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Hydrogen-Induced Dipoles and Sensing Principles of Pt-Ti-O gate Si-MISFET Hydrogen Gas Sensors

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Abstract

Distribution of hydrogen-induced dipoles in platinum-titanium-oxygen (Pt-Ti-O) gate structures of Si-MISFET hydrogen gas sensors has been observed by H-specific $^{1}H(^{15}N,\alpha\gamma)\,^{12}C$ nuclear reaction analysis (NRA). The sheet number of hydrogen-induced dipoles under N_2-diluted 1% H_2 atmosphere @50°C is estimated as $2.2x10^{14}/cm^2$. The averaged vertical components of dipole-moments is estimated as 82.5D, if the relative dielectric constant of modified TiOx layer and the sensing amplitude ΔV_g(V) are assigned by 114 and 624.4mV. We have found that the hydrogen-induced dipoles are generated in Pt-side modified TiOx layer, and also localized around specific thick pathway of the corridor originated from platinum grain-boundaries.

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Keywords: hydrogen gas sensors, Pt-Ti-O, Si-MOSFET, hydrogen-induced dipoles, nuclear reaction analysis, NRA, hydrogen microscope

1. Introduction

We have developed novel platinum-titanium-oxygen (Pt-Ti-O) gate Si-Metal-Insulator-Semiconductor hydrogen gas sensors [1-3]. The Pt-Ti-O gate Si-MISFETs have unique gate structures composed of titanium and oxygen accumulated around platinum grains on top of a novel mixed layer of nanocrystalline TiOx and super heavily oxygen-doped amorphous titanium formed on SiO_2/Si substrates. The Pt-Ti-O gate structures are schematically

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described in Figure 1. The sensing characteristics of Si-MISFET-type hydrogen gas sensors have been known to be well described by phenomenological Langmuir formula for isothermal dissociated hydrogen gases on the surface of palladium gates [4]. It leads to excellent fittings of the sensing amplitude of ΔV_g (V), *i.e.*, threshold voltage (Vth) shift, against hydrogen gas concentrations [3-4]. It has been explained that migrated dissociated hydrogen atoms on the Pt-surfaces reach to the surfaces of gate oxides through Pt grain boundaries and hydrogen induced dipole-moments cause the Vth shift depending on the hydrogen concentrations. The ΔV_g (V) can be described by

$$\Delta V_g = \Delta V_{gmax} \sqrt{C/C_0} / (1+\sqrt{C/C_0}) \quad (1)$$

where ΔV_{gmax} represents maximum sensing amplitude, and "central hydrogen concentration" (C_0) represents the hydrogen concentration to produce half-occupied states of adsorption sites on the surface of gate oxides [2,3]. One of the typical sensor characteristics in nitrogen-diluted 1% H_2 atmosphere is shown in Figure 2 [5].

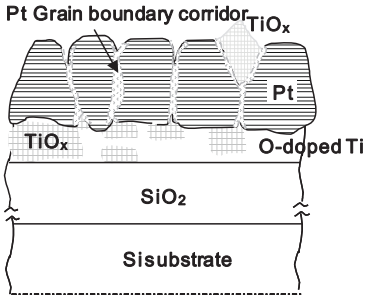

Fig. 1 Schematic structural model of Pt-Ti-O gate Si-MIS structures after air annealing Pt(15nm)/Ti(5nm)-gate Si-MOS structures at 400 °C for 2 h and post hydrogen annealing.

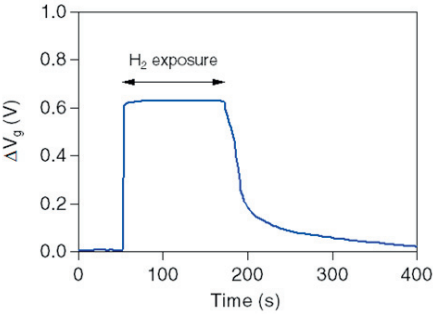

Fig. 2 A typical response curve of hydrogen sensing amplitude ΔVg for Pt-Ti-O gate Si-MISFET hydrogen gas sensors in nitrogen diluted 1.0% hydrogen gas. The sensor operation temperature is 115 °C.

As was discussed in the last paper [3], our Pt-Ti-O gate structures have two advantages of large ΔV_{gmax} and large C_0 compared with hitherto-developed Si-MOSFET hydrogen sensors. Two parameters of ΔV_{gmax} and C_0 for air-diluted hydrogen gas responses from several institutes [3] are shown in Table I and Fig. 3. The steep gradient of sensor characteristics of Pt-Ti-O gate structures is due to large value of ΔV_{gmax} of Table I. In general, Pt-gate structures make hydrogen atoms penetrate only grain-boundaries so that ΔV_g(V) is smaller compared with those of Pd-gates structures. The large ΔV_g(V) of Pt-Ti-O structures will be due to thick corridor.

Table I Two parameters of ΔV_{gmax} and C_0

Institutes	ΔVgmax(mV)	C_0 (ppm)	Range (ppm)
Hitachi	1365	4388	100-10,000
Tokyo Gas	830	130	1-10,000
THORN EMI	377	68.6	5-500
Okayama	194	30.1	8-800
Linköping	333	229	7-500

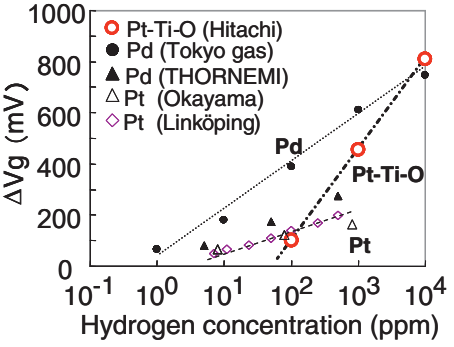

Fig. 3 Hydrogen sensing amplitude ΔVg vs. hydrogen concentration in air.

As the parameter C_0 represents a central hydrogen concentration to be measured, 4388ppm of C_0 seems to be nearly ideal value for the hydrogen detection apparatus toward explosion prevention with lower limit hydrogen concentration 4%, and also the large ΔV_{gmax} represents higher sensitivity for hydrogen gas detection. Although it can well describe sensor characteristics phenomenologically, it can not be said that physical pictures of hydrogen behaviour around platinum and titanium layers are clearly described. Direct evidence and/or quantitative measurements for hydrogen-induced dipoles have been strongly required from establishing hydrogen sensing

mechanism and/or clarifying TiOx-related surface physics. In this paper we apply “hydrogen microscope”, NRA (Nuclear Reaction Analysis) [6], to the Pt-Ti-O gate structures and analyze the hydrogen behaviour in the gate structures.

2. Experimental

2.1. *Sample preparation and TEM analysis*

In accordance with the sensor fabrication process reported in [1-3], we have applied the sensor chips to TEM observation. We have also prepared the test samples of the Pt-Ti-O gate MIS structures applied to NRA analysis. The test samples of Pt-Ti-O gate MIS structures are prepared by using Electron Beam (EB) evaporation of platinum and titanium on thermal silicon dioxide films (124nm) on p-type Si substrates, which had a resistivity of 10.5 Ωcm and (100) orientation inclined at an off-angle of four degrees in the [010] direction. Then, the samples composed of Pt(15 nm)/Ti(5 nm)/SiO_2(124 nm)/Si substrate were divided into small pieces (about 15 × 15mm), and were annealed in air at 400 ℃ for two hours and succeeding post hydrogen annealing.

The specific thick pathway of the corridor originated from platinum grain-boundaries is explicitly observed in Fig. 4(a) by Scanning Transmission Electron Microscopy (Hitachi HD-27700 Cs-corrected STEM). Associated TEM-EDX analysis clearly indicates that the thick corridors are composed of titanium and oxygen accumulated around platinum grains in Figs. 4(b), (c).

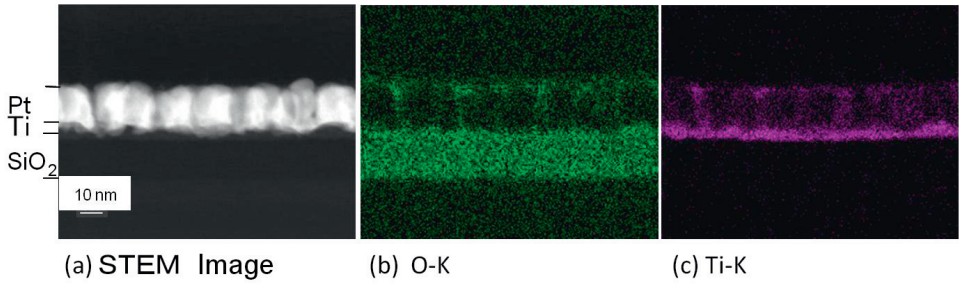

Fig. 4 STEM image (a), TEM-EDX analysis of Oxygen (b) and Titanium (c) for Pt-Ti-O gate structure(gate oxide thickness of SiO_2 is 18 nm).

The STEM image (Fig.4 (a)) and TEM-EDX analysis (Fig.4 (b) and(c)) for Oxygen and Titanium affirmatively confirm the concept of the Pt-Ti-O gate structure in Fig.1

2.2 *Analysis of Hydrogen distribution by Hydrogen microscope; NRA techniques*

As the depth resolution of NRA techniques [6], the 5MV Van der Graaf Tandem accelerator in the Microanalysis Laboratory (MALT) of the University of Tokyo, has been excellently improved within about 1nm, we think NRA is one of the best experimental methods to investigate the distribution of hydrogen-induced dipoles around modified TiOx layer. The $^{15}N^{2+}$ ion beam irradiates the surface of Pt-Ti-O samples, then the 4.43MeV γ-ray emittes from the following nuclear reaction between ^{15}N and ^{1}H,

$$^{15}N + {}^{1}H \rightarrow {}^{12}N + \alpha + \gamma\ (4.43\ \mathrm{MeV}) \qquad (2)$$

where the amplitude of γ-ray is proportional to the hydrogen concentration. As the resonant width is very narrow, 1.8 keV, the spatial resolution can be very narrow in principle. Since the nuclear reaction is resonated at 6.835 MeV (E_{res}), the incident Energy Ei and the stopping power (*dE/dz*) define the probing depth (z) as $z=(Ei-E_{res})/(dE/dz)$. The reaction depth position was calculated by the stopping power by using the atomic profiles of Pt,Ti,O, and Si from TEM-EDX analysis (Fig.4) of Pt-Ti-O gate sample.

Figure 5 shows hydrogen profiles depending on three conditions; (1) initial, (2) 1% H_2 in N_2 charged at 50°C 20min, (3) H_2 removed at 150°C 20min. The measurement temperature is fixed at -110ºC in order to keep the

distributed hydrogen atoms in the Pt-Ti-O structures. After all the measurements, the Pt-Ti-O sample was taken out from the experimental chamber, and annealed in air at 400ºC for 2h in order to extract the charged hydrogen gases. This sample was also measured by NRA apparatus. The measurement result is shown by white circle (○) in Fig.5. It indicates that all the charged hydrogen atoms in the modified TiOx layer disappear.

Figure 6 shows the converted hydrogen profile between hydrogen number-density vs. depth from Pt surface. We have found $2.2x10^{14}/cm^2$ hydrogen-induced dipoles around Pt/modified TiOx interface and also H_2 accumulation in corridors of Pt-layer. In general sensing amplitude ΔV_g can be described by using the averaged vertical components of dipole-moments μ and the relative dielectric constant ε of modified TiOx layer in combination with sheet number n of hydrogen-induced dipole moments,

$$\Delta V_g = \mu n/\varepsilon \quad (3)$$

We could determine the sheet number of hydrogen-induced dipole moments; however, the relative permeability ε of modified TiOx layer is not definite. If the relative permeability ε of modified TiOx layer is assumed to be 114 expected from bulk TiOx materials, and the ΔV_g are assigned by 624.4mV at 115ºC operation, the estimated vertical component of hydrogen-induced dipole moments become a too big value of 82.5D. We think that there will still remain a puzzle of the size of hydrogen-induced dipole-moments.

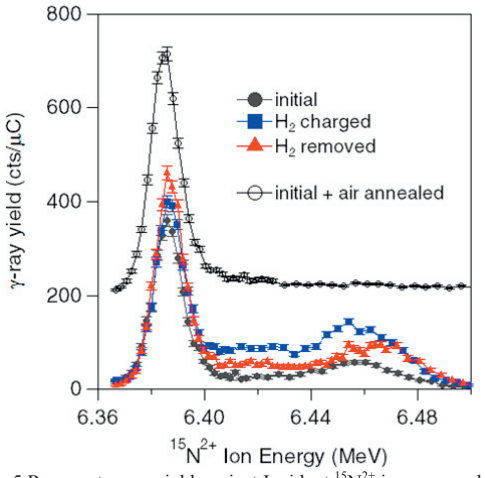

Fig. 5 Resonant γ-ray yield against Incident $^{15}N^{2+}$ ion energy dependence. The vertical origin of "Initial+air-annealed" shifts to 200.

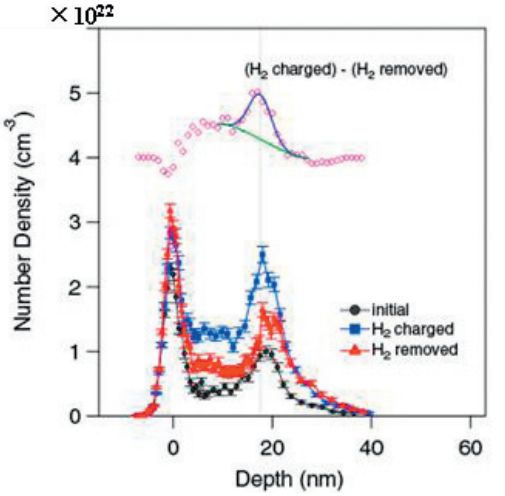

Fig.6 Hydrogen distribution in Pt-Ti-O gate structure

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