Sensing Requirements for Real-Time Monitoring and Control in Energy Production

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Abstract— Clean, efficient energy production, such as the gasification of coal (syngas), requires physical and chemical sensors for exhaust gas monitoring as well as real-time control of the combustion process. Following a description of syngas production from coal, we outline the sensing needs for this high temperature, chemically corrosive gas stream. The performance of devices based on the wide-bandgap semiconductor SiC, for monitoring gas composition, flame dynamics and temperature, as well as combustor structural integrity in this extreme environment are reviewed. We have developed a Pt-SiO_2-SiC micro-device with a dense Pt catalytic sensing film, for fast (<1s) detection of hydrogen containing species at 630 °C. Our SiC sensor can monitor the hydrogen concentration in a 350 °C simulated syngas ambient containing the common interferants CO_2, CH_4 and CO. Exposure to H_2S (~1000 ppm) and water vapor does not degrade the sensor performance.

I. INTRODUCTION

The world wide concern over the adverse effects from global warming, coupled with the rise of energy costs in developed countries has reinvigorated the need to identify clean and cost-effective sources of energy production. As the United States has large national reserves of coal, an attractive option in this country is to generate electricity from the gasification of coal. Minimizing total sulfur dioxide emissions is a concern, as a number of US sources of coal contain high levels of sulfur. Physical and chemical sensor systems to monitor and control the gasification process in real time are needed for highly efficient yet minimally polluting power production [1]. The gasification process is an extremely harsh environment; devices must operate in a chemically corrosive gas stream at temperatures up to 800 °C. In this paper we review the insertion opportunities for solid state sensors based on the wide-bandgap semiconductor SiC.

The integrated gasification combined cycle (IGCC) power plant is a minimally polluting, energy efficient and cost effective technique to generate electricity. The Wabash River Coal Gasification Repowering Project has demonstrated that a commercial utility can provide 262 MW of electricity, in a clean and efficient manner using locally mined high-sulfur Indiana bituminous coal [2]. The first step in producing electricity from coal is gasification, the generation of synthetic gas (syngas). In the Wabash project a 1950's steam turbine was retrofitted with a new syngas-fired combustion turbine. The total sulfur dioxide (SO_2) emissions from the entire plant was <0.1 lbs SO_2 emitted per MMBtu of coal input, well below the acid rain limits set by the Clean Air Act for year 2000 of 1.2 lbs/MMBtu. Note that syngas has multiple commercial uses in addition to consumption for energy generation; as syngas can also be processed to produce hydrogen, chemicals and fuels [3].

II. SENSING NEEDS FOR COAL GASIFICATION

Sensors for monitoring coal gasification must operate in a harsh environment in terms of temperature, as well as the presence of particulates, reducing gases, sulfur compounds and high temperature steam. In order to ascertain sensor insertion opportunities, we briefly summarize the gasification process, see ref [4] for a review of commercial IGCC plant performance. (i) In the typical gasification process, dry coal is gasified with steam and 95% (by volume) oxygen at ~1430 °C and 1,000 psia. (ii) The syngas is then cooled to ~550 °C to remove entrained solids and char, which is recycled back to the gasifier. A wet scrubber (~190 °C) removes the remaining solids, alkali salts, hydrogen halides and a portion of the ammonia. (iii) In order to reach the desired low SO_2 emission levels, H_2S and COS which exist at significant levels must be removed. COS is difficult to remove from the gas stream as is, so it is converted to H_2S via hydrolysis. The net H_2S content is then removed by an acid gas process at 40 °C. (iv) An activated carbon bed is used to remove Hg, as well as any volatile heavy metals such as As. (v) Finally any acid gas is removed from the syngas stream resulting in "sweet" or clean syngas. This clean fuel gas is humidified, depressurized through an expander to ~380 psia and heated

TABLE I.
Fuel composition for "clean" syngas from an IGCC Gasifier [2,4]

Species	Typical Concentration
H_2	24-39 %
O_2	0 – 0.2 %
CO	31 – 50 %
CO_2	5 – 9 %
CH_4	800 – 1000 ppm
H_2S	50 – 200 ppm
H_2O	5 – 15 %

to 280 °C and fed to the input of a gas turbine generator. A combination of gas turbines, steam turbines and fuel cells (hybrid design) powered by the clean syngas are used to generate electricity. Conceptual IGCC plant designs, which are based on equipment that is expected to be commercially available by 2010, forecast 600 MWe of electricity at 39 – 42% efficiency [4].

It is critical to monitor the quality of the clean syngas prior to the power generation units of the IGCC plant for optimal performance of the turbines as well as protection of sensitive downstream components. In Table I we list the typical fuel composition for an IGCC gasifier after acid cleanup. We are developing a solid-state gas sensor to monitor the net hydrogen concentration of the clean sygas fuel stream flowing at 1000 sccm at 350 °C [5]. The sensor must survive in a gas stream containing large amounts of CO, sulfur compounds at the 1000 ppm level (which are known to be lethal for metal catalysts) as well as up to 15 % water vapor. In addition the sensor response time should be fast enough to enable real-time control of the gasification and gas cleanup processes, and to respond to process upsets, which is in the range of seconds to under 1 minute [6].

III. SILICON CARBIDE SENSORS

The wide bandgap semiconductor SiC is well suited for sensing and electronic applications in high temperature chemically reactive environments. Table II lists the relevant electronic, mechanical and structural properties of the two commercially available polytypes, 6H-SiC and 4H-SiC. SiC electronic devices can operate at temperatures in excess of 900 °C due to the ~3 eV bandgap, as compared to 1.1 eV for Si. In order to modulate the carrier concentration in the semiconductor via an applied gate potential, a robust dielectric is need for metal/oxide/semiconductor (MOS) structures. SiC has a native oxide, SiO_2, which fulfills this need. For sensing applications, a number of groups have developed SiC based MOS and diode structures with a catalytically active metal gate (sensing film) to electronically detect various chemical species, see reviews in ref. [8, 9]. The high thermal conductivity of SiC ensures that the device will be in thermal equilibrium with its surroundings. The hardness and chemical inertness of SiC enables high pressure and chemically corrosive sensor applications. An additional advantage of the SiC materials system is the parallel development of high temperature bipolar and field-effect electronics. Down the road we envision the development of complete SiC based sensing systems, transducer coupled with control and readout electronics.

TABLE II
Electronic and mechanical properties of silicon carbide [7]

	6H-SiC	**4H-SiC**
Bandgap (eV)	3.02	3.26
Themal Conductivity (W/cmK)	4.9	4.9
Breakdown Field (MV/cm)	2 -3	2
Hardness (Mohs scale)	~9	~9
Corrosion resitance (acids & bases)	yes	yes

In the area of combustion monitoring SiC sensors have been shown to be sensitive to flue gases and automobile exhausts, including hydrogen, hydrocarbons, CO and NO_x [5, 8, 9, 10]. Fig. 1 shows a schematic view of our catalytic gate MOS gas sensor. At temperatures above 400 °C refractory metals such as Pt, Pd and Ir can efficiently dehydrogenate hydrogen containing gas species. Hydrogen then diffuses rapidly (µs) through the metal gate, and is adsorbed at sites at the metal/oxide interface giving rise to a dipole layer at the interface. This chemically induced polarization charge, shifts the potential of the MOS sensor and is monitored as the sensor signal. For an optimally chosen setpoint, we have shown that this simple description is valid for our catalytic gate $Pt/SiO_2/SiC$ gas sensors [11].

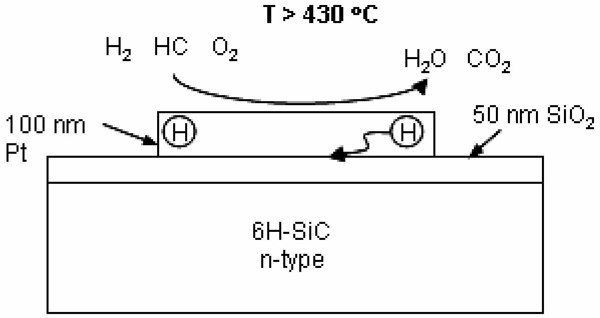

Figure 1. : Schematic of a SiC metal-oxide-semiconductor gas sensor with a Pt catalytic sensing film. The device can detect hydrogen containing gases at temperatures above 430 °C.

We have demonstrated that our SiC gas sensor can be used to monitor the net hydrogen content of "clean" syngas [5]. The 1cm^2 SiC sensor chip contains an array of 52 devices with a backside platinum heater to self heat the sample up to 670 °C. Sensing measurements were made under simulated syngas conditions by installing the device, mounted inside a robust sensor module, at the exhaust of an industrial reactor. The gas temperature and flow were 350 °C and 1000 sccm respectively, while the SiC chip was maintained at 630 °C for optimum device performance in terms of sensitivity and response time. The sensor response to 350 °C hydrogen gas was 240 mV/decade, in the 0.1-40 % H_2 range. This response is significantly higher than that at room temperature or predicted by theory, which is based on vacuum chamber data. All measurements were validated by an online mass spectrometer located downstream from the sensor. The SiC sensor can monitor the net hydrogen concentration in the presence of the following common interferants: CO_2 (40 %), CH_4 (5 %) and CO (40 %). The device performance was not degraded by exposure to ~1000ppm of H_2S or water vapor. For a device temperature of 630 °C the sensor response time is faster than 1 s [12]; therefore our SiC sensor is capable of real time syngas monitoring.

In addition to gas monitoring, the materials properties of SiC, given in Table I, have spurred development of a number of sensors for energy production. A SiC flame sensor is commercially available for gas turbine and control systems [13]. The device has been used for tracking the mode of the combustor, combustion flame dynamics and flame intensity in gas turbine power plants. Another group has reported on a UV flame sensor operating at 700 °C [14]. A SiC photodiode chip has been developed to determine the temperature of a natural gas combustion flame, with a sensitivity of 0.35% per 11 °C change in flame temperature in the 1480 to 1650 °C range [15]. In the area of physical sensors, devices for monitoring strain and pressure using 3C-SiC deposited on a Si substrates have been reported. The MEMS resonant strain sensor achieved a strain sensitivity of 66 Hz/ $\mu\varepsilon$ in a bandwidth from 10 – 20 kHz at temperatures above 300 °C [16] and the piezoresistive pressure sensor had a sensitivity of 63 μV/V*psi at 400 °C [17].

IV. OTHER SOLID STATE AND OPTICAL SENSORS

Solid state gas sensors based on metal oxides, most notably zirconium oxide, are widely used commercially, primarily for automotive combustion control applications. These devices are outside the scope of this paper; the reader is referred to the reviews in references [18, 19]. Commercial gas turbine combustors operate near the fuel-lean flame extinction limit in order achieve very low NO_x emission. A combustion oscillation monitoring sensor using flame ionization has been developed to address the problems associated with flame flashback and blow off [20]. For long term operation of power generation systems it is also important to monitor the structural integrity of gas turbine engines. Ceramic strain gages have been developed that can operate from room temperature to 1200 °C at strain levels up to 1000 $\mu\varepsilon$, with a near zero temperature coefficient of resistance [21].

A number of optical diagnostic techniques including absorption, infra-red emission and chemiluminescence are being successfully used to control combustion by monitoring temperature, pressure, mass flow, mole fraction of combustion intermediates, heat fluctuations, and flame front motion; as reviewed by Docquier [18]. These techniques have good spatial and temporal resolution but require line of sight optical access, which may not be possible for all systems. In-situ oxygen and carbon monoxide sensing using tunable diode laser spectroscopy have been demonstrated for real time combustion monitoring in waste incinerators and gas-fired power plants [22]. In addition fiber optical devices to monitor temperature and pressure may be imbedded into the combustion system

V. CONCLUSION

Clean, efficient energy production requires chemical and physical sensors that can operate in harsh, high temperature environments. In this paper the sensing needs for electricity generation from the gasification of coal were reviewed. We have discussed the insertion opportunities for SiC based solid state sensor for measuring gas composition, monitoring the combustion flame as well as its temperature, and the structural integrity of the combustor.

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REFERENCES

[1] B. T. Chorpening, D. Tucker and S. M. Maley, "Sensor Applications in 21st Century Fossil-fuel Based Power Generation", Proceedings of IEEE Sensors 2004, vol.3, pages1153 – 1156.

[2] C. G. Keller and J. Stulz, "Operating Experience at Wabash River Coal Gasification Repowering Project", Sixth Clean coal Technology Conference (Reno, NV), April 1998 (www.netl.doe.gov).

[3] D. Tucker, L. O. Lawson and R. S. Gemmen, "Preliminary Results of a Cold Flow Test in a Fuel Cell Gas Turbine Hybrid Simulation Facility ," ASME GT2003-38460, June 2003. (http://store.asme.org/search_cp.asp)

[4] J. Hoffmann, J. Tennant, G. J. Stiegel, M. Matuszewski, M. D. Rutkowski and R. L. Schoff, "Comparison of Pratt and Whitney Rocketdyne IGCC and Commercial IGCC Performance', Final technical report, June 2006, DOE/NETL-401/062006 (www.netl.doe.gov).

[5] R. Loloee, B. Chorpening, S. Beer and R. N. Ghosh, "Hydrogen Monitoring for Power Plant Applications using SiC Sensors", to be published in Sensors & Actuators B, 2007.

[6] B. T. Chorpening, NETL-DOE, private communication.

[7] S. Park, *SiC Materials and Devices, Semiconductors and Semimetals* vol. 52, Academic Press, New York, 1998, ch. 1, pp. 12-16.

[8] A.L. Spetz and S. Savage, “Advances in SiC field effect gas sensors”, *Silicon carbide recent major advances*, Editors : W.J. Choyke, H. Matsunami, and G. Pensl”, springer-verlag berlin Heidelberg 2004.

[9] A. L. Spetz et. al., “SiC Based Field Effect Gas Sensors for Industrial Applications”, Phys. Stat. Solidi A, vol. 185 pages 15-25 (2001).

[10] J. Schalwig, P. Kreisl, S. Ahlers, and G. Müller, “Response mechanism of SiC-based MOS field-effect gas sensors”, IEEE Sens. J., vol. 2, pages 394-402 (2002).

[11] P. Tobias, B. Golding & R. Ghosh, “Interface states in high temperature gas sensors based on SiC”, IEEE Sensors J. vol. 3, pages 543-547 (2003).

[12] R. N. Ghosh, P. Tobias, H. Hu, and M. Koochesfahani, "Fast solid state gas sensor characterization technique with millisecond resolution", Proc. IEEE Sensors 2005, pages 1411-1413 (2005).

[13] D. M. Brown, E. Downey, J. Kretchmer, G. Michon, E. Shu E and D. Schneider, ‘SiC flame sensors for gas turbine control systems”, Sol. St. Elec., vol. 42, pages 755-760 (1998).

[14] T. Toda, M. Hata, Y. Nomura, Y. Ueda, M. Sawada and M. Shono, “Operation at 700 degrees C of 6H-SiC UV sensor fabricated using N+ implantation”, Jap. J. Appl. Phys., Part 2 – Letters, vol. 43 (1A-B), pages L27-L29, (2004)

[15] D. M. Brown et. al, “Silicon carbide photodiode sensor for combustion control”, IEEE Sensors J., vol. 5, pages 983-988 (2005).

[16] R. G. Azevedo, “A SiC MEMS resonant strain sensor for harsh environment applications”, IEEE Sensors J., vol. 7, pages 568-576 (2007).

[17] C. H. Wu, C. A. Zorman, M. Mehregany, “Fabrication and testing of bulk micromachined silicon carbide piezoresistive pressure sensors for high temperature applications”, IEEE Sensors J., vol. 6, pages 316-324 (2006).

[18] N. Docquier and S. Candel, “Combustion control and sensors: a review”, Prog. Energy & Comb. Sci., vol. 28, pages 107-150 (2002).

[19] J.H. Visser and R. E. Soltis, “Automotive exhaust gas sensing systems”, IEEE Tran. Instrm. & Meas., vol. 50, pages 1543-1550 (2001).

[20] B. T. Chorpening, J. D. Thornton, E. D. Huckaby and K. J. Benson, “Combustion oscillation monitoring using flame ionization in a turbulent premixed combustor”, ASME J. Eng. Gas Turb. & Power Trans., vol. 129, pages 352-357 (2007).

[21] O. J. Gregory & X. Chen, “A low TCR nanocomposite strain gage for high temperature aerospace applications”, Proc. IEEE Sensors 2007, paper 6719 (2007).

[22] V. Ebert & J. W. Fleming, “Optical oxygen sensors using tunable diode laser spectroscopy: application to harsh reactive processes”, Proc. IEEE Sensors 2007, paper 6837 (2007).