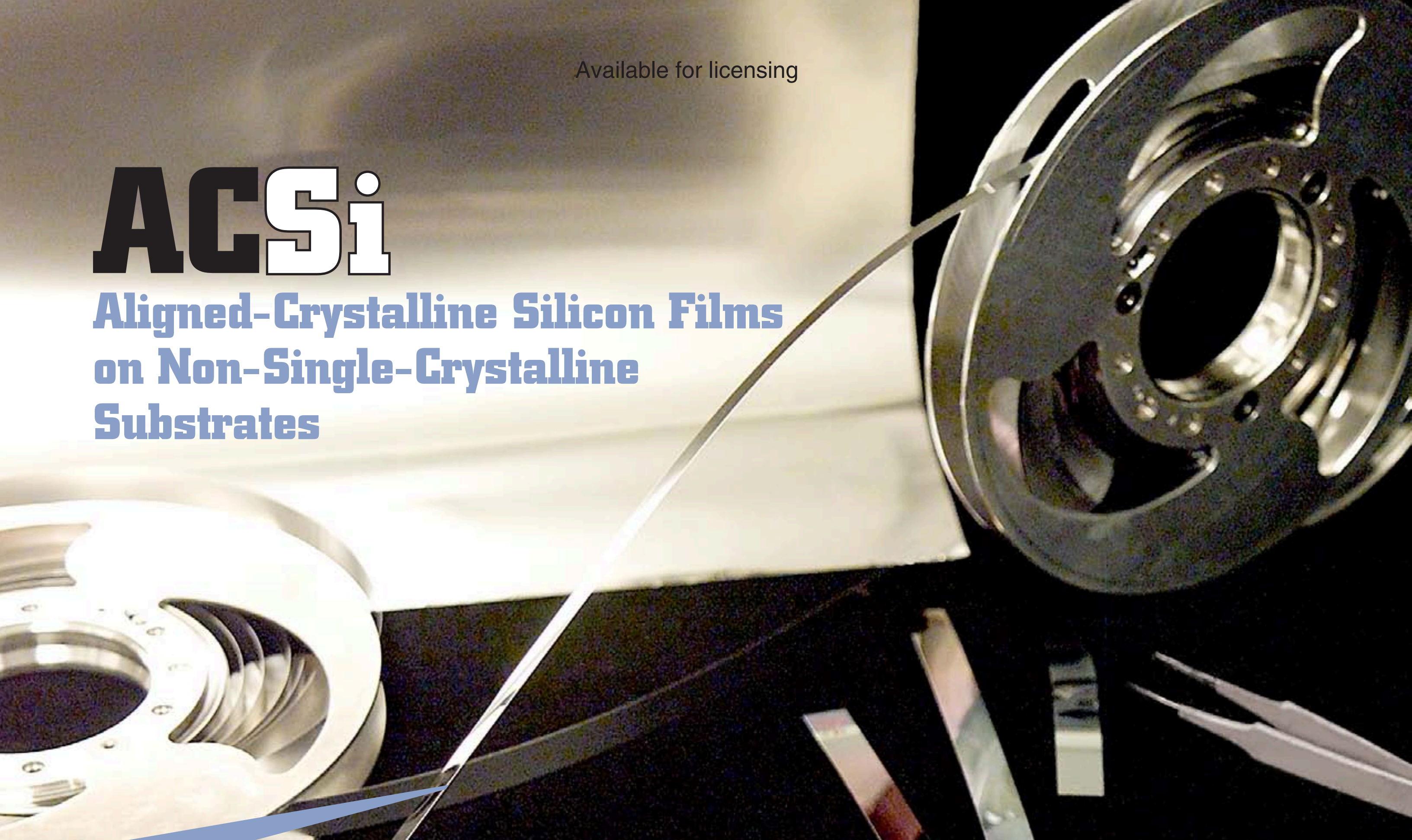
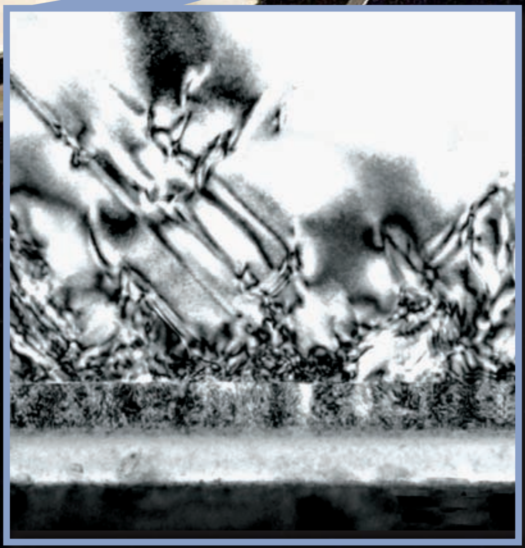
Available for licensing

ACSi

Aligned-Crystalline Silicon Films on Non-Single-Crystalline Substrates





Silicon films with near-single-crystalline quality and high carrier mobility

Continuous production on inexpensive, flexible, non-single-crystalline substrates

Fundamental impact on semiconductor industry: thin-film transistors and solar cells

Los Alamos
NATIONAL LABORATORY
EST. 1943

LA-UR-06-1165

ACSi

Aligned-Crystalline Silicon Films on Non-Single-Crystalline Substrates

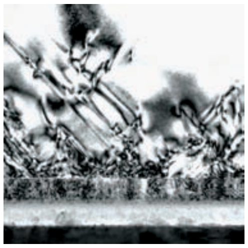
Technical Contacts: Alp Findikoglu (principal developer),
Woong Choi, and Vladimir Matias

Technology Transfer Contact:
John Russell (Team Leader), jrussell@lanl.gov

ABOUT THE COVER

The right side of the cover, below the reel of metal tape (our substrate), shows a progression of our ACSi film deposition process. At the right is a pile of raw silicon chips, the starting material of our process. Next (counterclockwise around the silicon wafer), are three strips of ACSi-coated tape. To their left are two patterned device prototypes: a solar cell and a thin-film-transistor array. Finally, below the silicon wafer, we show examples of the potential applications of such devices (TV and smart-phone display screens and solar-panels). The inset microscopic image, on left side of the cover, shows the cross section of our coated tape including the metal substrate (black), a multilayer buffer stack (grey and mottled B&W), and the near-single-crystalline silicon film (top 2/3 of the image). The reflective material behind the reels is a sheet of stainless steel—a possible future substrate for ACSi films.

Los Alamos
NATIONAL LABORATORY
EST. 1943



Executive Summary

ACSi

Aligned-Crystalline Silicon Films on Non-Single-Crystalline Substrates

Features

Our aligned-crystalline silicon (ACSi) film deposition process achieves high-performing, *near-single-crystalline* silicon films on low-cost, large-area, non-single-crystalline substrates by using ion-beam-assisted deposition (iBeam) texturing. No other technology combines the high performance of single-crystalline silicon wafers with the low cost of amorphous and polycrystalline silicon films on non-single-crystalline substrates. By providing a means to improve the performance (or reduce the cost) of silicon-based devices, such as solar cells and flat-panel displays, our ACSi technology promises to fundamentally alter the semiconductor industry.

Applications

Silicon (in either amorphous, polycrystalline, or single-crystalline form) is the most widely used material in the semiconductor industry, with multibillion-dollar applications in

- solar cells (films and wafers) and
- flat-panel displays (such as TV and computer monitors, mobile-phone and PDA displays, and electronic billboards).

Our ACSi process promises to vastly improve the quality of these products—offering high quality at a price comparable to lower-quality products currently available.

In addition, our process offers the option of manufacturing these products on a flexible substrate—leading to the development of

- durable solar cells that could be wrapped around a building or used as roofing shingles.
- curved or flexible TV monitors or computer screens, and
- electronic billboards of nearly any conceivable size.

Benefits

- Our ACSi technology improves the performance of silicon-based devices made on inexpensive amorphous or polycrystalline substrates.
- Our ACSi technology works with both nonconductive and conductive buffers—for application in the thin-film transistor or solar-cell markets.
- Our use of flexible substrates facilitates industrial-scale manufacturing (depositing films on reels of any length and width a manufacturer's deposition chamber can accommodate) and expands market possibilities to new flexible electronic products.

Technical Description

Silicon (in either amorphous, polycrystalline, or single-crystalline form) is the most widely used material in the semiconductor industry, with multibillion-dollar markets spanning electronics, solar cells, and flat-panel displays (e.g., for TVs, cell phones, and computer monitors). Our aligned-crystalline silicon (ACSi) technology achieves high-performing, *near-single-crystalline* silicon films on low-cost, large-area, non-single-crystalline substrates by using a new manufacturing process that includes ion-beam-assisted deposition (iBeam) texturing. Currently, no other technology combines the high performance of single-crystalline silicon wafers with the low cost of amorphous and polycrystalline silicon films on non-single-crystalline substrates. As such, our ACSi technology promises to make a major impact in the semiconductor industry by providing a new means to improve the performance (or reduce material and fabrication costs) of silicon-based devices, such as solar cells and flat-panel displays.

The iBeam texturing technique begins with any common amorphous substrate such as glass or even a flexible polycrystalline metal-alloy tape. On the substrate, we deposit a special buffer-layer stack that is either nonconductive or conductive, depending on the end-product's application (i.e., a flat-panel display or a solar cell). This buffer-layer stack, which includes several distinct layers of material with a total thickness of ~0.2 µm, serves two important purposes. First, it acts as a diffusion barrier. Second, it provides a highly oriented template surface for the growth of near-single-crystalline silicon films. Within the buffer-layer stack, the transition from a polyscrystalline or amorphous substrate to a highly oriented layer is achieved through the use of iBeam texturing. For the rest of our discussion, all layers of the multilayer architecture we use are electron-beam evaporated (or sputtered) in situ on a flexible, polycrystalline nickel-alloy tape, a corrosion-resistant Hastelloy C-276. This commercially obtained 1-cm-wide and 100-µm-thick tape is cleaned with solvents and polished, if necessary, to achieve a root mean square surface roughness of <10 nm, for a $5 \times 5\ \mu m^2$ area.

A nonconductive buffer-layer stack, formed by insulating oxides, is produced in a four-step process.

(1) A 5-nm-thick Y_2O_3 (yttrium oxide) nucleation-layer base is applied.

(2) A 10-nm-thick MgO (magnesium oxide) film is deposited via iBeam texturing while directing a 750 eV Ar^+ assist beam at the substrate at ambient temperature and with a 45° angle between

the ion beam and the substrate—forming a *biaxially oriented crystalline layer*.

Once established, this iBeam-textured layer serves as an epitaxial template for the growth of the subsequent layers that have a high degree of crystallographic orientation.

(3) An approximately 10- to 100-nm-thick layer of MgO is homoepitaxially grown at 500 °C.

(4) Finally, a 50- to 200-nm-thick layer of the cubic form of Al_2O_3 (gamma aluminum oxide, γ-Al_2O_3) is heteroepitaxially grown on the MgO layer at 550–750 °C.

A conductive buffer-layer stack, which is formed by conducting nitrides, is produced by a two-step application of TiN (titanium nitride). In this case, the iBeam-textured TiN layer is directly deposited on the metal tape after it has been reactively ion-etched and cleaned for about 30 seconds using a 750 eV ion mixture of Ar^+ and N^+.

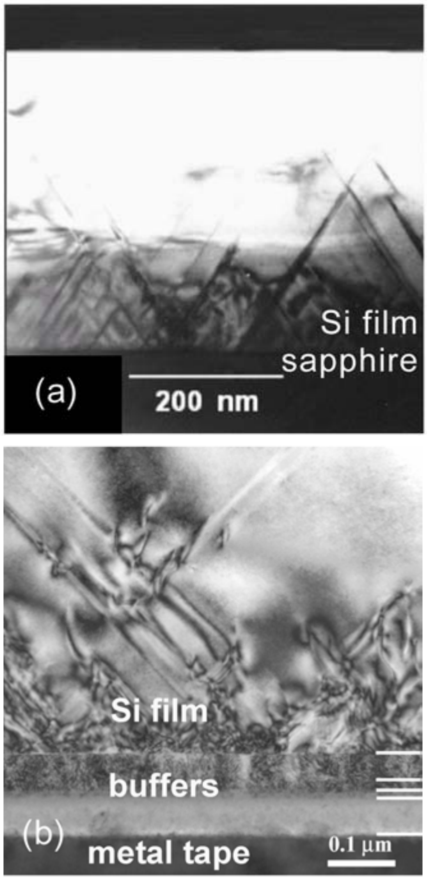
(1) A 10-nm-thick iBeam-textured TiN layer is deposited on the metal tape to achieve biaxial texture.

During iBeam-textured TiN deposition, 750 eV Ar^+ and N^+ beams, with an Ar to N_2 ratio of about 4, are directed at the substrate at an angle of 45° to the substrate.

(2) A 200- to 400-nm-thick TiN film is then homoepitaxially deposited at 550–700 °C using reactive sputtering to complete the conducting buffer-layer stack.

The carefully grown top surface of each buffer stack approaches single-crystalline order and provides the ordered and robust surface necessary to grow biaxially oriented grains (i.e., with preferred out-of-plane and in-plane crystallographic orientations) of near-single-crystalline silicon. The TEM images show that the microstructure of our ACSi film (b) on metal tape, where the non-conductive buffer layer termination is γ-Al_2O_3, is very similar to that of standard silicon film (a) on single-crystal Al_2O_3 (sapphire). These conductive and nonconductive buffer stacks are the heart of our innovation—allowing us to grow well-oriented, high-quality silicon films. The thickness of silicon films that we have deposited in situ on these buffer stacks ranges from 0.1 to 4 µm. We have created various dopant profiles (in situ during film growth, or ex situ by ion implantation) depending on the device application.

The silicon grows with $\langle 001 \rangle$ orientation perpendicular to the substrate and has an in-plane lattice constant of 0.54 nm. The crystallinity of the silicon films is determined by x-ray diffraction. In-plane and out-of-plane mosaic spreads of optimized silicon films are 0.8° and 1.3°, respectively, indicating near-single-crystalline

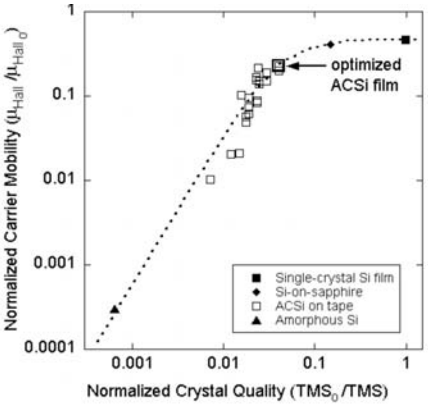


Tranmission electron microscopy (TEM) image of (a) a silicon film on single-crystal sapphire vs (b) our iBeam-buffered ACSi film on metal tape, showing the similar crystalline quality and structure of the silicon in the two films.

quality. To our knowledge, no other technology exists to achieve such high-quality silicon films on foreign, non-single-crystalline substrates.

Electronic devices based on such silicon films demonstrate improved electrical performance due to improved alignment and connectivity of the grains in the films. This near-single-crystalline quality leads to superior electrical characteristics, as indicated by a room-temperature Hall mobility of about 90 cm^2/V•s at a hole doping concentration of 4.4×10^{16} cm^{-3} for our 0.4-μm-thick ACSi films. These mobility values are within a factor of 2 of the best values reported for single-crystalline silicon films with similar doping concentrations on single-crystal substrates (~180 cm^2/V•s), and *almost 1000 times better* than what is achievable with amorphous silicon films (~0.1 cm^2/V•s). These results provide proof-of-concept for our new manufacturing process that does not require lattice-matched single-crystal substrates for deposition of well-oriented and high-performing silicon thin films.

Our studies have also revealed a strong dependence of normalized carrier mobility (Hall mobility normalized with respect to bulk single-crystal values and doping concentration) on normalized crystalline quality (defined as the inverse of total grain mosaic spread, normalized with respect to bulk single-crystal silicon) for our ⟨001⟩-oriented, 200- to 400-nm-thick silicon films grown on polycrystalline metal substrates (see graph at left). The carrier mobility, an indicator of electrical performance for applications such as thin-film transistors (TFTs) used in flat-panel displays, increases strongly with crystal quality, asymptotically approaching single-crystal values for our optimized ACSi films. A microscopic electronic model combining intragrain and grain-boundary scattering yields a decrease of the energy barrier height from 0.1 eV to $<10^{-3}$ eV and an accompanying decrease of trap density from 6×10^{11} cm^{-2} to $<3 \times 10^{10}$ cm^{-2} with increasing crystallinity. These results demonstrate that improving the intergrain alignment of sub-micron-sized grains in our ACSi films is an effective alternative to increasing grain size (for example, by laser annealing) in order to approach single-crystal-like performance.



Carrier mobility vs crystal quality, showing near-single-crystal values for our optimized ACSi films.

Also, we have been able to grow near-single-crystalline films of silicon on fused silica substrates using similar multilayer architectures, showing the flexibility of our iBeam process in terms of substrate choice. Furthermore, we have grown silicon films with thicknesses of up to 4 μm on standard metal-alloy substrates. These thick samples showed no discernible degradation in crystalline quality or electrical performance. Such thick films could be necessary for certain photovoltaics applications.

Competition

1. TFT applications—silicon films <1 μm thick:
    - (a) Amorphous-silicon films on glass—TFT-LCDs (liquid-crystal displays) made by Sharp and Samsung.
    - (b) Laser-crystallized silicon films on glass—low-temperature polysilicon (LTPS) TFT-LCDs made by Sharp and LG Philips.
    - (c) Organic semiconductor films on plastics (no large-scale production yet).
    - (d) Polycrystalline silicon films on metal foil (no large-scale production yet).

Silicon-based TFT manufacturing technologies in this list are widely used for flat-panel displays (>80% of world market). Other flat-panel displays, such as PM (passive matrix)-LCD and plasma display panels, have been excluded from this list because they do not use TFTs.

2. Solar cell applications—silicon films (>1 μm thick) or bulk silicon wafers:
    - (a) Single- and multicrystalline silicon wafers made by BP Solar, Kyocera, Sanyo, Sharp, and Shell Solar.
    - (b) Ribbon silicon wafers made by ASE Americas and Evergreen Solar.
    - (c) Amorphous silicon films made by Unisolar.
    - (d) Multicrystalline silicon films made by AstroPower (GE Energy) and CSG.

Silicon is the most widely used material for solar-cell applications (>90% of world market). Other materials have been excluded from this list because of their small market share.

Our iBeam texturing process produces an electronic component used to manufacture subsequent consumer products. Because manufacturers guard these component costs, we cannot provide absolute figures for comparison. In place of these figures, we establish a benchmark based on the dominant technology in the market and provide a relative cost comparison for all other technologies. For TFT applications, the dominant technology is amorphous silicon films on glass. Market drivers are a complex interplay between cost, performance, display resolution, and driving-electronics integration—each simultaneously affecting all other factors. For solar-cell applications, the dominant technology is single- and multicrystalline silicon wafers. The market driver for solar cell manufacturers is cell cost per unit of generated power.

Comparison matrix

TFT Applications

Fabrication Type	Cost[a] (per m^2)	TFT Performance[b] (mobility $cm^2/V \cdot s$)	Display Resolution	Integration of Driving Electronics[c]	Comments
Amorphous Silicon (a-Si) Films on Glass	Benchmark cost	~0.1	Modest	No	Dominant technology for large displays; uses glass substrates.
Laser-Crystallized Silicon Films on Glass	Large increase in cost[d]	10–100	High	Yes	High-performance, compact displays; uses glass substrates; nonuniform mobility.
Organic Semiconductor Films on Plastics	Decrease in cost	<1	Modest	Not available	Development stage for flexible displays; uses light and flexible plastic substrates.
Polycrystalline Silicon Films on Metal Foil	Product not yet available	10–100	High	Yes	R&D stage for flexible displays; uses flexible and inexpensive metal foil substrates; nonuniform mobility.
ACSi Films	Modest increase in cost (estimate ~$50)	>100	Highest	Yes	Combines the highest uniform performance and resolution with modest cost; can use inexpensive, flexible substrates.

[a] Estimated relative cost includes only materials cost (substrates and raw materials) and fabrication cost (thin-film deposition).

[b] TFT performance is compared based on average electron mobility, which is a measure of semiconductor performance.

[c] Integration of driving electronics with TFT panel improves display performance and reduces overall cost.

[d] Requires laser annealing on a-Si as separate fabrication process, which increases cost.

Solar Cell Applications

Fabrication Type	Solar Cell Cost[a]	Efficiency[b]	Comments
Single- and Multicrystalline Silicon Wafers	Benchmark cost	16%–23%	Dominant technology for solar cells.
Ribbon Silicon Wafers	Modest reduction (at least 20%)	15%–18%	Cost reduction due to use of ~200-µm-thick silicon wafers and continuous production.
Amorphous Silicon Films	Large reduction (at least 40%)	6%–15%	Cost reduction due to use of 1- to 3-µm-thick amorphous silicon films on inexpensive sheets.
Multicrystalline Silicon Films	Large reduction (at least 40%)	9%–15%	Cost reduction due to use of 1- to 30-µm-thick silicon films on inexpensive sheets.
ACSi Films	Large reduction (at least 40%)	>15%	Combines the cost and customizability advantages of silicon films with the high efficiency of silicon wafers.

[a] The parenthetical numbers are the estimated cost reduction with respect to the benchmark technology.

[b] This efficiency translates to generated power per unit area.

Principal applications and advantages

Our ACSi technology holds immediate promise for two specific applications: active-matrix LCDs and thin-film-based solar cells.

The most commonly used flat-panel displays in the market today are active-matrix LCDs, which use amorphous-silicon TFTs on glass substrates as active elements. However, amorphous silicon has very low carrier mobility, which causes limited circuit speed and necessitates the use of a large pixel size. These limitations, in turn, lead to low-resolution displays with low refresh rates. Also, glass, an inflexible material, cannot deliver the many potential benefits that flexible substrates offer such as rollable or nonflat displays. Our ACSi technology has commercial potential in flexible display applications because the carrier mobility in our silicon films is nearly 1000 times better than that in amorphous silicon films. The improved, uniform mobility of ACSi films on flexible substrates should allow the manufacture of displays with vastly improved resolution, refresh rates, and system reliability, combined with reduced manufacturing costs due to industrial-scale manufacturing. Our ACSi films can be deposited on reels of flexible substrate of any length and width that a manufacturer's deposition chamber can accommodate. This advancement in technology could have an industrywide impact in many current and future TFT applications such as flexible displays, TV and computer monitors, mobile-phone and PDA displays, iPods, portable DVD players, and electronic billboards.

The second application for our ACSi technology is in the photovoltaics market, which currently is dominated by (a) high-performing solar cells that use expensive single-crystal or multicrystalline bulk silicon wafers and (b) low-performing, inexpensive solar cells that use amorphous or polycrystalline silicon films on non-single-crystalline substrates. The ACSi technology combines the advantages (essentially the high performance of crystalline silicon wafers, and the low cost and versatility of films on non-single-crystalline substrates) of these two dominant technologies on a single platform. The high measured carrier mobility, and expected high carrier lifetimes (compared to amorphous silicon) makes the ACSi films promising for use in new solar-cell architectures on inexpensive substrates that can be flexible and sized according to customer need.

Our ACSi process can be used to manufacture flat-panel displays with active-matrix TFTs that are used in products of all kinds including flat-panel televisions, computer screens, cellular telephones, PDAs, iPods, portable DVD players, and electronic billboards. Our ACSi technology also provides manufacturers of silicon-based solar cells a process with which they can build a product that is better than single-crystalline silicon wafers in terms of cost, platform flexibility, and customizability and better than conventional silicon films in terms of electrical performance.

Other applications

Our ACSi process can also be used to manufacture silicon-based transistors for electronics applications such as radio-frequency silicon-on-insulator circuitry for cell phones and integrated circuits for fast processing.

Although we have so far demonstrated the applicability of our manufacturing technology for silicon, the most widely used material in the semiconductor industry, our approach could be extended to other materials. ACSi could integrate inexpensive amorphous and polycrystalline substrates with various oxide, nitride, and semiconductor films that would benefit from having a biaxially textured crystalline structure leading to improvements in electrical, chemical, or mechanical properties.

Summary

Silicon is the most widely used material in the semiconductor industry, with multibillion-dollar markets in electronics, flat-panel displays, and solar cells. Because the electrical performance of silicon is directly related to its crystal quality, amorphous silicon performs the poorest while single-crystal silicon performs the best. However, the high performance of crystalline silicon comes at a price—high cost—while low-performing amorphous silicon film offers important consumer benefits—low cost and customizability. For these reasons, crystalline silicon wafers and amorphous silicon films both find large markets today. Crystalline silicon wafers dominate the solar-cell industry (more than 90% of a $7 billion market in 2004) because they offer the best performance (solar cell efficiency), whereas the display industry tolerates the low performance of amorphous silicon (more than 80% of a ~$60 billion market in 2004) because amorphous silicon films offer low cost, large display area, and customizability, which are important for that industry. Our ACSi technology promises to offer a novel solution to this dilemma of choosing between high performance *and* low cost.

Our ACSi manufacturing technology promises to combine high performance and customizability *with* low cost. It will allow manufacturers to produce near-single-crystalline quality silicon films in a range of thicknesses on virtually any inexpensive substrate that suits customer needs—rigid or flexible, conductive or nonconductive, curved or flat, and with panel dimensions limited only by the manufacturers' deposition system. If we compare our film's electrical performance to that of amorphous silicon films that are normally grown on these cheaper substrates, we find that the carrier mobility of our films is *almost 1000 times better* than what is currently achievable with the amorphous film technology. These mobility values are within a factor of 2 of the *best* values reported for single-crystalline silicon films on single-crystal substrates. These high mobilities in our ACSi films will directly translate into high-performing TFTs for display applications. In the solar-panel application, the ACSi technology will make it feasible for the solar-panel industry to offer, at last, high-performance panels that any consumer can afford.

The flexibility of the metal tape we use, combined with low-cost manufacturing and top-notch performance, will make affordable, high-quality electronics products, such as flat-panel displays and solar cells, a reality. Our ACSi technology will allow manufacturers to supply the marketplace with cost-effective, high-quality silicon film products.