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40 Å Platinum–porous SiC gas sensor: Investigation sensing properties of H_2 gas

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ABSTRACT

The present paper reports on a new structure for H_2 gas sensing based on thin porous silicon carbide (PSiC) films. The PSiC layer has been formed by electrochemical etching of SiC films previously deposited onto p-type silicon substrate by pulsed laser deposition (PLD) using 6H-SiC target. Current–voltage (I–V) and current–time (I–t) characteristics have been measured. A thin platinum (Pt) film (40 Å thickness) deposited onto PSiC layer has been used as a catalytic metal. The Schottky diode parameters such as ideality factor (n), barrier height (ϕ_{Bp}) and series resistance (R_S) have been evaluated under different concentrations of H_2 gas. The experimental results show that upon exposure to H_2 gas the barrier height, the ideality factor and the series resistance change significantly. The different changes in the electrical parameters of the structure (increase and decrease as a function of the H_2 concentration) have been explained by the formation of two inversion layers. The first one forms as soon as the gas is in contact with the sensor and the second when the concentration reaches 90 ppm. Subsequently, the effect of gas concentration on the maximum sensitivity value of the sensor has been investigated. A high sensitivity ($\Delta I/I$) value around 86% is found at about 1 V bias voltage. In addition, the response and recovery times were determined to be around 55 s and 160 s, respectively. Finally, the structure shows a reversible response for low gas concentration at room temperature.

1. Introduction

Recently, hydrogen has attracted attention for use in a fuel battery for producing clean energy. The gas sensor based on a semiconductor, such as silicon, porous silicon, can be easily integrated with other electronic circuits, which promises to be an important factor for realizing an intelligent sensor device in the future. However, these materials are not hard enough to be used in hazardous medium. Moreover, SiC is more popular than Si in some applications because it has high breakdown field, high thermal conductivity and high carrier saturation velocity [1]. Recently sensors using semiconductors with large energy band gap such as silicon carbide and diamond film as substrates are developed for severe condition operation [2–4]. The type of silicon carbide widely used is 6H-SiC. Actually, the attention is increasing for using SiC in thin layer deposited onto p-type silicon. A gas sensor device based on the Schottky contact between catalytic metal and Si has been demonstrated to exhibit an output response to change in gas concentration of 1 V or less [5–8]; the same output response is exhibited by a device based on MISiC and that is currently in development [9–12]. Both devices are thought to employ basically the same gas sensing mechanism, which is based on a process of adsorption of gas molecules, dissociation to atoms, diffusion to an interface between catalytic metal and a semiconductor, and production of a polarized layer and a drop in potential. Recently, some new devices based on SiC have been proposed in an effort to increase an output response to gas. Each of these devices has a structure that includes a metal oxide layer placed between catalyst metal and semiconductor [13]. In the present study, we fabricated a new structure based on Pt (40 Å)/thin porous SiC/silicon (Pt–PSiC structure) in an attempt to improve the structure response to hydrogen gas. Current–voltage (I–V) and current–time (I–t) characteristics of the structure have been obtained.

2. Experimental procedure

The SiC deposition onto silicon substrate has been performed by a pulsed laser deposition technique, using a hot pressed

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polycrystalline p-type 6H-SiC as a target (supplied by Goodfellow). The silicon substrate with a resistivity of 6 Ω cm was mounted on a plate which is attached on the top of a rotating cylinder. During the deposition, the plate is heated at 500 °C by halogen lamps placed on a fixed water-cooled reflector. The deposition is performed at a pressure of 10^{-6} Torr. The laser pulses have been produced by a Lambda Physik Compex 102 KrF laser excimer. The deposition parameters were irradiation wavelength $\lambda=248$ nm, maximum pulse energy $E_{max}=600$ mJ and pulse duration $\tau=25$ ns [14]. After the growth of the SiC layer, an aluminum (Al) Ohmic contact layer with a thickness of 4900 Å has been deposited by thermal evaporation on the back side of silicon substrate, followed by an annealing in air ambience at 600 °C for 1 h. The SiC layers deposited onto silicon have been porosified by anodization at a constant current density of 10 mA/cm^2 for 10 s in a HF/ethylene glycol (1/1 by volume) solution. The electrochemical setup was a standard three electrode configuration with SiC(p) structure as a working electrode, a platinum (Pt) sheet as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. The electrochemical process was performed using a potentiostat–galvanostat model EG&G PAR 362 [14]. After formation of PSiC layer, a thin platinum (99.995% purity) layer has been evaporated onto PSiC to form a Schottky contact. The thickness of Pt layer measured by Rutherford Backscattering Spectroscopy (RBS) at 2.0 MeV was 40 Å. The Pt layer served as a catalytic gate. The current–voltage (I–V) measurements were performed at room temperature with different concentrations of H_2 gas on 40 mm^2 area of Pt–PSiC structure using an electrometer Keithley 6485 and a voltage/current source ITECH 6121.

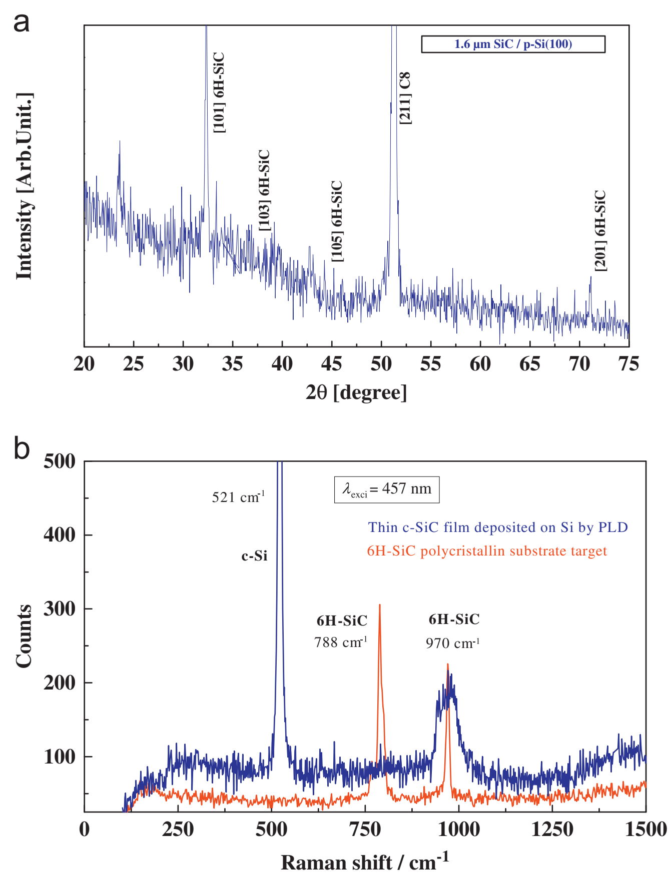

Fig.1. (a) XRD pattern of thin c-SiC film deposited on Si by PLD and (b) Raman spectra of thin c-SiC film deposited on Si by PLD.

3. Results and discussion

Fig. 1a and b shows XRD pattern and Raman spectra of a thin SiC layer deposited on Si, respectively. The XRD spectrum peaks (Fig. 1a) of the deposited film were identified using an ASTM data base as a crystalline 6H–SiC material [15]. Also, the Raman spectrum (Fig. 1b) clearly indicates that the deposited film is crystalline by the presence of the peak at 970 cm^{-1} corresponding to the longitudinal optical phonon (LO) of 6H-SiC material. Fig. 2 shows a plan view and cross-sectional SEM images of the silicon carbide layer anodized at a constant current density of 10 mA/cm^2 for 10 s. The surface appears porosified with formation of spherical shape cavities in the substrate, as shown in the cross-sectional view (Fig. 2**)**. These results have been discussed in detail in our previously published work [15].

The current–voltage (I–V) characteristics of the Pt–PSiC structure have been measured in the bias voltage range of −1.5 V to +1.5 V under air and various H_2 gas concentrations (Fig. 3). Fig. 3 shows a rectifying behavior for different atmospheres.

Also, it shows that at a given bias voltage value, the forward current is lower for a 30 ppm H_2 concentration than for air ambient indicating that the structure becomes more resistive in the presence of hydrogen (curves a and b). This can be due to the hydrogen passivating effect of Pt–PSiC structure.

The increase of H_2 gas concentration leads to the increase of current to reach a maximum value for a 90 ppm concentration (curves c and d) then decreases (curves e and f).

The striking feature suggests that, as a function of the gas concentration, probably two mechanisms of conduction occur, the first one for H_2 concentrations below 90 ppm and the second for concentrations higher than this value.

The thermionic emission theory can be used for the analysis of electrical characteristics of Pt–PSiC Schottky barrier structures.

The junction current expression given by this theory is as follows [16,17]:

$$I \cong I_s\left[\exp\left(\frac{qV}{nkT}\right)-1\right] \qquad (1)$$

where n is the ideality factor and I_s is the saturation current given by

$$I_s = aA^{**}\,T^2\,\exp\left(\frac{-q\phi_{Bp}}{kT}\right) \qquad (2)$$

where q is the electron charge, V is the forward applied voltage, a is the junction area (40 mm^2), T is the measurement temperature (295 K), k is the Boltzmann constant, A^{**} is the effective Richardson constant for p-type SiC (76 A cm^{-2} K^{-2}) and ϕ_{Bp} is the barrier height for p-type PSiC.

For a bias voltage, V, greater than $3kT/q$, the forward I–V characteristics are linear in the semi-log scale.

Using Eq. (2), the barrier height (ϕ_{Bp}) is determined from the following relation:

$$q\phi_{Bp} = kT\,\ln\left[\frac{aA^{**}T^2}{I_s}\right] \qquad (3)$$

In the usual way the ideality factor n is derived from the slope q/nkT, and the saturation current I_s from the intercept at $V=0$. It is preferable to bias forwardly the sensor to monitor the gases which cause a change in diode parameters that can be calculated from the Schottky diode theory. In reverse bias, the enhancement of the localized electric field around metals which are deposited on very small features of PSiC can considerably change the behavior of the Schottky contact. In this case, the reverse bias current becomes a strong function of the applied voltage which