Sensing Mechanism of InP Hydrogen Sensors Using Pt Schottky Diodes Formed by Electrochemical Process

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1. Introduction

Use of hydrogen gas is rapidly increasing recently due to increased use of fuel cells as a new clean energy source. Thus, accurate monitoring of hydrogen concentration by a suitable sensor is very important to avoid hazardous explosion. Preferably, the material for such a sensor is a well established semiconductor which can realize, by onchip integration, an integrated wireless sensor chip to be incorporated in the sensor network [1].

Pursuing such an idea, we have recently found that electrochemical deposition of Pt, a well known catalytic metal, onto InP, a well-established and surface sensitive material, realizes a highly sensitive hydrogen sensor [2] whose sensitivity is much higher than that of the Pt/AlGaN sensor we first investigated [3]. To proceed further, understanding of the sensing mechanism is indispensable.

The purpose of this paper is to investigate both experimentally and theoretically the sensing mechanism of our Pt/InPhydrogensensordiode formed on n-InPbythe electrochemical process.

2. Fabrication and Characteristics of Sensor Diodes

The hydrogen sensor had a Pt/n-InP Schottky diode structure formed on n^+ InP substrate. The Pt front Schottky contact was formed on the n-InP epitaxial layer by our pulsed electrochemical process [4], using 1 M solution of (HCl + H₂PtCl₆). The process consisted of anodic etching of the semiconductor and subsequent metal deposition in the same electrolyte by changing the pulse polar **M** observation showed that nanometer-sized Pt particles precipitated on the n-InP surface in a selfassembled fashion. For the same electrochemical conditions, the particle size remained almost the same, and its number density increased with time. Finally, a smooth



Fig.1 On-transient responses of the reverse current observed in air for various hydrogen pressure, $P_{\rm H2}$

and uniform Pt film was obtained by uniform coverage with size-controlled nano-particles. I-V and C-V measurements indicated that the diodes have high Schottky barrier height (SBH) values of 750-810 meV and excellent ideality factors of 1.0-1.1. The SBH values are much higher than those of the conventional vacuum deposited diodes with SBHs of 350-450 meV. We attribute this improvement to reduced interface disorder due to the extremely low processing energy of the electrochemical processposure to hydrogen in the air ambient caused marked increase of the diode current both in the forward and reverse directions, as shown in Fig.1 for the reverse current. Response speeds and saturation current levels depended on the hydrogen partial pressure, P_{H2}. The on-off transient response is shown in Fig.2. Current responded to "on" and "off" of hydrogen in air sharply and sensitively with reproducible on- and off-current levels.

We also found that ambient gas has large effects on the sensing characteristics. For example, on-response of the diode measured in vacuum is shown by open circles in **Fig.3**. As compared with **Fig.1**, the response is much faster and saturates to nearly the same current level. Measured





Fig.3 On-transient responses observed in vacuum for various P_{H2} . Open circles: experiment, solid curves: theory (Eq.(1)).





off- transients are compared in **Fig.4** for threes cases of 1) in air, 2) in vacuum and 3) in nitrogen. Both in vacuum and in nitrogen atmosphere, off transients became very slow. These results indicate that oxygen in the ambient affects strongly on-off transients of the Pt/InP sensor diode.

3. Hydrogen Sensing Mechanism

1)Proposed sensing mechanism

We propose the following sensing mechanism:

(1)Hydrogen molecules dissociate on the Pt surface and form atomic hydrogen, H*. (2) H* diffuses through the Pt layer and reaches the Schottky interface after a delay time t_d. (3) H* is adsorbed at the adsorption sites at the Schottky interface through a rate equation for adsorption sites, including the adsorption time constant, _a, desoprtion time constant, _d, and the sheet density of total adsorption sites, N_{ao}. (4) H*-adsorbed sites form an interface dipole layer with a monolayer level thickness. (5) Due to the dipole, SBH changes and this causes change of the diode current.

An analysis based on the above mechanism gives the following equation for the reverse current $I_0(t)$ at time t.

$$(\log I_0(t)) / (\log I_0()) = 1 - \exp(-(t-t_d)/)$$
 (1)

where $^{-1} = _{a}^{-1} + _{d}^{-1}$, $(logI_{0}()) = N_{a0}/(1 + _{a}/_{d})$, is a constant and represents increment due to hydrogen. $_{a}^{-1}$ is most likely proportional to the H* concentration at interface.

2)Comparison with experiments

Figure 5 shows the C^{-2} -V plots taken during hydrogen exposure in air. Straight line characteristics are seen, and they are shifted with hydrogen exposure, keeping the same slope. This confirms directly that hydrogen exposure causes change of the SBH values, as assumed in (5) of the above.

Examples of fitting of Eq.(1) to measured currents are shown by solid curves for data in vacuum shown in **Fig.3**. They excellently fit the experimental data plotted in the log scale. Similar excellent fitting was obtained also for the data in air shown in **Fig.2**. Thus, main features of experiment can be explained by the above model.

The values of the time constant obtained by fitting are plotted vs. P_{H2} , in **Fig.6**. In vacuum, d seems to be large, and d is controlled by a. On the other hand, d seems to become smaller in air due to presence of oxygen which



Fig.5 C⁻²-V plots taken during hydrogen hydrogen exposure in air.



Fig.6 Values of $% \mathcal{B}_{\mathrm{B}}$ obtained by fitting vs. hydrogen pressure, $P_{\mathrm{H}2}$

makes response slower and the current saturation level much more dependent on P_{H2} . Theoretically, is expected to be proportional to square root of P_{H2} , giving a slope of -1/2 in **Fig.6**, if supply of H is controlled by the equilibrium mass reaction law between H₂ and H*. Experimentally, a slope of -1/2 is obeyed only for small P_{H2} values in vacuum, and a slope of -2/3 is seen for other cases. This is due to non-equilibrium effect together with presence of oxygen causing a strong reaction between H* and oxygen on the Pt surface. Further work is needed to elaborate these points.

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