Materials Availability Expands the Opportunity for Large-Scale Photovoltaics Deployment

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Solar photovoltaics have great promise for a low-carbon future but remain expensive relative to other technologies. Greatly increased penetration of photovoltaics into global energy markets requires an expansion in attention from designs of high-performance to those that can deliver significantly lower cost per kilowatt-hour. To evaluate a new set of technical and economic performance targets, we examine material extraction costs and supply constraints for 23 promising semiconducting materials. Twelve composite materials systems were found to have the capacity to meet or exceed the annual worldwide electricity consumption of 17 000 TWh, of which nine have the potential for a significant cost reduction over crystalline silicon. We identify a large material extraction cost (cents/watt) gap between leading thin film materials and a number of unconventional solar cell candidates including FeS_2, CuO, and Zn_3P_2. We find that devices performing below 10% power conversion efficiencies deliver the same lifetime energy output as those above 20% when a 3/4 material reduction is achieved. Here, we develop a roadmap emphasizing low-cost alternatives that could become a dominant new approach for photovoltaics research and deployment.

Introduction

An affordable electricity supply is essential for meeting basic human needs, and yet 30% of the world population remains effectively without reliable or sufficient electricity (*1*). With forecasts of over 30 TW (10^{12} W) of new power needed by 2050, the carbon emissions associated with the expansion,

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or even continuation, of current fossil-fuel-based electricity generation would make maintaining atmospheric CO_2 concentrations near their current levels of 379 ppm an insurmountable challenge (*1–3*). Solar photovoltaics (PV) are frequently cited as a promising but an economically unrealistic large-scale supply option for a low-carbon future (*4*). By one recent estimate, the U.S. could achieve 69% of electricity and 35% of total energy consumption by 2050 entirely with existing PV technologies but may require almost half a trillion dollars in subsidies (*5*). Even with current PV module production at 3,800 MW/year, it remains less than 3% of all new generation capacity (*6*). How realistic is a future where solar PV amounts to a significant fraction of generation (*5, 7, 8*)? To be a viable alternative to fossil fuels, PV must expand dramatically and form a new, far larger industrial sector.

Background

A typical polycrystalline silicon PV cell produces electricity, amortized over a 20 year lifetime, at above 20¢/kWh (variations in insolation may lead to costs as low as 16¢/kWh) with life-cycle carbon emissions as low as 32 g CO_2/kWh (*9, 10*). This is more than twice the average cost of the two fastest growing alternatives, namely, wind at 4−10¢/kWh (∼20 g CO_2/kWh) and natural gas at 5−7¢/kWh (∼400 g CO_2/kWh) (*6, 9*). Lifetime costs of PV-generated electricity are the summation of module, balance of systems (BOS), and operation management (OM) costs. Recent estimates show BOS and OM costs declining at over 5% per year, whereas module costs vary with the market fluctuations of material feed stocks. Today, modules represent ∼54% of the total installed cost for existing PV technologies, notably mono- and polycrystalline silicon, where silicon processing is estimated to be ∼85% of the energy input of the finished module (*10–13*). Aggressive development of nonsilicon-based PV materials has changed the PV landscape, offering exciting near-term cost reductions for material systems like copper indium gallium selenide (CIGS) and cadmium telluride (CdTe). Quantifying material cost and the availability of these and other emerging material systems provides a critical metric to guide future research and development decisions toward a greatly expanded solar cell industry of the future.

Forecasts of the future costs of vital materials have a high-profile history. In 1980, Paul Ehrlich and Julian Simon made a public wager on the future price change of chrome, copper, nickel, tin, and tungsten (*14*). Ehrlich and his colleagues waged a total of $1000, or $200/metal. In 1990, as Simon had predicted, the inflation-normalized price of all five metals had dropped to ∼$430 because cheaper plastics and ceramics replaced more costly metals, lowering demand and subsequently the price of those metals (*14*). Today, however, that basket of five metals is now valued at over $1500. Continued demands for higher-purity and thus valued materials have been the driver of this reversal of the initial Ehrlich−Simon wager (*15–19*). For example, the average quality of copper ore has gone from 2.4% to 1% in the last 100 years. The fraction of recoverable zinc that has already been placed in use is 19%, and indium, a secondary metal byproduct of zinc mining, has seen its price increase 400% in the past five years due to an increase in demand from the digital display market (*20, 21*). Here, we explore such material limits for PV expansion by examining the dual constraints of material supply and least cost per watt for the most promising semiconductors as active photogenerating materials.
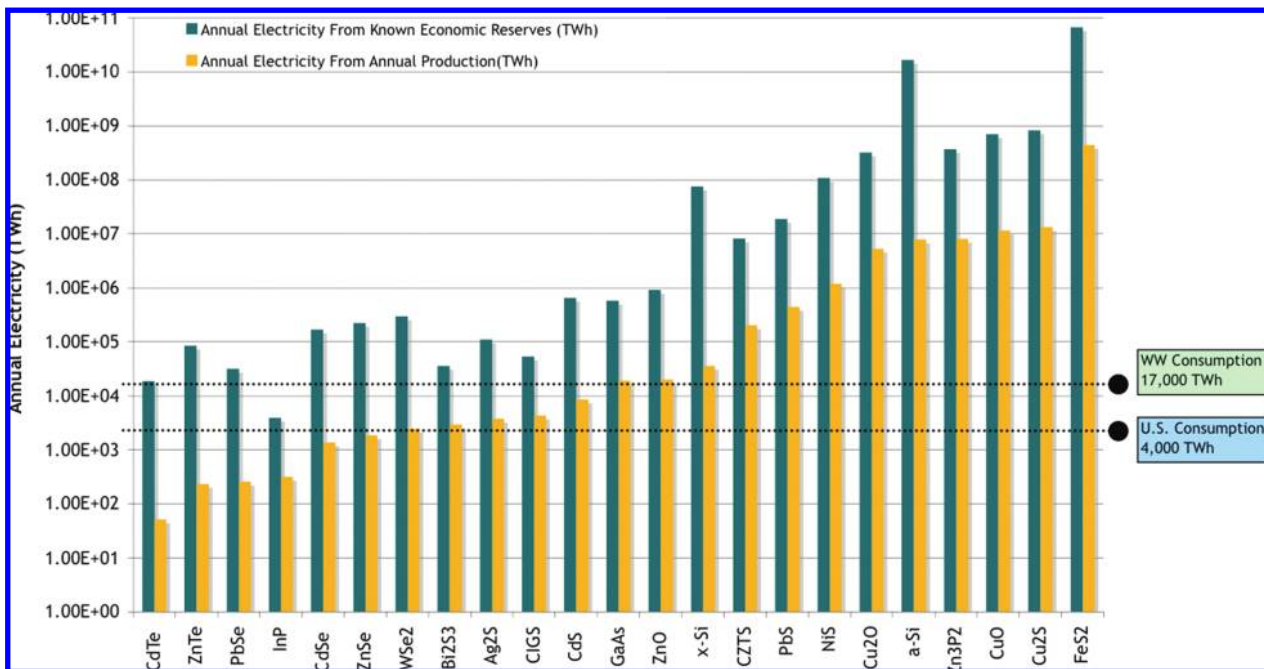
FIGURE 1. Annual electricity production potential for 23 inorganic photovoltaic materials. Known economic reserves (also known as Reserve Base) and annual production are taken from the U.S. Geological Survey studies (21). Total U.S. and worldwide annual electricity consumption are labeled on the figure for comparison.
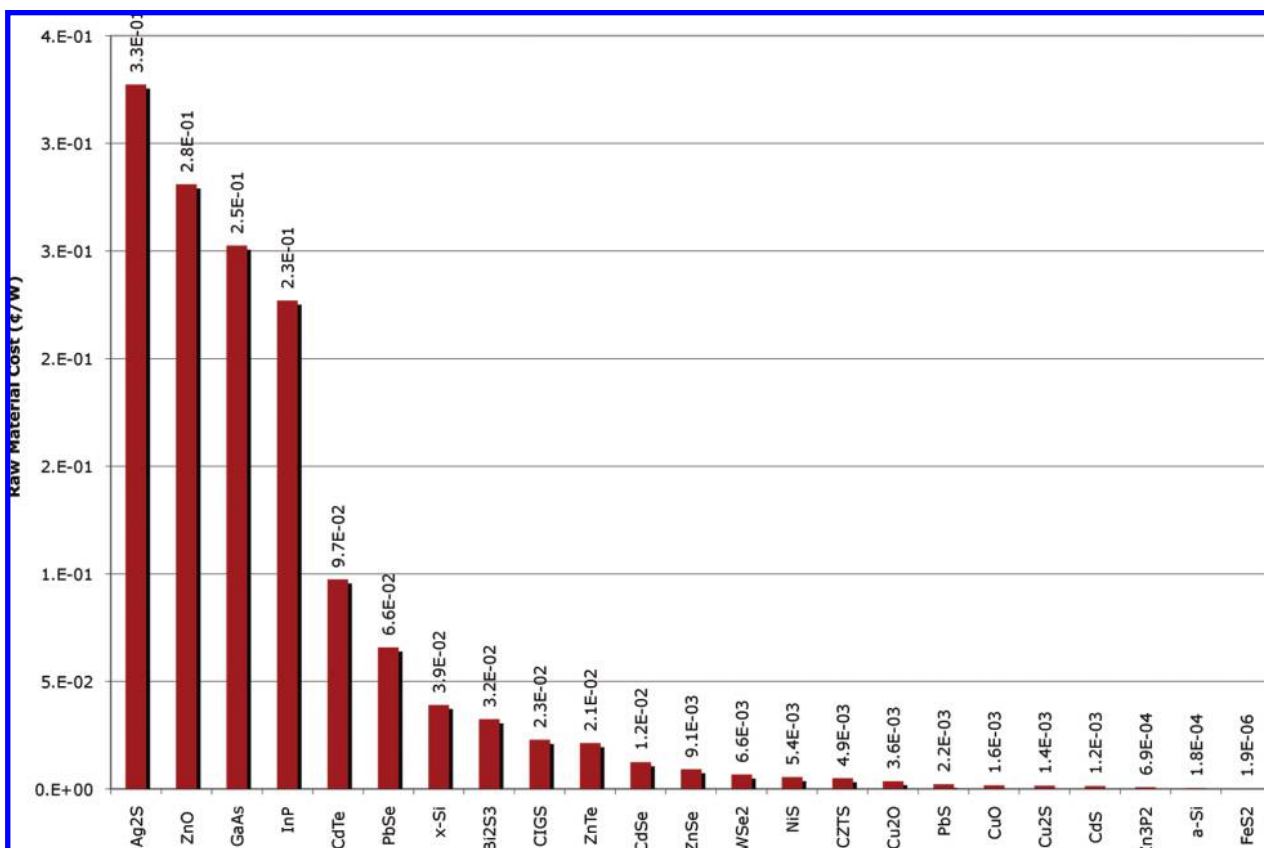

FIGURE 2. Minimum ¢/W for 23 inorganic photovoltaic materials. Component cost contribution in ¢/W is a strong indicator of value for future deployment. Calculated values for all 23 compounds evaluated are shown. The range of costs are between 0.327¢/W for Ag₂S and <0.000002¢/W for FeS₂. While the actual dollar figure per watt for material extraction will appear small compared to the entire cost of an installed PV system, the cost of processing the material for PV grade applications is a larger cost contributor and should be evaluated further.

Methods

Model Overview. We developed a model to evaluate the maximum annual electricity contribution from 23 potential photovoltaic technologies. We consider single junction limits for all 23 inorganic semiconductors as active photogenerating materials. We do not evaluate the role these materials could
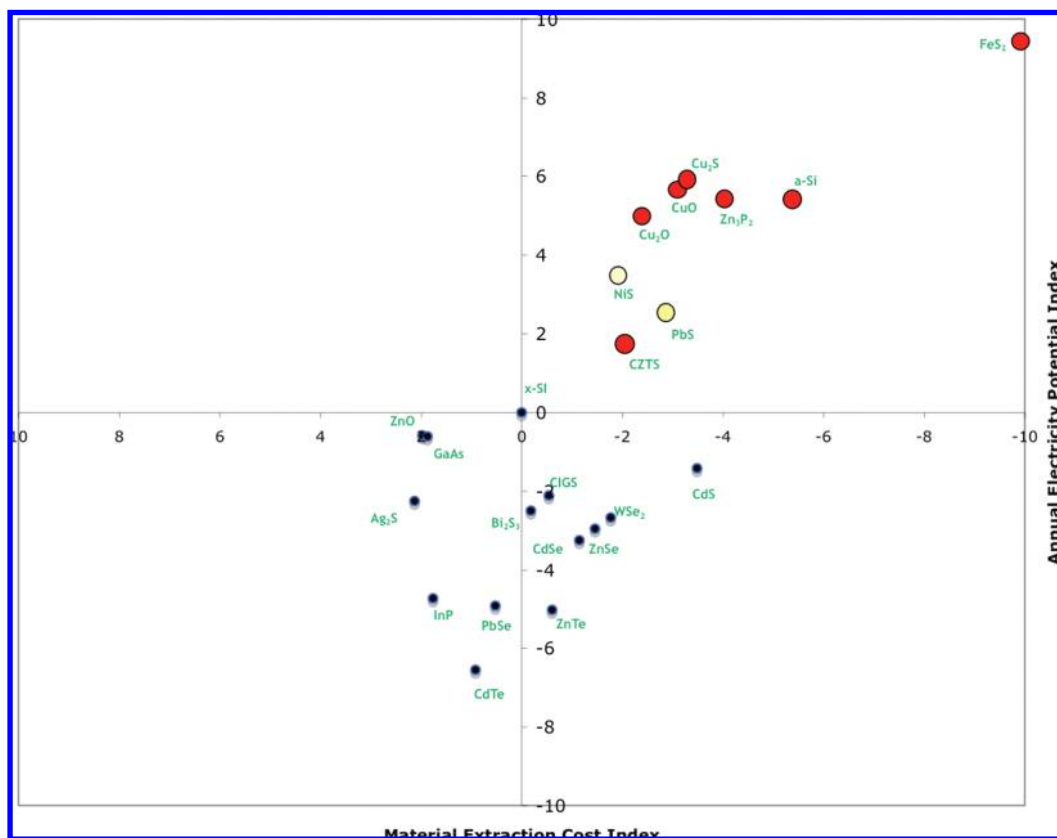
FIGURE 3. Four-quadrant plot of indexed results. By indexing both model results from Figure 1 and the cost from Figure 2 to modeled values of x-Si, materials that exhibit the greatest long-term potential are identified. All index values are calculated as the natural logarithm of the calculated value divided by the calculated result for x-Si. The most attractive materials for large-scale future deployment are highlighted red and are in the upper right-hand quadrant. Materials highlighted in yellow are attractive by this analysis but have low performance limits that will lead to a disproportionately larger balance of systems cost per watt. These materials indicated in yellow are also candidates for quantum confinement to tune the bandgap higher and yield a higher η.

play in other PV configurations, such as window layers, part of a multijunction stack, or as a dye-sensitized device. Prior work to address maximum electricity potential focused on leading thin film alternatives to crystalline silicon (x-Si), namely, CIGS and CdTe (*22–25*). In each case, material availability of a particular elemental species emerged as a strong constraint. For example, one such hypothetical analysis demonstrated that a CdTe device with a cell thickness of 2 μm and operating at 10% power conversion efficiency was found to be capable of producing 0.3 TW per year before material scarcity was to become a limiting factor (*25*). Our results confirm this finding, even when the devices perform close to their maximum theoretical limit, but also reveal several compounds that are not hindered by abundance constraints.

Theoretical Limits for Power Conversion Efficiency (η) and Material Intensity (β) Defined. Model calculations are based on the theoretical limits in both minimum material intensity (β) and maximum power conversion efficiency (η). Minimum material intensity values are defined as the absolute minimum mass of semiconducting material required for achieving a single pass absorption of 85%. These β values are calculated by multiplying the material density by a calculated material thickness (t). Thickness was determined by solving the following integral function for I/I_o equal to 0.85 over λ values between 280 nm and the bandgap energy of each material:

$$\frac{I}{I_o} = \frac{\int_{280nm}^{\lambda_{bg}} (\lambda)\,d\lambda - I_o(\lambda)e^{-\alpha(\lambda)t}\,d\lambda}{\int_{280nm}^{\lambda_{bg}} I_o(\lambda)\,d\lambda}$$

I_o is the wavelength-specific intensity of the AM1.5G solar spectrum, I/I_o is the fraction absorbed by the material, and α is the material absorption coefficient (*26, 27*). Where full absorption data were not available, thickness was estimated on the basis of absorption lengths ($1/\alpha$) at representative wavelengths. Performance (η) was taken as 100% of each semiconductor's theoretical power conversion efficiency limit, also known as the single junction thermodynamic limit based on published energy bandgap values (*28–30*).

Total Electricity Potential Calculation. Total annual electricity potential P in terawatt hours (TWh) is calculated by the following equation:

$$P = \frac{I \cdot \eta \cdot A \cdot C \cdot H}{\beta \times 10^{12}}$$

where I is the solar spectrum intensity taken as a global air mass index (AM1.5G) of 1000 W/m², A is the annual production per mineral in metric tons, C is the capacity factor for operation taken at 20%, and H is the number of hours per year (*21, 31*). Material intensity values of β are in units of metric tons per square meter. Because theoretical limits are used for η and β values, resulting P values are a best-case scenario and may slightly overstate what is actually achievable in industry.

Because commercial PV technologies have already demonstrated lifetimes up to and exceeding 30 years, there is a cumulative production benefit if, in years two and beyond, all of the mined material were again converted into PV devices. To address this, we calculate and show the total electricity potential using known economic reserves as a second measure of an upper limit. Yet, economic reserves

will vary greatly on current market conditions of supply and demand, making forecasts of future mineral stocks and production rates (A) highly variable and uncertain. Therefore, this analysis remains rooted in comparing all semiconductor compounds' total PV productivity based on one year of mineral exhaustion.

Cost Model Framework. The focus of our analysis is on mineral abundance, total extraction potential, and extraction cost. A framework for material cost analysis includes mineral extraction and processing costs, where $C_T = C_e + C_p$. The cost of extraction (C_e) is given by $C_e = a/g$, and the cost of mineral refining (C_p) is given by $C_p = b \cdot \Delta G$, where a and b are constants, g is ore grade or mineral content of the raw ore, and ΔG is the Gibbs free energy of transforming the mineral into useable metal (32). Material processing costs (C_p) are complex and mineral-specific. In most cases, $C_p > C_e$ and may exceed the extraction cost by several orders of magnitude. Due to limited industry experience and data on the costs associated with solar grade processing for non-traditional material systems, C_p values remain uncertain and are omitted from this analysis. While this area deserves further investigation, the C_p/C_e ratio has been proven to be highly uniform for a wide range of minerals examined in this study, and hence exclusion of C_p does not discriminate against any one material system (32–36).

Cost Modeling. Material extraction costs C_e are expressed in cents per watt (¢/W) for each semiconductor compound with x components and are calculated by

$$C_e = \frac{\beta}{\eta \cdot I} \sum_{n=1}^{x} C_n \left[\frac{(x_n)(M_n)}{\sum_{m=1}^{x} (x_m)(M_m)} \right]$$

where C_n is the mined cost per material n given in cents per kilogram, x_n and x_m are the molar quantities of an individual species in the semiconducting compound, M_n and M_m are the molar masses of an individual species in the semiconducting compound, and I is the solar spectrum intensity taken as a global air mass index (AM1.5G) (21, 31).

Results and Discussion

Abundance and Cost Analysis. We estimated the electricity contribution and cost impact of material extraction to a finished solar module by calculating the maximum TWh and minimum ¢/W of each of the 23 compounds evaluated (Figures 1 and 2). PV materials that could achieve extraction costs lower than x-Si at 0.039¢/W and demonstrate equal or greater electricity production potential versus x-Si include FeS_2, Zn_3P_2, and a-Si (Figure 3). Iron pyrite (FeS_2) is significantly more attractive in both cost and availability than all other compounds, whereas several of the leading thin-film technologies like CdTe are not able to meet the large-scale needs. The two materials PbS and NiS are both promising, but outside of a quantum confined system, they will be hampered by disproportionately higher BOS and installation costs due to low power conversion efficiencies. Furthermore, some unusual candidate compounds, like ZnO,
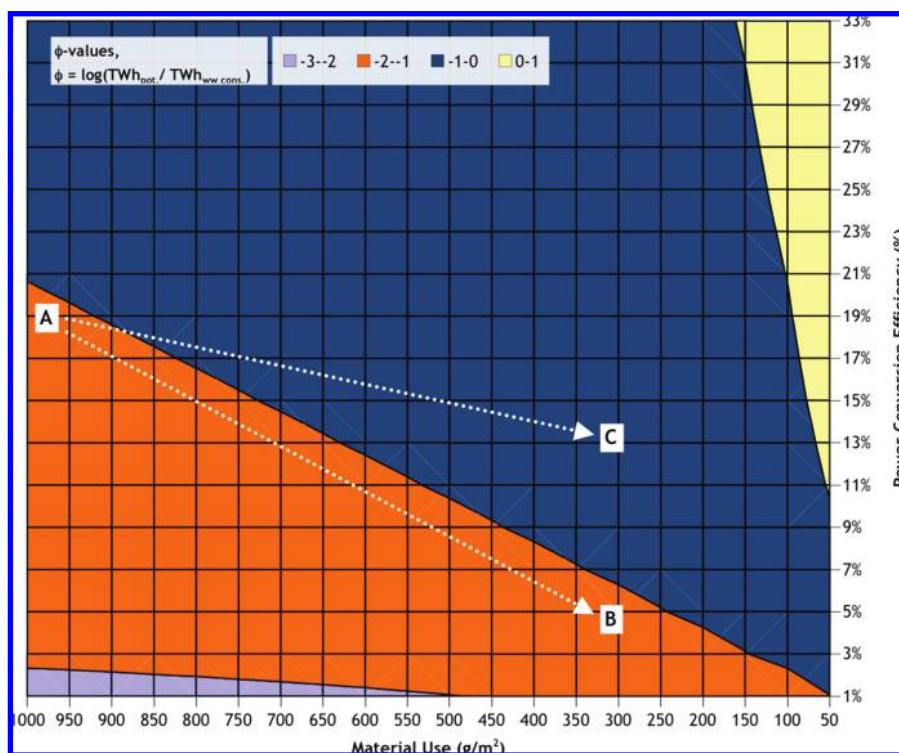

FIGURE 4. Sensitivity phase plot of total electricity production potential by both material usage and power conversion efficiency for x-Si. This analysis highlights the total TWh potential of x-Si for varying material usage and performance values. Phi values (ϕ) are calculated as the natural logarithm of the calculated maximum annual electricity potential (as described in Figure 1) divided by worldwide electricity consumption. Each point on the graph represents a different ϕ value based on the discrete material usage and performance values at that point. Shaded regions represent separate brackets of ϕ values. Implicit in this analysis is the assumption that by minimizing material usage there may be an associated reduction in cost, yet there may also be a downward shift in performance. The sensitivity analysis for x-Si shows that given today's technology benchmarks (point A) there is a 10^{-1} multiplier on worldwide demands. By following a contour from point A to point B, ϕ values are held constant. At point B, a low-efficiency cell (~4%) with much lower material consumption has the same potential benefit as a material at point A. Low-efficiency materials may face disproportionate cost hurdles in the balance of system and installation costs. For this reason, a less aggressive performance reduction at the same material reduction (point C) would increase ϕ values by 1 order of magnitude while decreasing total installed cost reduction.

have a high abundance but fail to meet an acceptable limit on cost, and some compounds, like CdS, show favorable cost but a low production potential, making them candidate technologies primarily for niche markets.

Silicon Comparison. Its important to compare results of these novel material systems to silicon, the second most abundant element in the earth's crust at 28% of the lithosphere by mass (37). Despite its abundance, silicon has an annual production that trails that of copper by 145,000 metric tons and a cost of extraction of ~$1.70/kg, as compared to the $0.03/kg for iron (21). This disparity in costs is traced to the energy input of 24 kWh/kg for useable metallurgical-grade silicon from silica (SiO_2) as opposed to the 2 kWh/kg for converting hematite (Fe_2O_3) to iron (31, 32). While both processes are already quite efficient, the Gibbs free energy of processing silica is a fixed thermodynamic barrier that will always be present. Crystalline silicon is further disadvantaged by a weighted photon flux absorption coefficient two orders of magnitude smaller than that for FeS_2, thereby requiring a much larger material input to achieve the same absorption properties (26). Our analysis highlights a photovoltaic future that may not be dependent on either silicon technologies or currently popular thin films.

Power Conversion Efficiency Limits. The physics and economics of photovoltaic technologies are linked by performance measures. The dominant performance benchmark has been power conversion efficiency (PCE), where an optimum is determined by open circuit voltage (V_{oc}) and short circuit current (J_{sc}), as given in the relationship $\eta = (V_{oc}J_{sc}FF)/P_{in}$, where FF is the material fill factor and P_{in} is the incident solar energy. For a single junction PV cell, there is an optimal bandgap of ~1.3 eV that yields a maximum PCE of 33%, as set forth by Shockley and Queisser (28, 30). Large bandgap materials, like ZnO, sacrifice the low-energy wavelengths in the red part of the spectrum, thereby lowering J_{sc}, whereas small bandgap materials, like PbS, absorb a broader part of the spectrum but at the expense of lowering the V_{oc} (29). Since the early 1950s, the evolution of the PV industry has favored high-efficiency materials (28, 29). These technologies shaped the market for PV into one of high-value electricity alternatives for remote power and more recently high-value grid-tied electricity. Low-efficiency cell types were not significantly investigated, regardless of cost.

In addition to providing a guide of promising materials to investigate for the large-scale expansion of the PV industry, this analysis also illustrates the opportunity for new manufacturing techniques to increase the total TWh output of promising but relatively more expensive materials by sacrificing per-unit efficiency. To explore this, a two-variable sensitivity analysis between material consumption and performance was performed on x-Si, the dominant technology today (Figure 4). Crystalline silicon at a PCE of 19% and material consumption of ~1 kg/m^2 will produce between 10^{-2} and 10^{-1} times the current global annual electricity consumption. This is annual electricity production based on one year of mineral extraction. Total contribution would increase if annual production were integrated over the entire lifetime of the cell. An equivalent total output is possible with a device at 4% PCE and a material consumption of 0.3 kg/m^2. By contrast, FeS_2 could achieve between 10^2 and 10^3 times the current global annual electricity consumption using the same performance and material assumptions as x-Si.

As stated earlier, low-PCE devices may be hampered by disproportionately high area-related BOS costs. While there exist technology-specific PCE thresholds for achieving a commercially viable PV cell, such thresholds are moving targets and must be considered separately from this analysis. Therefore, these findings point to lower-cost alternatives than traditional thin films, such as nanocomposites or organics, that may sacrifice some performance in order to utilize less material and innovative low-cost processing. Presently, state of the art nanotechnology PV cells fabricated with inorganic materials reach ~3% in PCE but with <300 nm thick films, thereby utilizing far less material then their thin film predecessors (38–41). Both lower cost and faster throughput are the key potential benefits to this new generation of PV devices.

Our analysis demonstrates a major opportunity for fruitful new research and development based on low cost and commonly available materials. Aggressive targets for PV growth, while noble, may be challenging with either traditional silicon-based technologies or the emerging chalcogenide-based thin films. Rather, this analysis shows that there exist other material systems that satisfy both parameters of a least cost per watt and high theoretical performance. These materials may also be fabricated as low-performance alternatives to traditional thin films, such as nanocomposite photovoltaics. Such an approach will utilize far less material, achieve further cost reductions, and increase the rate of production without sacrificing total TWh potential.

Supporting Information Available

Model inputs and assumptions, details of the mineral abundance analysis, and additional analysis on modern industrial technologies versus the theoretical limits. This information is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Holdren, J. P. Presidential address - Science and technology for sustainable well-being. *Science* **2008**, *319* (5862), 424–434.

(2) Hoffert, M. I.; Caldeira, K.; Benford, G.; Criswell, D. R.; Green, C.; Herzog, H.; Jain, A. K.; Kheshgi, H. S.; Lackner, K. S.; Lewis, J. S.; et al. Advanced technology paths to global climate stability: Energy for a greenhouse planet. *Science* **2002**, *298* (5595), 981–987.

(3) *Intergovernmental Panel on Climate Change (IPCC): Climate Change 2007- Impacts, Adaptation, and Vulnerability*; Cambridge University Press: Cambridge, U. K., 2007.

(4) Green, M. A. *Power to the people: sunlight to electricity using solar cells*; University of New South Wales Press: Sydney, Australia, 2000.

(5) Zweibel, K.; Mason, J.; Fthenakis, V. By 2050 solar power could end US dependence on foreign oil and slash greenhouse gas emissions. *Sci. Am.* **2008**, *298* (1), 64–73.

(6) U.S. Energy Information Administration, International Energy Outlook, 2007; U.S. Department of Energy: Washington, DC, 2007.

(7) Service, R. F. Solar energy - Is it time to shoot for the sun. *Science* **2005**, *309* (5734), 548–551.

(8) Lewis, N. S.; Nocera, D. G. Powering the planet: Chemical challenges in solar energy utilization. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103* (43), 15729–15735.

(9) Kammen, D. M.; Pacca, S. Assessing the costs of electricity. *Annu. Rev. Environ. Res.* **2004**, *29*, 301–344.

(10) Fthenakis, V. M.; Kim, H. C.; Alsema, E. Emissions from Photovoltaic Life Cycles. *Environ. Sci. Technol.* **2008**, *42* (6), 2168–2174.

(11) Knapp, K.; Jester, T. Empirical investigation of the energy payback time for photovoltaic modules. *Solar Energy* **2001**, *71* (3), 165–172.

(12) Alsema, E. A. Energy pay-back time and CO2 emissions of PV systems. *Prog. Photovoltaics* **2000**, *8* (1), 17–25.

(13) Rogol, M.; Choi, P.; Conkling, J.; Fotopoulos, A.; Peltzman, K.; Roberts, S. *Solar Annual 2006 - The gun has gone off*; Photon Consulting: Boston, MA, 2006.

(14) Tierney, J. Betting on the Planet. *The New York Times*, 1990.

(15) Solow, R. M. Economics of Resources or Resources of Economics. *Am. Econ. Rev.* **1974**, *64* (2), 1–14.

(16) Slade, M. E. Trends in natural-resource commodity prices - An analysis of the time domain. *J. Environ. Econ. Manage.* **1982**, *9* (2), 122–137.

(17) Nordhaus, W. D. Allocation of Energy Resources. *Brookings Pap. Econ. Activity* **1973**, (3), 529–570.

(18) Hotelling, H. The Economics of Exhaustible Resources (Reprinted from Journal of Political-Economy, Vol 39, Pg 137−175, 1931). *Bull. Math. Biol.* **1991**, *53* (1−2), 281–312.

(19) Withagen, C. Untested hypotheses in non-renewable resource economics. *Environ. Resour. Econ.* **1998**, *11* (3−4), 623–634.

(20) Gordon, R. B.; Bertram, M.; Graedel, T. E. Metal stocks and sustainability. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103* (5), 1209–1214.

(21) U.S. Geological Survey: Mineral commodity summaries 2007; U.S. Geological Survey: Washington, DC, 2007.

(22) Andersson, B. A.; Azar, C.; Holmberg, J.; Karlsson, S. Material constraints for thin-film solar cells. *Energy* **1998**, *23* (5), 407–411.

(23) Zweibel, K. *The Terawatt Challenge for Thin-Film PV: A Work in Progress*, January 2006 version); NREL Internal Report, National Renewable Energy Laboratory: Washington, DC, 2006.

(24) Zweibel, K. Baseline Evaluation of Thin-Film Amorphous Silicon, Copper Indium Diselenide, and Cadmium Telluride for the 21st Century. *Electrochem. Soc. Proc.* **1999**, *99* (11), 3–15.

(25) Andersson, B. A. Materials availability for large-scale thin-film photovoltaics. *Prog. Photovoltaics* **2000**, *8* (1), 61–76.

(26) Altermatt, P. P.; Kiesewetter, T.; Ellmer, K.; Tributsch, H. Specifying targets of future research in photovoltaic devices containing pyrite (FeS2) by numerical modelling. *Sol. Energy Mater. Sol. Cells* **2002**, *71* (2), 181–195.

(27) Palik, E. D.; Ghosh, G.; Knovel (Firm). *Handbook of optical constants of solids*; Academic Press: San Diego, CA, 1998.

(28) Shockley, W.; Queisser, H. J. Detailed Balance Limit of Efficiency of P-N Junction Solar Cells. *J. Appl. Phys.* **1961**, *32* (3), 510−519.

(29) Bube, R. H. *Photovoltaic Materials*; Imperial College Press, Distributed by World Scientific: London, 1998.

(30) Hanna, M. C.; Nozik, A. J. Solar conversion efficiency of photovoltaic and photoelectrolysis cells with carrier multiplication absorbers. *J. Appl. Phys.* **2006**, *100* (7).

(31) Green, M. A. *Solar cells: operating principles, technology, and system applications*; Prentice-Hall: Englewood Cliffs, NJ, 1982.

(32) Chapman, P. F.; Roberts, F. *Metal resources and energy*; Butterworths: London, 1983.

(33) Morita, K.; Miki, T. Thermodynamics of solar-grade-silicon refining. *Intermetallics* **2003**, *11* (11−12), 1111–1117.

(34) Engh, T. A.; Simensen, C. J.; Wijk, O. *Principles of metal refining*; Oxford University Press: Oxford, U. K., 1992.

(35) Bodsworth, C. *The extraction and refining of metals*; CRC Press: Boca Raton, FL, 1994.

(36) Moore, J. J. *Chemical metallurgy*; Butterworths: London, 1981.

(37) Emsley, J. *Nature's building blocks: An A-Z guide to the elements*; Oxford University Press: Oxford, U. K., 2001.

(38) Gur, I.; Fromer, N. A.; Geier, M. L.; Alivisatos, A. P. Air-stable all-inorganic nanocrystal solar cells processed from solution. *Science* **2005**, *310* (5747), 462–465.

(39) Gledhill, S. E.; Scott, B.; Gregg, B. A. Organic and nano-structured composite photovoltaics: An overview. *J. Mater. Res.* **2005**, *20* (12), 3167–3179.

(40) Tian, B. Z.; Zheng, X. L.; Kempa, T. J.; Fang, Y.; Yu, N. F.; Yu, G. H.; Huang, J. L.; Lieber, C. M. Coaxial silicon nanowires as solar cells and nanoelectronic power sources. *Nature* **2007**, *449* (7164), 885–888.

(41) Wu, Y.; Wadia, C.; Ma, W. L.; Sadtler, B.; Alivisatos, A. P. Synthesis and photovoltaic application of copper(I) sulfide nanocrystals. *Nano Lett.* **2008**, *8* (8), 2551–2555.