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TPD Detection of Hydrogen Absorbed in GaAs during Electrochemical Hydrogen Evolution Reaction

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Temperature programmed desorption (TPD) technique was employed to detect hydrogen absorbed in n-GaAs during electrochemical hydrogen evolution reaction (HER). It was found that 5.63×10^{15} atom cm^{-2} of D atom which is equivalent to 10 monolayers adsorption was absorbed in GaAs after HER for 12 h at -1.5 V (vs. Ag/AgCl) in 0.5 M D_2SO_4/D_2O.

It is well known that surface states play important roles in semicondutor electrochemistry. The potential distribution at semiconductor/electrolyte interfaces is significantly altered by introduction of surface states.1) The kinetics of electrochemical reactions at semiconductor electrodes are also affected by surface states. Surface states may act as a mediator for electron transfer leading to larger current2) or as recombination centers leading to smaller photocurrent.3) Spectral response of photocurrent may be extended to a longer wavelength range due to the excitation via surface states.4) Thus, the knowledge of the nature and origin of surface states is very important to understand the electrochemical characteristics of semiconductor electrodes. In some cases, surface states are introduced during electrochemical processes and the electrochemical characteristics of the semiconductor electrode change accordingly. Yoneyama et al. demonstrated that surface states were formed during photoelectrochemical hydrogen evolution reaction (HER) at p-GaP electrode, leading to higher photocurrent and extension of spectral response.5) They suggested that impregnated hydrogen is the origin of the surface states based on several indirect evidences.

In this paper we proved directly that hydrogen is *absorbed* in GaAs during electrochemical HER by employing temperature programmed desorption (TPD) technique.

n-GaAs single crystal wafers (Si doped : 0.84 x 10^{18} cm^{-3}) were obtained from Laser Diode, Inc. An ohmic contact to the crystal was made by using In metal and ensured by heating at 250 °C for 20 min in He atmosphere. The electrode surface was etched in HNO_3-HCl (1:1, v/v) before each experiment. Electrochemical HER was carried out in 0.5 M D_2SO_4/D_2O solution, since the background level of $H(H_2)$ is relatively high in a TPD apparatus. D_2SO_4 (Merck Corp., 96-98%) and D_2O (Merck Corp., NMR grade) were used to prepare electrolyte solution. The electrochemical HER was carried out potentiostatically with a potentiostat (Nikko Keisoku NPGS-301s) in an ordinary three electrode cell at room temperature after the solution was deaerated by passing purified He gas for at least 30 min.

TPD measurement was carried out by using an apparatus of High Vacuum Lab., Dept. of Nuclear Engineering, Faculty of Engineering, Hokkaido University.[6)] The block diagram of the apparatus is shown in Fig. 1. The volume of the analysis Chamber was 1.0 x 10^{-3} m^3 and its ultimate pressure was 5 x 10^{-6} Pa. After the HER treatment GaAs was rinsed thoroughly with H_2O in air to remove D_2O and D_2SO_4 on the surface and transferred to the analysis chamber. The sample was heated by an infrared light furnace (1.2 kW) with a heating rate of 10 K min^{-1} up to 550 °C to avoid the decomposition of GaAs. The desorbing D_2 gas (M/e=4) and HD gas (M/e=3) were detected by a quadrupole mass spectrometer (QMS). The sensitivity of the QMS for HD and D_2 gas was 2.53 Pa A^{-1} and 3.73 Pa A^{-1}, respectively.

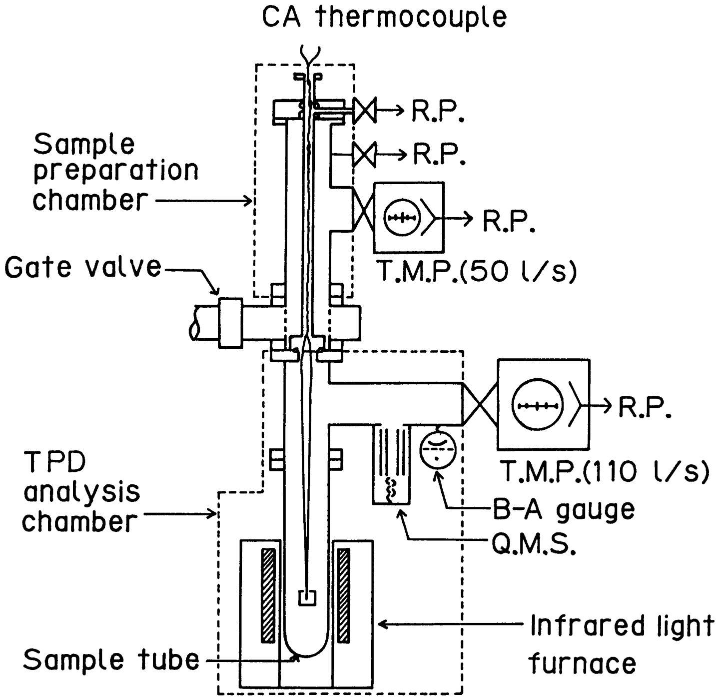

Fig. 1. Temperature programmed desorption (TPD) apparatus.

Figure 2 shows TPD spectra of D_2 (M/e=4) and HD (M/e=3) desorbed from GaAs at which HER took place for 12 h at -1.5 V in 0.5 M D_2SO_4/D_2O. The inset of Fig. 2 shows the time course of the cathodic current during HER. The current increased with time as was the case in photoelectrochemical HER at p-GaP,[5)] suggesting the change of the nature of the electrode during HER. The TPD spectra show that D atom is really contained in GaAs. The spectrum of HD shows a peak around 320 °C and the spectrum of D_2 is very broad. Several possibilities can be considered as the reason for the fact that the amount of HD desorbed was higher than that of D_2. As mentioned before, background level of H_2 (M/e=2) in the TPD apparatus was quite high compared with that of HD (M/e=3) and D_2 (M/e=4), suggesting the existence of high concentration H source in the system. One possible H source is residual water in the vacuum system. Thornton et al. reported that H_2O dissociated partially on GaAs (110).[7)] Since GaAs was rinsed with H_2O before transfer to the vacuum chamber, GaAs surface should be covered with large amount of water which also acted as a H source. The number of desorbed gas molecules, N, can be calculated by using[8)]

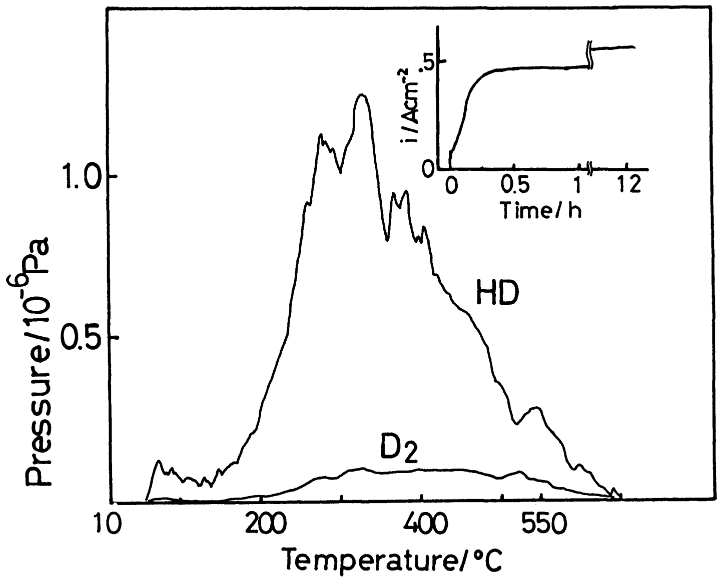

Fig. 2. TPD spectra of D_2 (M/e=4) and HD (M/e=3) of n-GaAs at which HER took place for 12 h at -1.5 V in 0.5 M D_2SO_4/D_2O. Inset : Time dependence of cathodic during HER.

$$N = \frac{s}{A\,kT_0}\int_0^\infty \Delta P\,dt \qquad (1)$$

where A is the surface area of the sample, T_0 is the room temperature, k is the Boltzmann constant, s is the speed of exhaust which is 3.0×10^{-3} m^3 s^{-1} for HD and 1.9×10^{-3} m^3 s^{-1} for D_2, respectively and ΔP is the pressure difference before heating and at time t after heating. By integrating the area of each spectrum according to Eq. 1, the number of desorbed HD and D_2 is calculated as 4.97×10^{15} molecules cm^{-2} and 3.32×10^{14} molecules cm^{-2}, respectively. Thus, the total number of desorbed D atom is 5.63×10^{15} atom cm^{-2} ($=4.9 \times 10^{15} + 2 \times 3.32 \times 10^{14}$). Since the surface density of atoms exposed at the (100) face of GaAs is

6.27×10^{14} atom cm^{-2} and hydrogen adsorbs on both Ga and As atomically[9)] the amount of D atom desorbed is equivalent to ca. 10 monolayers of adsorption.[10)] This result suggests that the hydrogen (D) atom is not only adsorbed on the surface of GaAs but also absorbed in GaAs during HER. Furthermore, it is rather difficult to think that adsorbed hydrogen existed on GaAs surface after the exposure to air. If GaAs was dipped in 0.5 M D_2SO_4/D_2O for 12 h and then rinsed by H_2O, the amount of desorbed HD was only less than 1/10 of that of Fig. 2. Thus, it is concluded that the HER induces the absorption of hydrogen into GaAs lattice.

The effects of absorbed hydrogen on the change of the nature of the electrode and the increase of HER rate are under investigation.

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10) The roughness factor is not taken into account in this estimation. Since single crystal was used, roughness factor should not be too large.

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