Laser-Doped SiC as Wireless Remote Gas Sensor based on Semiconductor Optics

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Abstract. An uncooled SiC-based electro-optic device is developed for gas sensing applications. P-type dopants Ga, Sc, P and Al are incorporated into an n-type crystalline 6H-SiC substrate by a laser doping technique for sensing CO_2, CO, NO_2 and NO gases, respectively. Each dopant creates an acceptor energy level within the bandgap of the substrate so that the energy gap between this acceptor level and the valence band matches the quantum of energy emitted by the gas of interest. The photons of the gas excite electrons from the valence band to the acceptor level, which alters the electron density in these two states. Consequently, the refractive index of the substrate changes, which, in turn, modifies the reflectivity of the substrate. This change in reflectivity represents the optical signal of the sensor, which is probed remotely with a laser such as a helium-neon laser. Although the midwave infrared (3-5 μm) band is studied in this paper, the approach is applicable to other spectral bands.

Introduction

Accessing the harsh combustion environments requires advanced materials and packaging that limit the applicability of conventional semiconductor gas sensors [1]. The semiconductor-based gas sensors generally produce electrical signal with poor sensitivity and long response time. This paper presents a new type of gas sensor that produces optical signal. Loloee et al. [2] developed a hydrogen gas sensor by fabricating a metal-oxide-semiconductor (MOS) capacitor in an n-type SiC (Pt-SiO_2-SiC) and demonstrated its operation up to 620°C. Neudeck et al. [3] presented a SiC-based Schottky diode hydrogen sensor with improved gain even though the operating temperature was below 150°C. Spetz et al. [4] fabricated a metal-insulator-SiC-field-effect-transistor (MISiCFET), Pt/TaSi$_x$/SiO_2/6H-SiC, for sensing reducing gases such as H_2, hydrocarbons and CO over a wide temperature range of 100-700°C. The performance of solid state gas sensors, however, deteriorate owing to junction breakdown and electromigration. Additionally, the sensor functionality relies on the gas contacting the sensor, which is often difficult to implement in harsh environments at high temperatures. For such hazardous conditions, optical detection provides a nonintrusive, remote sensing mechanism for measuring the temperature and chemical concentration, and for identifying the chemicals [5]. This paper presents a noncontact chemical sensor, which has been fabricated by doping four regions of a SiC substrate with four different dopants for sensing four gases. The as-received substrate was an n-type 6H-SiC of nitrogen concentration 5×10^{18} cm^{-3}.

Experimental Procedure

Sensor Fabrication and Testing. The spectroscopic data, particularly the spectral emission lines of the chemicals of interest, which are CO_2, CO, NO_2 and NO in this study, are listed in Table 1. Another critical datum is the dopant element that produces an energy level corresponding to the energy of a photon emitted by the chemical. The dopant elements for these gases and their acceptor levels [6] in 6H-SiC are listed in Table 1. Although the NO_2 photon energy and the P dopant energy level differ by 0.05 eV, the P-doped 6H-SiC enables detecting NO_2 because the dopant energy level is sufficiently broad to cover this difference. Sensors are fabricated by incorporating dopants into different regions of a 6H-SiC substrate using a laser metallorganic chemical vapor diffusion (LMOCVD) technique [7].

Table 1. Gas absorption spectroscopic data for dopant selection.

Gas	Emission wavelength [μm]	Photon Energy [eV]	Dopant	Dopant energy level [eV]
CO_2	4.32	0.29	Ga	$E_V + 0.29$
CO	2.35	0.52	Sc	$E_V + 0.52$
NO_2	6.25	0.19	P	$E_C - 0.14$
NO	5.26	0.23	Al	$E_V + 0.23$

The characteristic photons of a given chemical excite electrons from the valence band to the dopant energy level, altering the electron density in the valence band and dopant levels. This modifies the refractive index of the substrate and, consequently, the reflectance of the substrate changes. The sensor response is the change in the reflectance of the doped substrate   This semiconductor optics, i.e., the semiconductor properties and the optical sensor response, is the fundamental principle of the optical gas sensor in this paper. A helium-neon (He-Ne) laser beam of wavelength 632.8 nm is used to probe the sensor response. The power of the He-Ne laser that is reflected off the sensor is measured with a Si photodetector.

Results and discussion

The optical properties of the doped samples were measured to verify whether the dopants create appropriate absorption peaks for sensing operation. A Varian Cary 500 spectro-photometer was used for measurements in the wavelength range 0.2 – 3 μm and a Bruker Vertex 70 FTIR spectrometer equipped with a Helios infrared micro-sampling accessory was used in the wavelength range 2.5 to 25 μm. The spectroscopic data of different samples doped with Ga, Sc, P and Al are presented in Figs. 1-4, respectively. The Ga-doped sample (Fig. 1) shows relatively high
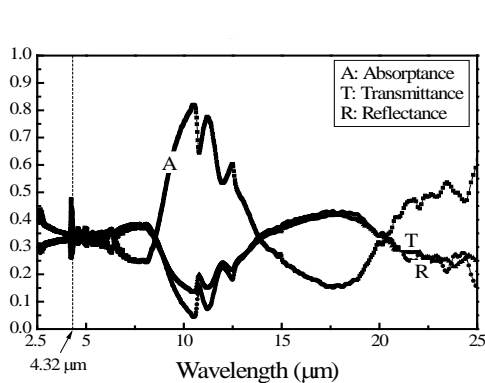

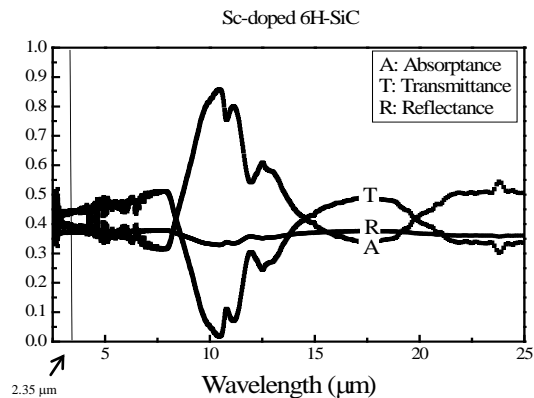Fig. 1. Optical data for Ga-doped CO_2 sensor.

Fig. 2. Optical data for Sc-doped CO sensor.

absorptance (47.3%) at 4.32 μm and this wavelength corresponds to the energy of each photon (0.29 eV) emitted by CO_2. The Al-doped sample (Fig. 4) exhibits an absorptance of 35.1% at 5.26 μm that corresponds to the energy of each photon (0.23 eV) emitted by NO.
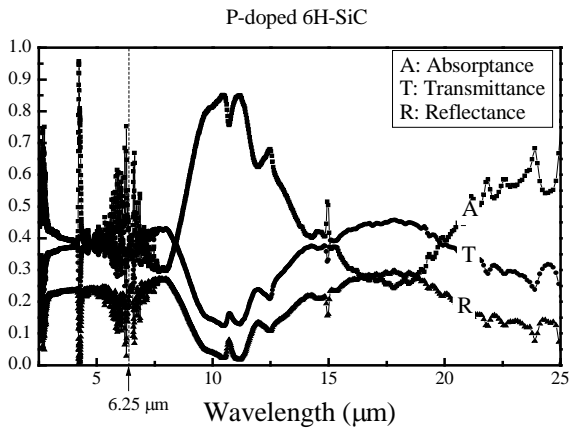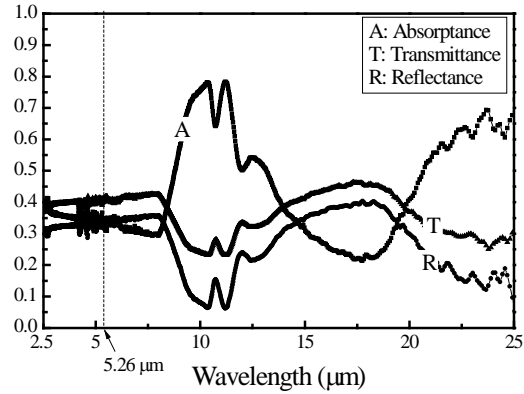

Fig. 3. Optical data for P-doped NO_2 sensor.

Fig. 4. Optical data for Al-doped NO sensor.

When the electrons are excited from the valence band to the acceptor level by the photons of a gas, the refractive index of this gas-excited doped 6H-SiC (n_g) depends on the wavelength (λ), temperature (T), gas concentration (c) and gas type, i.e., $n_g = n_g(\lambda,T,c)$. The deviation of n_g from the refractive index of the doped sample (n_a) in air , i. e., $n_a = n_a(\lambda,T)$, is expressed as $\Delta n = n_g(\lambda,T,c) - n_a(\lambda,T)$. This deviation in refractive index (Δn) is an important parameter that shows the selectivity of the sensor for a particular gas. The values of Δn are plotted in Figs. 5-8 for different doped samples exposed to the photons of CO_2, CO, NO_2 and NO gases, respectively. The Ga dopant energy level is $E_V + 0.29$ eV in 6H-SiC, which matches with the photon energy of 0.29 eV corresponding to the MWIR wavelength of 4.32 μm emitted by the CO_2 gas. So the transition of
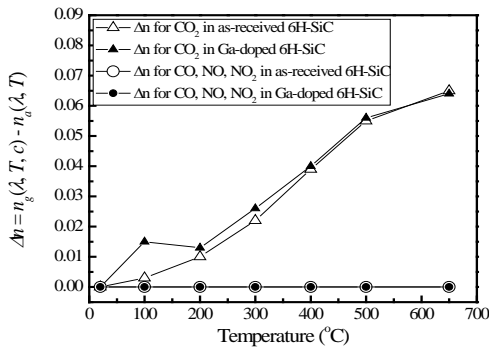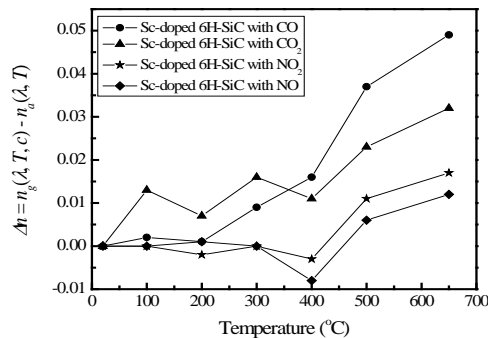

Fig. 5. Ga-doped 6H-SiC as CO_2 gas

Fig. 6. Sc-doped 6H-SiC as CO gas

electrons from the valence band to the Ga energy level would be caused only by the CO_2 photoexcitation. In Fig. 5, the curve for CO_2 gas is, therefore, distinctly different from the curves of CO, NO and NO_2 gases, indicating that the Ga-doped 6H-SiC can be used as a CO_2 gas sensor. Similarly, the Sc-, P- and Al-doped samples exhibit distinct changes in the refractive indices at high temperatures of the CO, NO_2 and NO gases, respectively. For these three cases (Figs. 6-8), other

gases also affect the refractive index at high gas temperatures, because the dopants were found to create additional absorption peaks in the substrate corresponding to certain emission peaks of the other gases. To prevent this type of multiple gas-effect on the refractive index and to achieve gas-selective sensing, intrinsic SiC epilayer can be used to fabricate the sensor and optical filters can be used to select only the photons of interest.
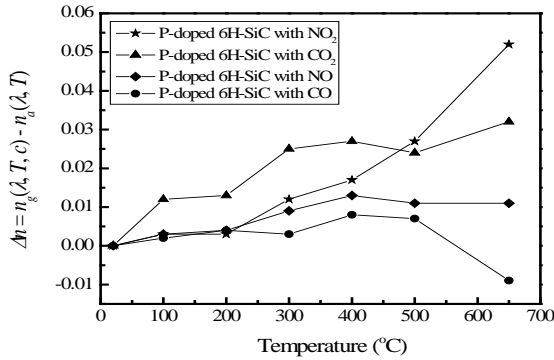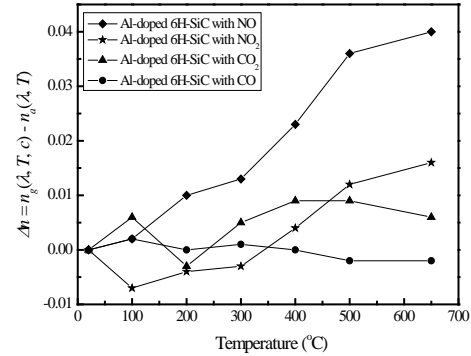

Fig. 7. P-doped 6H-SiC as NO_2 gas

Fig. 8. Al-doped 6H-SiC as NO gas

Summary

Nonintrusive, remote sensors have been fabricated by doping different regions of an n-type 6H-SiC substrate with Ga, Sc, P and Al to detect CO_2, CO, NO_2 and NO gases, respectively. The sensors operate based on the principle of semiconductor optics and produce optical signal instead of electrical signal as in conventional gas sensors. The optical response of the sensor is due to changes in its reflectance caused by the photons of a gas. This response is measured with a He-Ne laser beam in this study. Since the reflectance depends on the refractive index, the data pertaining to the changes in refractive index indicate that the doped samples can be used as gas sensors.

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