

Microfabricated Gas Sensors Detect Hydrogen over Wide Range of Concentrations

Leak detection and monitoring of flammable or explosive concentrations of gas for safe use, storage, and handling are among the potential industrial applications for the high-temperature hydrogen gas sensors developed by NASA Glenn Research Center in conjunction with the Electronics Design Center at Case Western Reserve University. The sensors are microfabricated and micromachined using microelectromechanical-systems-based technology to minimize size, weight, and power consumption. The sensor technology development also depends on the use of nanomaterials and silicon carbide (SiC) as an electronic semiconductor. Microfabricated sensors are small and lightweight, and consume minimal power. Compared with conventional sensors, these devices often have superior high-temperature performance, chemical resistance, and mechanical toughness.

Silicon-based microelectronic sensors that utilize a Schottky diode have been developed. This type of diode exhibits the "Schottky effect," which results in rectifying behavior in the current of electrons leaving a metal surface when an external electric field is applied. Each sensor has a temperature detector and a heater on the same chip. The architecture of the Schottky diode makes the sensors highly sensitive to specific adsorbed gases. A picture and schematic drawing of the combined hydrogen-sensitive Schottky diode is shown in Figure 1. The detector and heater allow optimization of sensor response and recovery time. These microfabricated hydrogen sensors are highly sensitive to low concentrations of hydrogen gas. The concentration range of the combined two sensor systems—Schottky diode and resistor—is 10 ppm to 100% in nitrogen. A number of them can be placed in an area to monitor hydrogen leaks in safety applications. With hardware and software to monitor the sensors, the location and magnitude of a leak can be determined.

In space transportation applications, hydrogen propellant leaks pose significant operational problems. In 1990, hydrogen leaks on the Space Shuttle while on the launch pad temporarily grounded the fleet until the source of the leak could be identified. As recently as July 1999, the launch of a Space Shuttle mission was delayed for two days due to an ambiguous signal using the present leak-detection system. Thus, the detection of explosive concentrations of fuel continues to be of interest wherever fuel is used.

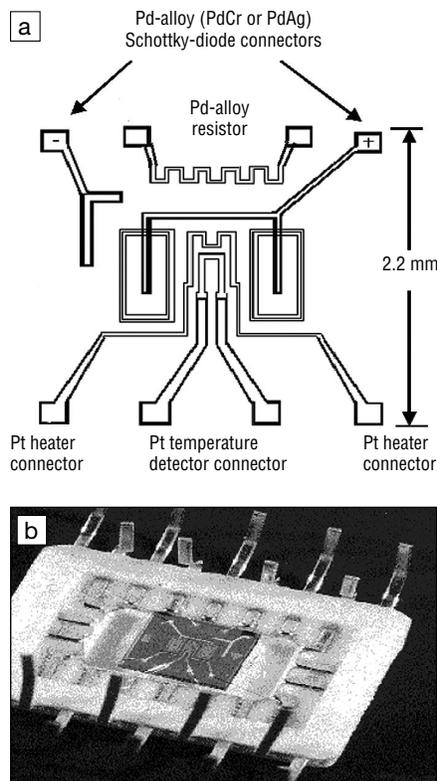


Figure 1. (a) Schematic diagram of the silicon-based hydrogen sensor. The Pd alloy Schottky diode (rectangular regions) resides symmetrically on either side of a heater and temperature detector. The Pd alloy resistor is included for high concentration measurements. (b) Picture of the packaged sensor.

In response to this problem, efforts were made at NASA Glenn to develop microfabricated point-contact hydrogen sensors for locating leaks. One component of this leak-detection program is the fabrication of Pd-alloy hydrogen sensors on Si substrates. Two different hydrogen detection approaches are used depending on the

Technology Advances provides up-to-date reports of materials developments that show potential to bridge the gap between research innovation and application of advanced materials technologies. If you encounter or are involved with materials research that shows potential for commercialization and would like to present these developments, contact Renée G. Ford, Renford Communications, Ltd., P.O. Box 72, Harrison, NY 10528-0072; tel. 914-967-0955; fax 914-967-7927; or e-mail renford@compuserve.com.

hydrogen concentration range. The detection of low concentrations of hydrogen involves the use of palladium (Pd) alloy Schottky diodes on a silicon substrate. This type of sensor is based on metal-oxide-semiconductor (MOS) technology such as that used in the semiconductor electronics industry. The gas-sensing MOS structures are composed of a hydrogen-sensitive metal deposited on an oxide adherent to a semiconductor. When the oxide is a very thin layer ($\sim 50 \text{ \AA}$), the MOS structure forms a Schottky diode. The advantage of a Schottky diode in gas-sensing applications is its high sensitivity. Furthermore, this type of sensor does not need oxygen for operation. If required, the detection of higher concentrations of hydrogen (up to 100%) is accomplished using a resistor whose resistance is dependent on the hydrogen concentration.

The complete hydrogen sensor system using palladium silver (PdAg) or palladium chrome (PdCr) Schottky diodes and PdCr resistors (depending on the application) have been packaged and combined with electronics for use in a number of applications. The sensors are integrated with on-chip temperature detectors and heaters for operation in a wide variety of environments. The sensor microfabrication allows the sensor packages to have minimal size, weight, and power consumption and thus to be placed in a number of locations. Hardware and software ("smart" electronics) have also been interfaced with the sensor to provide signal conditioning and control. The overall approach is to determine the magnitude and position of a leak in a region by correlating the signal from a number of these small sensor packages. The long-term objective of the leak-detection project is to produce a postage-stamp-sized fuel/oxygen sensor array that includes the power and communications support structure to make it a stand-alone system.

While the hydrogen sensor has been primarily developed for leak-detection applications, work is currently underway in applying the hydrogen sensor technology to process monitoring applications including fuel cells and electrical transformer monitoring.

Opportunities

The hydrogen sensor technology is being commercialized. NASA Glenn seeks industrial partners to cooperatively develop new applications for this technology.

Source: For the technology: Gary W. Hunter, NASA John H. Glenn Research Center at Lewis Field, Mail Stop 77-1, Cleveland, OH 44135-3191, USA; tel. 216-433-6459; fax 216-433-8643; and e-mail Gary.W.Hunter@grc.nasa.gov.

Lead-Free Active Solder Economically Joins Most Inorganic Materials

Active solders that are capable of joining most inorganic materials including light metals, refractory metals, ceramics, and composites as well as aluminum, copper, and steels, are being developed by Materials Resources International (MRi). These lead-free active solder alloys, which contain additions of active elements such as Ti and rare-earth metals, join materials in air at low temperature (<450°C), have fluxless application, do not require pre-metallization, and keep solder where needed due to their limited solder flow. The S-Bond® alloys made by MRi, due to their reactive element additions, interact with surfaces to lower surface tension differences thus lowering capillary spreading forces. In addition, the alloy's apparent viscosity decreases its tendency to flow.

Active solders contain reactive elements that enable the molten solder to directly wet and bond to oxides and other ceramic-like substrates or layers that typically exist on many corrosion-resistant metals, such as aluminum, titanium, and/or stainless steels. These solders do not flow; therefore techniques for use in joints are part of the processing methods. These techniques overcome the alloys' low capillary flow and prevent the molten solder from infiltrating interconnected porosity in foams that typically could absorb high capillary brazes and solders. Two alloys have been developed: One is

Alloy 220, which is Sn-Ag-Ti-based, and the other is Alloy 400, which is Zn-Ag-Al-based. Both have rare-earth elemental additions that enable wetting and surface reactions to occur at normal soldering temperatures (>450°C). Once the *active* solders are molten, the active elements migrate to the joint interface and react with the joint surfaces. The rare-earth elements (lanthanides) are believed to lower the energy of reaction with oxides, nitrides, and other surface compounds during heating in air, allowing the active element in the solders to interact with the metal surfaces of the joints, causing alloying or atomic-level bonds.

Active solders are thermally and electrically conductive alloys that can join most inorganic materials in an economic, one-step joining process. Applications include the joining of many conventional and emerging thermal management devices such as diamond heat spreaders, graphite foam-core heat exchangers, aluminum-matrix composites, electronic packages, thermo-syphons, and heat pipes fabricated from the most advanced materials. S-Bond® has been used to investigate the technology for economically fabricating both lightweight structures and graphite-foam thermal-management devices. Figure 1 illustrates the types of joints that the Sn-based active solders have achieved in joining aluminum metal matrix composites for electronic package structures. The active solder (represented as the lighter area in the center) has dissolved a bit of the aluminum matrix and wetted the

ceramic (SiC) particles, creating a metallurgically sound joint. The joining of graphite foams is another emerging technology. Figure 2 shows a joint where graphite foam has been joined to an aluminum base. The micrograph illustrates the interaction of the active solder with the aluminum base while it adhered to and encapsulated the graphite webs on the foam. These graphite foams have been recently incorporated into heat exchanger cores that have 3–4 times the performance of brazed aluminum fin-tube heat exchangers. In recent work, MRi with its partners (POCO and Oak Ridge National Laboratories) has shown that S-Bond®-joined graphite foam has liquid cooling heat transfer coefficients of over 20,000 W/m² K. This is more than 10 times the best technology previously available.

Opportunities

MRi is pursuing partners to develop applications in which active solders offer a joining solution in the areas of diamond heat spreaders, graphite foam core heat exchangers, thermal bases for power electronics, cold plates for use in telecommunications and high-power servers, and a range of computer chips and interconnects for electronic packages.

Source: Ronald Smith, Materials Resources International, 811 W. Fifth Street/Unit 2, Lansdale, PA 19446, USA; tel. 215-631-7111; fax 215-651-7115; e-mail solution@voicenet.com; and URL <http://www.materialsresources.com>.

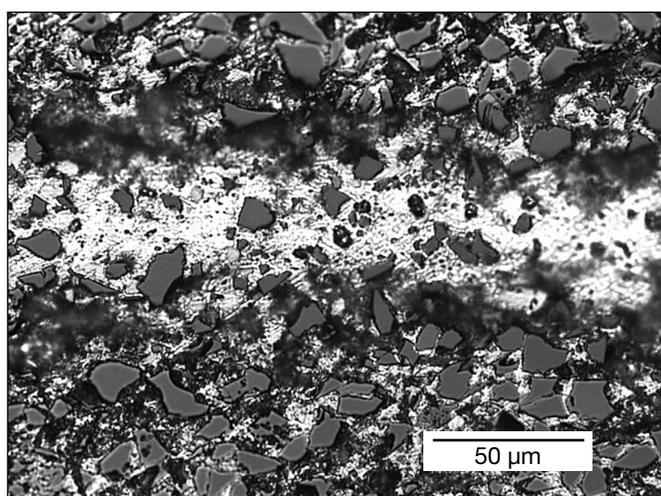


Figure 1. Micrograph of a metal matrix composite joint, Al/SiC, joined to Al/SiC, using a Sn-Ag-Ti + rare-earth active solder (S-Bond® Alloy 220).

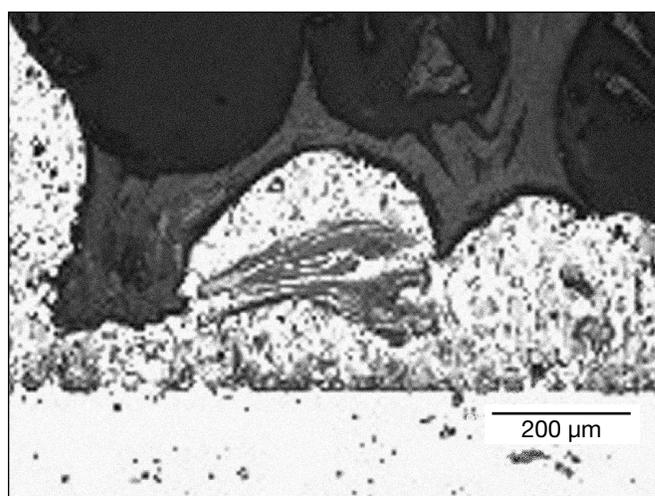


Figure 2. Microstructure of a graphite foam/aluminum base plate joint made with a Sn-Ag-Ti + rare earth-active solder (S-Bond® Alloy 220). The larger dark phase is a piece of the graphite web and the more distributed gray phase is SnTi intermetallics; the light phase is a Sn-Ag matrix of the S-Bond® alloy.

Superlattice Process Controls Size of Si Nanocrystals on Si Wafers

A process that allows the preparation of size-controlled silicon (Si) nanocrystals on 4-in. Si wafers with a nanocrystal density of up to $10^{19}/\text{cm}^3$ and a crystal diameter down to 1.8 nm has been developed at the Max Planck Institute of Microstructure Physics (MPI), Halle, Germany. This process produces well-passivated Si nanocrystals with a desired size arranged in layers and separated by high-quality silicon dioxide (SiO_2). The preparation is based on the growth of SiO/SiO_2 superlattices and is compatible with Si technologies. It enables, independent from each other, control of particle size, particle density, and position. In addition, the high density of crystals and the independent control exists and is preserved even for the smallest sizes. This cannot be achieved with porous Si, Si-ion implantation into high-quality oxides, or by using Si-rich silica (SiO_x) films. After high-temperature annealing, the superlattice films are composed of a desired number of crystallized layers that are dense and without pores or other porous structures. The nanocrystals exhibit strong room-temperature photoluminescence in the red and near-infrared spectral region without degradation. The wavelength of the photoluminescence can be tuned from 860 nm to 750 nm by adjusting the size of the nanocrystal.

In this process (shown schematically in Figure 1), amorphous SiO/SiO_2 superlattices are grown using a simple reactive evaporation process with silicon monoxide (SiO) powder in either a vacuum or an oxygen atmosphere. Annealing the films at high temperatures ($\sim 1100^\circ\text{C}$) results in phase separation of the ultrathin SiO layers into nanometer-sized Si clusters surrounded by amorphous SiO_2 . Figure 2 shows a cross-sectional transmission electron

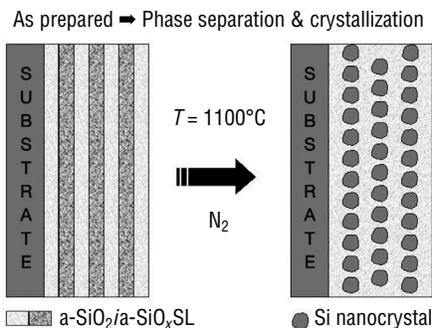


Figure 1. Fabrication of amorphous SiO/SiO_2 superlattice and thermally induced phase separation and crystallization.

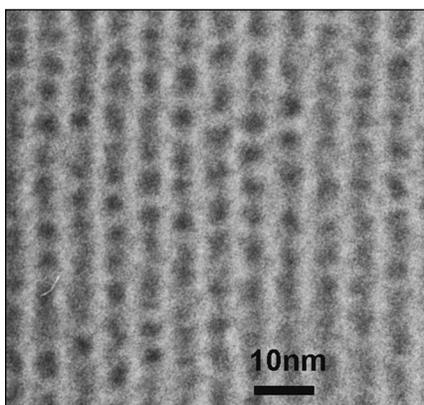


Figure 2. Cross-sectional transmission electron microscope image of layer-arranged Si crystals (~ 3 nm) closely separated by oxide.

micrograph of a sample after crystallization. Size control is realized by specifying the thickness (1–7 nm) of the active SiO layers, which also limits the maximum size of the nanocrystals and strongly restricts

the size distribution. The density of the nanocrystals can be adjusted by the thickness of the buffer SiO_2 layer. For example, in Figure 2 a thickness of ~ 3 nm was used. The position of the nanocrystal is controlled by that of the SiO layers in the growth direction and by selecting a specific area on the wafer by lithography.

This process enables the economic production of high-density arrays of randomly oriented silicon nanoclusters or nanocrystals with a narrow size distribution. It is expected that the same approach of using a superlattice structure and ultrathin Si suboxides as the active layer can be reproduced by different techniques such as reactive sputtering, chemical vapor deposition, or molecular-beam-epitaxy growth, and will result in a similarly simple control for ordered arranged Si nanocrystals. Within the layer, the density of the nanocrystals and the thickness of the surrounding oxide buffer can be controlled by the stoichiometry of the active SiO_x layer. The highest density of Si nanocrystals with this method can be achieved for $x = 1$.

Potential applications for this technique include light-emitting structures based on silicon. In addition, erbium (Er) doping of the structure shows a strong enhancement of the 1.54- μm Er luminescence. This enhancement is a result of the coupled emission process of the Si nanocrystals and Er^{3+} ions in the vicinity of the nanocrystal, which might be of interest for small-sized and low-cost Er amplifiers.

Opportunities

The Max Planck Institute is interested in establishing industrial collaborations for further development of this process.

Source: M. Zacharias, J. Heitmann, and U. Gösele, Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany; tel. 49-345-558-2729; fax 49-345-551-1223; e-mail zacharias@mpi-halle.de; and URL <http://www.mpi-halle.mpg.de/~nanopart>.

