deionized water with a frequency of 10 Hz (triangles) and 20 Hz (diamonds). A silicon cantilever with identical configuration was used as a control (circles). Inset is a photo of the piezocatalysis system. (b) Proposed mechanism of piezocatalysis at the piezoelectric–water interface.

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State of raw materials 2013

Overview and new frontiers

By Eileen De Guire

How far can we push materials? That core question defines the discipline that is materials science.

The question implicit in the Materials Genome Initiative is, “must innovation be at the mercy of known materials?” The finite set of raw material compositions and the limited ways that chemistry and processing allow them to be combined impose limitations on the structure, chemistry, and, ultimately, properties of manufactured components. Materials science, in many ways, has been a materials selection and product design problem, not a “materials design” problem.

MGI flips the question, and asks what properties are desired, and how can we use what we know about structure at the electronic and atomic levels, to engineer materials with specified properties from first principles?

However, MGI is only a formalization of a trend. The discovery of nanomaterials—actually, the discovery of ways to observe nanomaterials—opened the door to engineering materials on length scales not previously imagined. This required development of newer, more powerful characterization tools, but also computational methods that allow modeling across length scales that span many orders of magnitude. After all, even nanomaterial-based products interact sooner or later with users on a “people scale.”

The ability to model, synthesize, and characterize materials on such small scales led, perhaps inevitably, to researchers challenging boundaries, stretching theories, and demanding that materials deliver more of their intrinsic potential.

To this end, a group of researchers embraced the challenge of identifying the “grand challenges” of ceramic science at a NSF-sponsored workshop in spring 2012. They asked what are the compelling scientific questions that, if answered, could lead to the development of game-changing new materials, like oxide-based electronic devices? What questions, if answered, could lead to superior performance of existing materials, like maintaining the intrinsic strength of glass? The article in this issue, “Expanding the frontier—Grand challenges in ceramic science,” by

Gregory Rohrer describes eight grand challenges identified at the workshop, with the caveat that there are likely more.

Some research groups are already developing new materials that push the frontier of traditional materials. In the lead article of this issue, for example, Xudong Wang writes about a new class of materials—piezoelectronics—that are semiconductors with piezoelectric properties and use strain to engineer the band gap. Their fascinating properties are just starting to be explored, and could yield big dividends in energy and process industry applications.

New materials development has a practical side, too, and it behooves manufacturers to proactively address occupational health and safety issues. Especially in the realm of nanomaterials, new questions arise about materials handling and worker exposure in production environments. The medical community is responding with research on how nanomaterials enter, move through, and interact with living organisms. The Center for Disease Control’s National Institute for Occupational Safety and Health works with manufacturers on a voluntary basis to develop safe protocols for nanomaterial manufacturing. See the article, “NIOSH research and resources for safe handling of nanomaterials,” for details.

While we wait to see what new, previously unimagined materials and applications await us

across the frontier, the “Mineral Commodity Summaries 2013” report published by the United States Geological Survey reminds us that the manufacturing economy is the “here and now.” Its health depends on access to reliable supplies of raw materials.

The numbers tell the story. The report estimates the value of mineral raw materials produced at mines in the US was \$76 billion, up from \$74.8 billion in 2011. The value of domestic raw materials combined with domestic recycled materials is estimated to be in the neighborhood of \$2.4 trillion in 2012. According to the USGS report, 2012 represented the third straight year of growth for the mineral production industry.

Minerals contribute to the US gross domestic product on several levels—mining, processing, and manufacturing. For the second consecutive year, the contribution of minerals to GDP grew.

The economy’s harbinger construction industry fuels demand for minerals and products like cement, sand and gravel, and gypsum that are used almost exclusively for construction, not to mention the mineral raw materials used to make steel, windows, tile, fixtures, etc.

Imported minerals continue to be important to US manufacturing. According to the report, more than half of the consumption of 41 minerals in 2012 was imported. Eighteen of the 41 commodity minerals were 100 percent imported. This is about the same level of import-dependence as 2011 and 2010.

Abrasives, manufactured

The United States manufacturing sector strongly influences the markets for manufactured abrasives—fused aluminum oxide and silicon carbide—particularly in the aerospace, automotive, furniture, housing, and steel industries. In the US and Canada, two companies produced 10,000 tons of fused alumina valued at \$1.7 million in 2012. Likewise, two companies produced 35,000 tons of silicon carbide abrasives in 2012 valued at \$26 million. In 2012 China was the world's leading producer of manufactured abrasives. Plants operating nearly at capacity produced 695,000 tons of fused alumina and 450,000 tons of silicon carbide.

Domestic resources of raw materials to produce fused alumina are limited. However, adequate resources exist in the Western Hemisphere. Domestic resources are more than adequate to produce silicon carbide. Imports, especially from China, and high operating costs continue to challenge North American abrasives manufacturers, who are likely to further curtail production.

Bauxite and alumina

As in previous years, nearly all bauxite consumed in the United States in 2012 was imported, and more than 95 percent was converted to alumina. More than 90 percent of the alumina went to primary aluminum smelters, leaving less than 10 percent for non-metallurgical uses, such as abrasives, chemicals, and refractories.

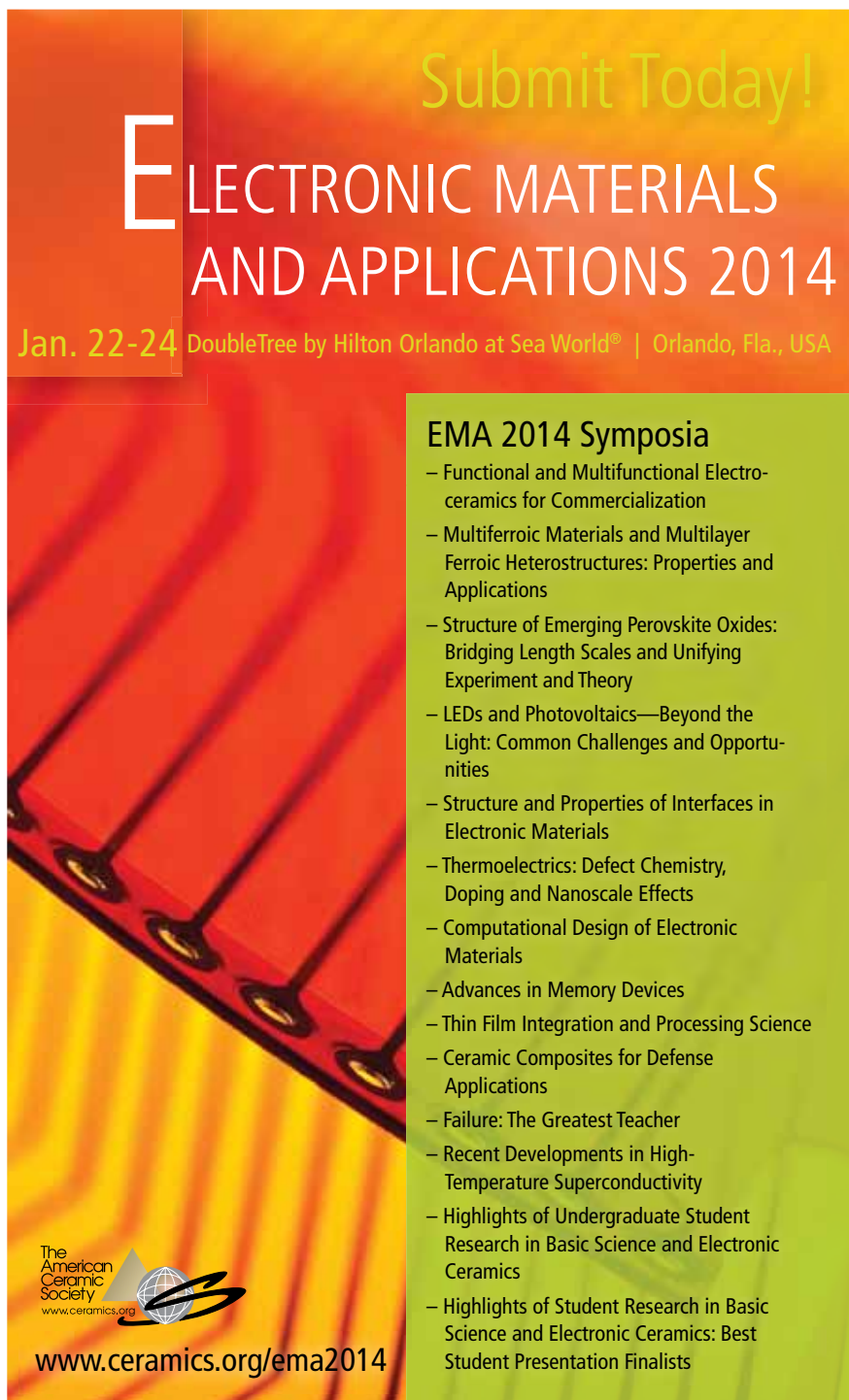
Annual US alumina production capacity was 5.64 million tons, with four Bayer refineries operating throughout the year. Globally, alumina production increased by five percent in 2012 over 2011 levels. Worldwide bauxite production increased slightly in 2012 compared with 2011 with increased production levels in Australia, Brazil, China, Guinea, and India. However, the increases were largely offset by declining production in Indonesia, which enacted strict mine export tariffs during 2012.

Boron

Two companies in southern California produced borates in 2012, and most of the boron products consumed in the United States were manufactured domestically. In 2012, the glass and ceramics industries remained the leading domestic users of boron prod-

ucts, consuming an estimated 80 percent of the total borates marketplace. Boron also was used as a component in abrasives, cleaning products, insecticides, and in the production of semiconductors.

Global consumption of borates is expected to increase in 2012 and the coming years, spurred by strong demand



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in the Asian and South American agricultural, ceramic, and glass markets. In particular, boron consumption in the global fiberglass industry was projected to increase by seven percent annually through 2013, spurred by a projected 19 percent increase in Chinese consumption. World consumption of borates is projected to reach 2.0 million metric tons by 2014, compared with 1.5 million metric tons in 2010, with most of the increased demand coming from glass and ceramics industries. China is expected to increase imports from Chile, Russia, Turkey, and the US during the next several years. Continued investment in new refineries and technologies and the continued increase in demand were expected to fuel growth in world production during the next several years.

Cement

US plants produced about 71 million tons of portland cement and 2.0 million tons of masonry cement at 98 plants in 35 states. Although the economic recovery helped boost production levels above 2009–2011 levels, production continued to be very low compared with levels during 2002–2007, when it exceeded 90 million tons per year. Sales volume in 2012 was 51 million tons less than the record level achieved in 2005. The cement market generated \$7.5 billion in sales, and most of it was used to make concrete, worth at least \$41 billion.

Manufacturing clinker for cement releases a great deal of carbon dioxide. The US Environmental Protection Agency published the results of the first mandatory reporting survey (2010) of the cement industry's greenhouse gas emissions. Carbon dioxide reduction strategies by the cement industry mainly aim at reducing emissions per ton of cement product rather than by a plant overall. Approaches include installation of more fuel-efficient kilns, partial substitution of noncarbonate sources of calcium oxide in the kiln raw materials, and partial substitution of supplementary cementitious materials, such as pozzolans, for portland cement in the

finished cement products and in concrete. Many portland cement substitute materials, especially fly ash and ground granulated blast furnace slag, react with the lime released by the hydration of portland cement and develop good hydraulic cementitious properties.

Clays

In 2012 about 180 companies operated approximately 750 clay pits or quarries and recovered about 25.7 million tons valued at \$1.57 billion. Specific clays and products made from them include ball clay for floor and wall tile, sanitaryware, and other uses; bentonite for drilling mud, absorbents, iron ore pelletizing, foundry sand bond, and other uses; common clay for brick, lightweight aggregate, cement, and other uses; fire clay for heavy clay products, refractory products, and other uses; fuller's earth for absorbents and other uses; and kaolin for paper and other uses. Increased commercial and residential housing construction is likely to slightly increase sales of common clay and fire clay for heavy clay products and ball clay for ceramic tile and sanitaryware manufacture. Kaolin production is likely to increase slightly as ceramic markets increase and paper markets stabilize.

Feldspar

US feldspar production in 2012 was valued at about \$39 million. Feldspar is ground to about 20 mesh for glassmaking and to 200 mesh or finer for most ceramic and filler applications. During 2012, glassmakers used about 70 percent of domestic feldspar supplies, with 30 percent going to pottery and other uses.

The glass industry uses most of the feldspar it consumes to manufacture container glass, which was a moderately stable industry despite some competition in baby food, fruit juices, mineral water, and wine container segments. Additionally, increased use of postconsumer glass collected through local government and neighborhood recycling programs competes with traditional raw materials, such as feldspar.

Residential flat glass markets improved slightly in 2012, but sluggishly. Automotive glass markets increased also. In 2013 fiberglass consumption for thermal insulation is forecast to expand in line with housing and commercial building construction in the US through 2013. Another growing segment in the glass industry is solar glass, used in the production of solar cells.

Iron and steel

The iron and steel industry and ferrous foundries produced goods in 2012 valued at \$112 billion. About 48 companies produce raw steel in the US at about 108 minimills representing a combined production capability of about 118 million tons. Most are located in the established steelmaking Great Lakes region encompassing Indiana, Ohio, Michigan, and Pennsylvania.

China accounted for about 47 percent of world steel production. According to the World Steel Association, world apparent steel consumption (ASC) was expected to increase by 2.1 percent to 1.41 billion tons in 2012, and increase by 3.2 percent to 1.46 billion tons in 2013. ASC in China, the world's leading producer and consumer of steel, is expected to increase by 2.5 percent and by 3.1 percent in 2012 and 2013, to 640 million tons and 659 million tons, respectively. ASC for North America is expected to increase by 7.5 percent in 2012 to 130 million tons and by 3.6 percent in 2013 to 135 million tons. ASC for India is expected to increase by 5.5 percent and 5.0 percent in 2012 and 2013, respectively. The global steel industry has been struggling from the impact of the debt crisis in Europe and slowing demand and oversupply in China.

Kyanite and related

Commercially produced mullite is synthetic, produced from sintering or fusing such feedstock materials as kyanite or bauxitic kaolin. Natural mullite occurrences typically are rare and uneconomic to mine. Refractories consume about 90 percent of the kya-

nite-mullite output. Most refractories, 60–65 percent, are used for ironmaking and steelmaking and the remainder for manufacture of chemicals, glass, nonferrous metals, and other materials.

Crude steel production in the United States, which ranked third in the world in steel production, increased by six percent in the first eight months of 2012 compared with that of the same period in 2011, which increased consumption of kyanite-mullite refractories. Demand for refractories in iron and steel production is expected to grow during the next several years, depending on the rate of increase in steel production. Growth also is anticipated for refractories to produce other metals and to meet increasing production of cement, ceramics, glass, and mineral products.

Lithium

Globally, lithium end-use markets include ceramics and glass, batteries,

lubricating greases, air treatment, metals, polymers, pharmaceuticals and primary aluminum production. Demand for lithium in batteries expanded significantly in recent years with growing demand for rechargeable lithium batteries in portable electronic devices and electric tools.

Batteries, especially rechargeable batteries, are expected to provide the largest growth potential for lithium compounds. Besides electronic devices, major automobile companies are developing lithium batteries for electric vehicles and hybrid electric vehicles.

Lithium supply security has become a top priority for Asian technology companies. Strategic alliances and joint ventures have been, and are continuing to be, established with lithium exploration companies worldwide to ensure a reliable, diversified supply of lithium for Asia's battery suppliers and vehicle manufacturers.

Platinum group metals

Catalysts to decrease emissions in light- and heavy-duty vehicles continue to make up the leading demand sector for PGMs. Most motor vehicle manufacturers now routinely substitute palladium for the more expensive platinum in gasoline-engine catalytic converters. Up to 25 percent palladium is routinely substituted for platinum in diesel engines. The chemical-processing industry and petroleum-refining industry also use PGM catalysts. High-purity crystals for the electronics industry are grown in PGM crucibles. Machines for manufacturing fiberglass, liquid-crystal displays, and flat-panel displays have PGM components.

Average annual prices for palladium, platinum, rhodium, and ruthenium were lower in 2012 than in 2011 because of economic concerns. Volatility throughout the year reflected external effects such as labor disputes and investor buying and selling.

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The sole US-based mining company expanded its mines and is testing new precious metals refinery technology.

Canada plans to launch a new platinum and palladium exchange-traded fund that would be backed by physical metal held at the Royal Canadian Mint and intended for long-term investment rather than short-term investment on price fluctuations. Investors will be able to redeem the physical metal.

Soda ash

The total value of domestic soda ash (sodium carbonate) produced in 2012 was estimated to be about \$1.6 billion. Nearly half of the 14.5 million ton capacity of domestic soda ash producers is used by the glass industry. Other uses include chemicals, soap and detergent, desulfurizers, and pulp and paper.

The largest deposit in the world is in the Green River Basin in Wyoming. China recently announced discovery of a large trona deposit in Tongbai County, ranking it the largest trona deposit in Asia and second only to the Wyoming deposit.

Overall global demand for soda ash was expected to increase by 1.5 percent to two percent annually for the next several years, with most of the growth expected to be in China, India, Russia, and South America. If the domestic economy and export sales improve, US production may be higher in 2013. If the reports about a new trona discovery in China are confirmed, China may become the lowest-cost soda ash producer in Asia and a strong competitor with the US in the Far East soda ash markets.

Talc and pyrophyllite

Domestic talc production in 2012 was estimated to be 623,000 tons valued at \$22 million and generated sales of about 571,000 tons valued at \$90 million. Sales in 2012 were about seven percent more than on 2011. Talc is used to produce ceramics (primarily refractories) paint, paper, plastics, roof-

ing, and cosmetics. About 260,000 tons was imported.

Production of pyrophyllite, the aluminum silicate hydroxide mineral $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$, decreased slightly from 2011 levels. It is used to manufacture refractory products, ceramics, and paint. Sales of pyrophyllite declined slightly in 2012 because of the slow recovery of those sectors of the economy.

No issues loom with access to talc or pyrophyllite. The US is self-sufficient in most grades of talc and related minerals. Domestic and world resources exceed estimated reserves by about fivefold.

Tungsten

More than one-half of the tungsten consumed in the US was used in cemented carbide parts for cutting and wear-resistant materials, primarily in the construction, metalworking, mining, and oil- and gas-drilling industries. The remaining tungsten was consumed to make tungsten heavy alloys for applications requiring high density; electrodes, filaments, wires, and other components for electrical, electronic, heating, lighting, and welding applications; steels, superalloys, and wear-resistant alloys; and chemicals for various applications. The estimated value of apparent consumption in 2012 was \$1 billion.

World tungsten supply was dominated by Chinese production and exports, but China also was the world's leading tungsten consumer. China's government has regulated its tungsten industry by limiting the number of exploration, mining, and export licenses; limiting or forbidding foreign investment; imposing constraints on mining and processing; and establishing quotas and imposing export taxes on tungsten materials. China's government plans to expand exploration and increase ore reserves in approved mines, to control tungsten mine production, to improve its tungsten-processing technology, and to increase the development and sales of value-added downstream tungsten products.

Yttrium

Phosphors for color televisions, computer monitors, temperature sensors, trichromatic fluorescent lights, and X-ray-intensifying screens use the rare-earth yttrium, which is mined as bastnaesite in the US. China, however, produces most of the world's supply of yttrium. India expects to become a significant producer with the opening of a new monazite processing plant. Although prices for yttrium metal and oxides were relatively stable for the first three quarters of 2012, they decreased significantly in the fourth quarter because of reduced demand, mostly in the energy and defense sectors.

Yttria-stabilized zirconia applications include alumina-zirconia abrasives, bearings, seals, high-temperature refractories, jet-engine coatings, oxygen sensors in automobile engines, simulated gemstones, and cutting tools. The optical and lasing properties of yttrium-containing garnets make them useful for medicine, communications, sensing, industrial cutting and welding, nonlinear optics, photochemistry, high-temperature superconductors, and photoluminescent devices.

Zirconium and hafnium

Zircon is a coproduct from the mining and processing of heavy minerals. Typically, zirconium and hafnium are contained in zircon at a ratio of about 50 to 1. Two firms mined zircon from surface operations in Florida and Virginia. Ceramics, foundry applications, opacifiers, and refractories are the leading end uses for zircon. Other end uses of zircon include abrasives, chemicals, metal alloys, and welding rod coatings. The leading consumers of zirconium metal and hafnium metal are the nuclear energy and chemical process industries. China plans to increase its nuclear power development, which would likely increase demand for nuclear-grade zirconium and hafnium, which are used for nuclear fuel cladding. ■