Diamond Film Based Structure for Gas Sensing Applications

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Abstract

A new microelectronic gas sensor utilizing plasma enhanced chemical vapor deposited (PECVD) diamond in conjunction with a catalytic metal has been built and tested for gas detection. The device is fabricated in a layered Pd/ i-diamond/ p-diamond Schottky diode configuration on a variety of supporting substrates. The performance of the device for H_2 detection has been examined in terms of sensitivity, linearity, response rate, and response time as a function of temperature and hydrogen partial pressure. Analysis of the steady state reaction kinetics confirm that the hydrogen adsorption process is responsible for the barrier height change in the diamond Schottky diode. The use of diamond film technology opens the door to the development of a microelectronic gas sensor which can operate at a wider and higher temperature range than the present silicon technology.

I. Introduction

Catalytic-gate microelectronic gas sensors such as the Schottky diode, MOS capacitor, and MOSFET using silicon based technology have been investigated extensively[1-7] in the past decade. Many interesting applications have been demonstrated and practical devices have been commercialized. Extensive research has been performed to improve gas sensitivity and selectivity through the use of a perforated gate structure[8]. And most recently, by the incorporation of catalyst and adsorptive oxide layers into the MOS system[9-10]. However, the relatively limited temperature operating range (<150°C) of the silicon based device has prevented the widespread utilization of these sensors, particularly for the detection of toxic gas for the combustion process and *in situ* emission control at high temperature. Recent advances in the plasma enhanced chemical vapor deposition (PECVD) process have resulted in the realization of high quality polycrystalline diamond films for device applications. Microelectronic devices such as Schottky diodes, and field-effect-transistors FETs[11] have been fabricated for high temperature applications. It would thus be possible to utilize the diamond technology for gas sensors operating at considerably higher temperatures than those based on silicon technology.

In this paper, we present the first prototype polycrystalline diamond based gas sensing structure for hydrogen gas detection. Major advantages of using the polycrystalline diamond thin film based structure for gas sensing applications are wider (or higher) temperature operating range, simplicity in the fabrication process, flexibility in the choice of substrates, and compatibility with silicon microfabrication technology. Moreover, PECVD diamond films possess many desirable material properties such as good thermal conductivity, chemical inertness, electrical stability, and compatibility with hostile environments.

II. Sensor Fabrication and Characterization Method

The diamond-based gas sensor was fabricated in a layered Pd/ i-diamond/ p-diamond Schottky diode configuration as shown in Fig. 1. The PECVD diamond film can be deposited on a variety of substrates such as W, Mo, Si, SiN, etc. Boron doped p-type polycrystalline diamond films 5-10μm thick were deposited on the prepared surface of the substrates via *in situ* boron compound solid source doping method using PECVD. A thin intrinsic (undoped) diamond interfacial layer was then deposited on the p-diamond layer. Typical process parameters for the growth of these films were: pressure, 40 torr; substrate temperature, 850°C; gas flow rate, 500 sccm hydrogen and 5 sccm methane; microwave power, 1500 watts. The growth rate was nominally 0.5 microns per hour. Films were then annealed for one minute at 850°C in argon. Raman spectroscopy of these diamond films is shown in Fig. 2. The film shows the typical characteristic Raman peak of a diamond at 1332cm^{-1}. Finally, a palladium electrode 1000 Å thick and 1mm in diameter was thermally evaporated on the diamond surface.

The device-under-test was placed on a probe station equipped with a heated stage in an atmosphere controlled test chamber. A predetermined amount of hydrogen was introduced into the chamber. The steady state and transient responses of the devices to H_2 were measured as a function of H_2 partial pressure and temperature by I-V and ΔI-t methods using a Hewlett Packard 4145 meter. The operating temperature of the device was controlled to ±1°C of the desired temperature during the measurement.

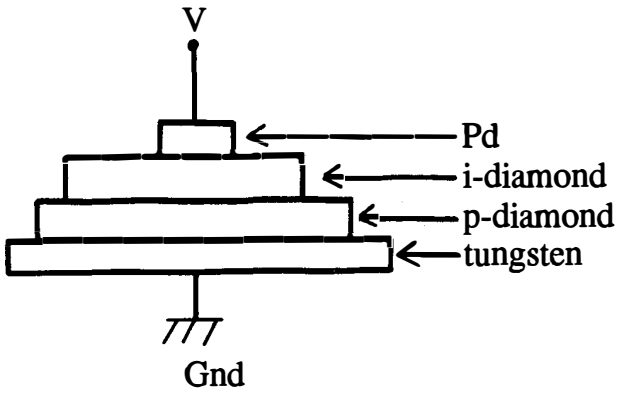

Fig. 1. Diamond based gas sensor fabricated in a layered Pd/ i-diamond/ p-diamond Schottky diode

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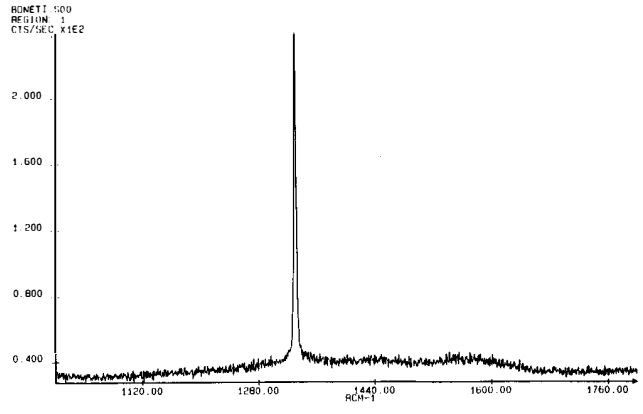

Fig. 2. Raman Spectra of PECVD Diamond

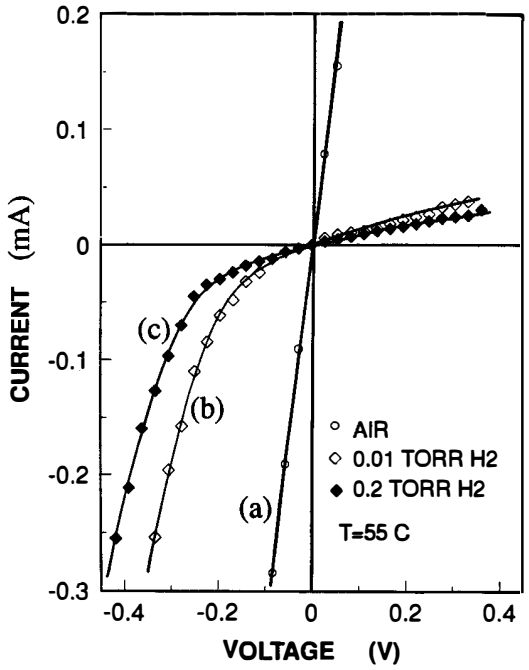

Fig. 3. I-V Characteristics of Pd/ i-Diamond/ p-Diamond Schottky Diode Hydrogen Sensor at T=55°C: (a) in air, (b) in 0.01 Torr H_2, and (c) in 0.2 Torr H_2.

III. Results and Discussion

A. H_2 Sensing Characteristic

Typical I-V characteristics of the polycrystalline diamond based gas sensor before and after exposure to H_2 are shown in Figs. 3, and 4 for two type of devices operating at 55 and 200°C, respectively. The figures show a large change in the I-V characteristics of the sensor, shifted from near ohmic to rectifying behavior upon the devices exposure to the H_2 gas. The effect is reproducible and repeatable upon adsorption/ desorption of hydrogen gas. Figure 5 shows the detection sensitivity, ΔI, versus hydrogen partial pressure for the device operated at 55°C, under a fixed (-0.4 V) forward bias voltage. The figure shows a rapid increase in ΔI upon H_2 adsorption at low hydrogen partial pressures, followed by a trend to saturation at higher H_2 partial pressures.

Adsorption transient behavior of the diode upon exposure to hydrogen gas was measured by monitoring the current of the device as a function of time, at fixed forward bias voltage. Typical transient responses of the diode as a function of H_2 partial pressures at a constant room temperature and at fixed H_2 partial pressure for several operating temperatures are shown in Figs. 6 and 7, respectively. In general, the initial adsorption rate, $[\Delta(\Delta I)/\Delta t]_{initial}$, increases with hydrogen partial pressure or temperature, while the adsorption time constant, (time required for the measured ΔI to reach e^{-1} of its saturation value) decreases with increasing hydrogen partial pressure or temperature. At room temperature, as the concentration of hydrogen increases from 0.1 torr to 2 torr, the initial adsorption rate increases from 0.002 mA/sec to 0.022 mA/sec with the corresponding response time decreasing from 168 sec to 22 sec. As the temperature increases, the initial adsorption rate increases from 0.019 mA/sec to 0.069 mA/sec and the response time constant decreases from 20 sec to 9 sec.

A typical repeatability test of the sensor for the detection H_2 (concentration: 100%, flow rate: 10 ml/min) in an open air (1 atm.) background is shown in Fig. 8. The device shows a response and recovery time in seconds upon turning of the H_2 gas on/off, exhibiting that the response to hydrogen is fast, sensitive, reproducible, and repeatable.

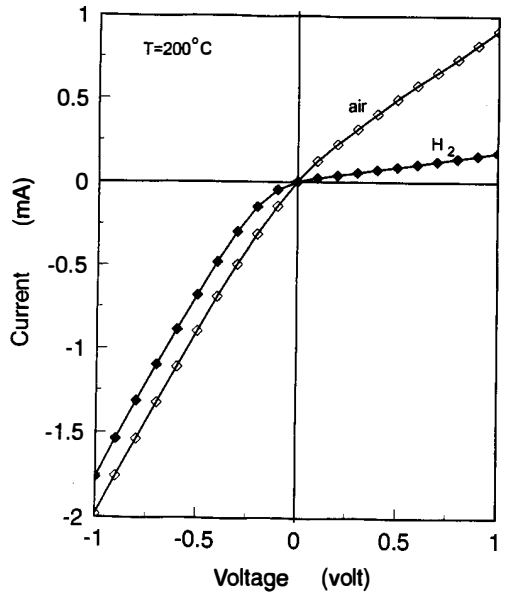

Fig. 4. I-V Characteristics of Pd/ i-Diamond/ p-Diamond Schottky Diode Hydrogen Sensor at T=200°C: (a) in air, (b) in H_2.

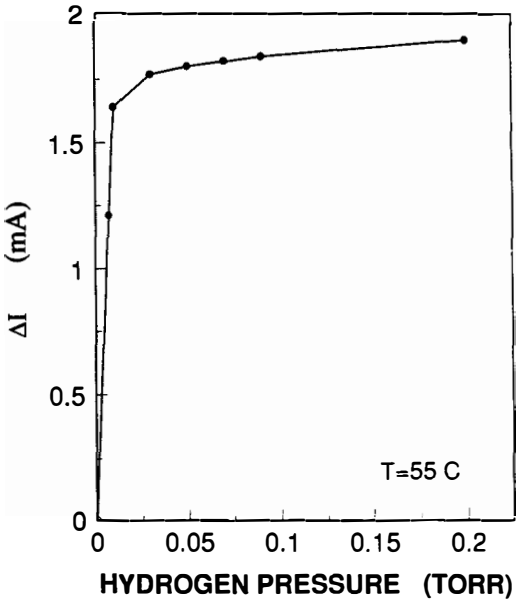

Fig. 5. Detection Sensitivity, ΔI, versus hydrogen partial pressure at 55°C.

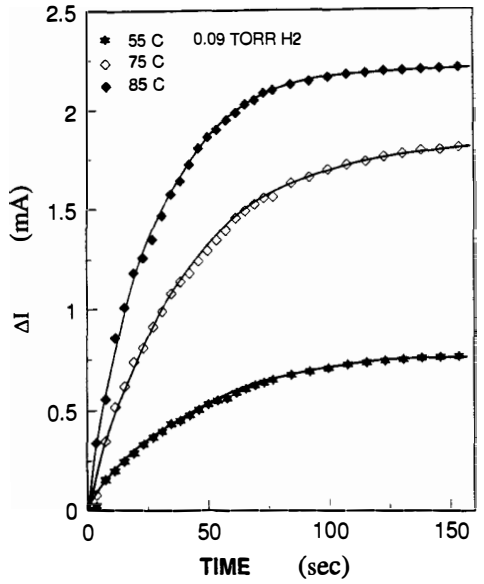

Fig. 6. Adsorption Transient Behaviors of Pd/ i-Diamond/ p-Diamond Hydrogen Sensor upon Exposure to 0.09 Torr Hydrogen at Various Temperatures.

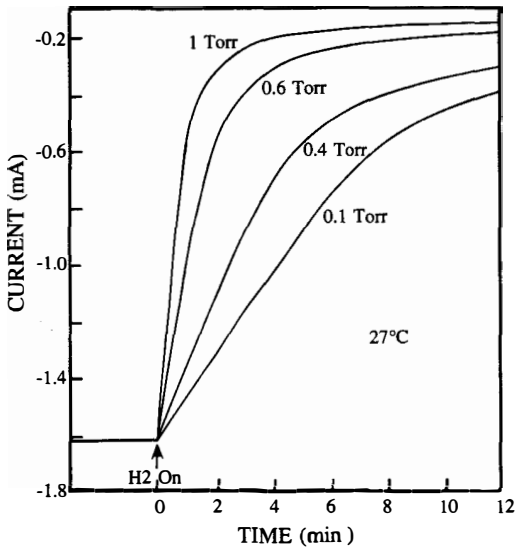

Fig. 7. Adsorption Transient Behaviors of Pd/ i-Diamond/ p-Diamond Hydrogen Sensor upon Exposure to various Hydrogen concentration at a constant temperature

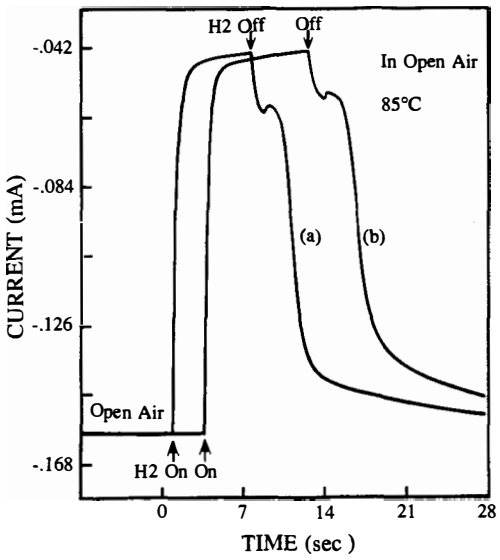

Fig. 8. Repeatability Test of Pd/ i-Diamond/ p-Diamond Hydrogen Sensor for Hydrogen Detection in Open Air Environment.

B. Detection Kinetic Analysis

The hydrogen reaction kinetic on the Pd-diamond based structure can be explained by considering the following hydrogen reaction kinetics[1].

$$H_{2(g)} \rightleftharpoons 2H_a \rightleftharpoons 2H_{ai} \quad (1)$$

where *g* and *a* stand for gaseous and adsorbed species, respectively. In this case, Eq. (1) describes the H_2 dissociative chemisorption on the Pd surface, solid state diffusion of atomic hydrogen through the metal film, and finally adsorption of atomic hydrogen at the Pd-diamond interface. Since the measured adsorption time constant is much larger than the hydrogen diffusion time through the 1000Å Pd film (solid state diffusion coefficient of atomic hydrogen in the metal[12] is 10^{-6} cm^2s^{-1}), we can assume that the equilibrium between hydrogen adsorbed on the surface, H_a, and hydrogen adsorbed on the Pd-diamond interface, H_{ai}, is established rapidly. Then, under the steady state condition in Eq. (1), the hydrogen coverage, θ, at the interface can be put in the form

$$\theta/(1-\theta) = (c_1/d_1)^{1/2}(P_{H2})^{1/2}. \quad (2)$$

But the barrier height of a Schottky barrier diode is related to the I-V characteristics[13] by

$$I = AA^{**}T^2 \exp(-\phi_b/\phi_T)[\exp(V/n\phi_T) - 1][1-\exp(-V/\phi_T)] \quad (3)$$

where k is the Boltzmann constant, T is in °K, A^{**} is the effective Richardson constant, A is the junction area, n is the ideality factor, and $\phi_T = kT/q$. Therefore, if we assume that the change in barrier height, $\Delta\phi_b$, induced by hydrogen adsorption is proportional to the hydrogen coverage, θ, i.e. $\Delta\phi_b = \Delta\phi_{max}\,\theta$. Where $\Delta\phi_{max}$ is the maximum barrier change, and θ is defined as $0 < \theta < 1$. Then Eq. (2) can be reduced to

$$(1/\Delta\phi) - (1/\Delta\phi_{max}) = (1/\Delta\phi_{max})(d_1/c_1\, P_{H2})^{1/2}. \quad (4)$$

Thus, according to the I-V relation of the Schottky diode (Eq. 3), under a fixed temperature and low bias voltage, the change in barrier height $\Delta\phi_b$ due to hydrogen adsorption is

$$\Delta\phi_b = \phi_T \ln(I_o/I_{og}) \quad (5)$$

and it follows that,

$$\Delta\phi_{max} = \phi_T \ln(I_o/I_{og(max)}) \quad (6)$$

where I_o and I_{og} are the current measured in the environment without and with hydrogen gas respectively. $\Delta\phi_{max}$ is the maximum barrier height change and $I_{og(max)}$ is the corresponding current measured at a fixed temperature.

Substituting Eqs. (5) and (6) into Eq. (4), we get

$$1/(\ln(I_o/I_{og})) = 1/(\ln(I_o/I_{og(max)}) + [1/(I_o/\ln(I_{og(max)})](d_1/c_1)P_{H2}^{1/2}. \quad (7)$$

Thus Eq. (7) describes a linear plot of $1/\ln(I_o/I_{og})$ versus $(1/P_{H2})^{1/2}$. Figure 9 shows that the plots of $1/\ln(I_o/I_{og})$ versus $(1/P_{H2})^{1/2}$ for the Schottky diode is indeed linear. Thus, the experimental data obtained in this work from I-V measurements confirms the hydrogen reaction kinetics in the Pd-diamond based Schottky diodes is consistent with that in the silicon based Pd-MOS system[1].

The activation energy E_a for H_2 detection can be obtained by investigating the device initial transient response rate, $\Delta I/\Delta t$, upon exposing the device to a fixed H_2 pressure with temperature ranging from 27°C to 85°C. According to the Lennard-Jones model, the initial rate of the adsorption process is given by

$$\Delta\theta/\Delta t = k_{ads} \exp(-E_A/kT) = (1/\ln(I_{og(max)}/I_o))(1/I_{og})(\Delta I_{og}/\Delta t). \quad (8)$$

Thus, the adsorption activation energy of hydrogen can be determined from the slope of $\ln[(1/I_{og})(\Delta I_{og}/\Delta t)]$ versus 1/T plot. The adsorption activation energy is 2.95 kcal/mole in 0.09 torr H_2. The low hydrogen adsorption activation energy of the device explains the observed high sensitivity and fast response to the hydrogen gas at low temperatures utilizing the Pd-diamond based structure.

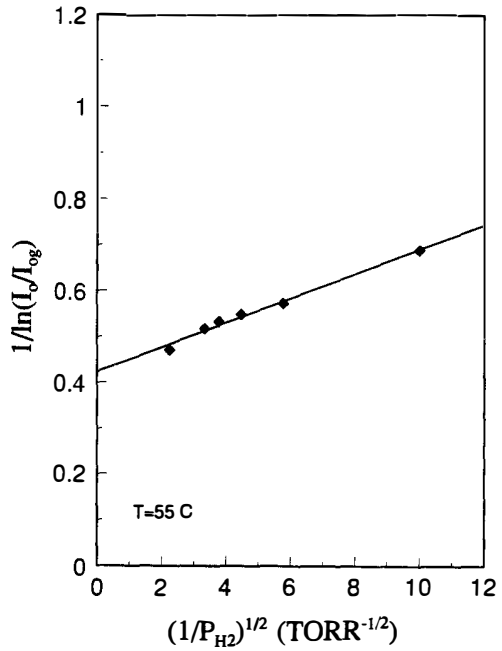

Fig. 9. Hydrogen Reaction Kinetic Analysis under Steady State Condition for Pd/ i-Diamond/ p-Diamond Hydrogen Sensor: Plot of $1/\ln(I_o/I_{og})$ versus $(1/P_{H2})^{1/2}$.

IV. Conclusions

The utilization of PECVD diamond technology for gas sensing application is achieved. Hydrogen detection performance of the device at low, medium, and high temperature ranges (27°C, 85°C, 200°C) have been demonstrated and analyzed. The hydrogen sensitivity is high, repeatable, and reproducible. This study has shown that the barrier height of the Pd-diamond Schottky diode increases upon hydrogen adsorption. This effect leads to the change of the I-V characteristics from near ohmic to rectifying behavior. Hydrogen reaction kinetics have been analyzed. This polycrystalline diamond based hydrogen sensing technology should have many applications due to its reproducibility, sensitivity, and performance over a wide temperature range. The findings open the door for the development of diamond based high temperature gas sensor which could be used for detection of combustible gas and *in situ* emission control.

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