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EFFECT OF THE Ru^{+++} TREATMENT ON THE ELECTROCHEMICAL HYDROGEN EVOLUTION REACTION AT GaAs ELECTRODES

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The electrochemical hydrogen evolution reaction (H.E.R.) both at n-GaAs and p-GaAs electrodes in dark was accelerated significantly by the dip treatment in $RuCl_3$ solution but the photocurrents at p-GaAs decreased by the treatment. These results and impedance analyses show that the Ru^{+++} treatment introduces not only catalytic surface for H.E.R. but also surface states which act as recombination centers.

Recently, strong attention has been paid to the effect of the deposition of metal[1-3] or of the adsorption of metal ions[4,5] on the kinetics of electrochemical reactions at semiconductor electrodes. The modification of semiconductor surface by metals which catalyze the hydrogen evolution reaction (H.E.R.) has been reported to increase the photoconversion efficiency of the photoelectrochemical H.E.R. at p-type semiconductors significantly.[6,7] Bockris *et al*. correlated the shift of potential by the metal treatment both at p-Si under illumination[8] and at n-Si in dark[3] with the exchange current density of H.E.R. at the metals which were used for the treatment and stressed the importance of the catalytic role of the adsorbed metals. The energetic information for this treatment is, however, not provided well and several models have been proposed. In this communication, we investigated H.E.R. not only at naked and Ru^{+++} treated n-GaAs electrodes in dark but also at naked and Ru^{+++} treated p-GaAs electrodes of three different carrier concentrations under pulsed illumination. Results show that the dark currents due to H.E.R. both at n- and p-GaAs electrodes increased by the treatment but the photocurrents, i.e., the difference between the currents under illumination and those in the dark, at p-GaAs electrodes decreased, suggesting the introduction of surface states which act as recombination centers.

The H.E.R. in dark at n-type semiconductors is accompanied with no complication due to carrier recombination and its study provides us with fundamental information for the elucidation of the mechanisms of the photoelectrochemical H.E.R. at p-type semiconductors. The current-potential relation of a thoroughly etched n-GaAs electrode[9] in dark is shown in Fig. 1 (——). The overpotential for H.E.R. at n-GaAs is rather large but is decreased by the Ru^{+++} treatment[10] (---). The large overpotential in dark at n-GaAs which could not be due to surface recombina-

tion and significant decrease by the Ru^{+++} treatment mean that the catalytic activity of GaAs itself for H.E.R. is low and enhanced significantly by the Ru^{+++} treatment.[11] Accordingly, the Ru^{+++} treatment is expected to increase the photoconversion efficiency at p-GaAs. Thus, the current-potential relations of naked and Ru^{+++} treated p-GaAs electrode[12] under pulsed illumination[13] were studied. Although the dark current increased significantly by the Ru^{+++} treatment as was the case at n-GaAs, the photocurrents decreased. The higher the carrier concentration, the smaller the photocurrents and at a Ru^{+++} treated p-GaAs of 1.09×10^{19} cm^{-3}, only small bumps were observed in the current-potential relation by the illumination as shown by arrows in Fig. 2. Thus, the Ru^{+++} treatment accelerates H.E.R. in dark but decreases the photocurrent efficiency. These results suggest that the Ru^{+++} treatment introduces not only a catalytically active surface for H.E.R. but also surface states within the energy gap which act as recombination centers. To prove the introduction of surface states, the impedance measurements were carried out at naked and Ru^{+++} treated p-GaAs electrodes.[14] The results were analysed by using an equivalent circuit shown in Fig. 3 which takes into account the contribution of surface states. Typical examples of the plots between the imaginary component of the admittance due to surface states and modulation frequency at naked and Ru^{+++} treated p-GaAs are shown in Fig. 3. The results clearly show that the Ru^{+++} treatment increases the surface states capacitance quite significantly.[15] Actually, the impedance of naked p-GaAs can be analysed very well without considering surface state components in the equivalent circuit

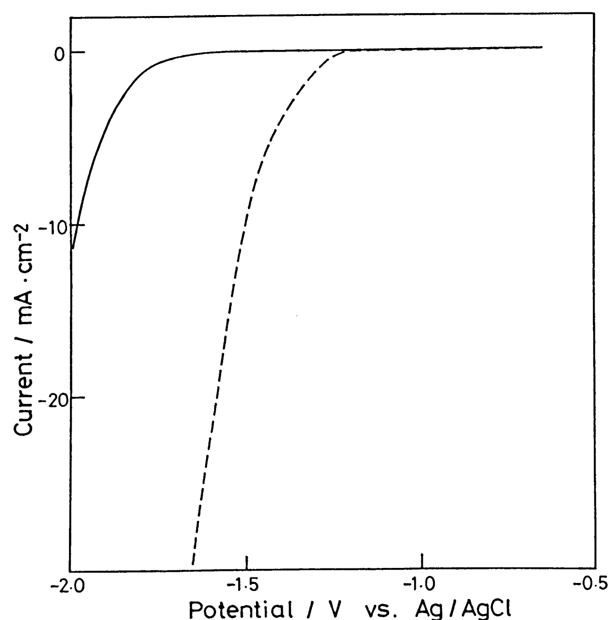

Fig. 1. Current-potential relations of thoroughly etched (——) and Ru^{+++} treated (---) n-GaAs in 1 M KOH. Sweep rate: 5 mV/s.

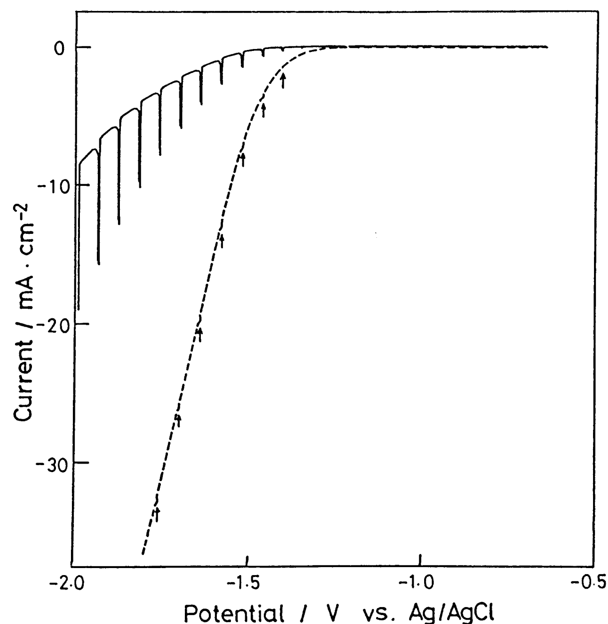

Fig. 2. Current-potential relations of thoroughly etched (——) and Ru^{+++} treated (---) p-GaAs under pulsed illumination in 1 M KOH. Arrows point small bumps. Sweep rate: 5 mV/s.

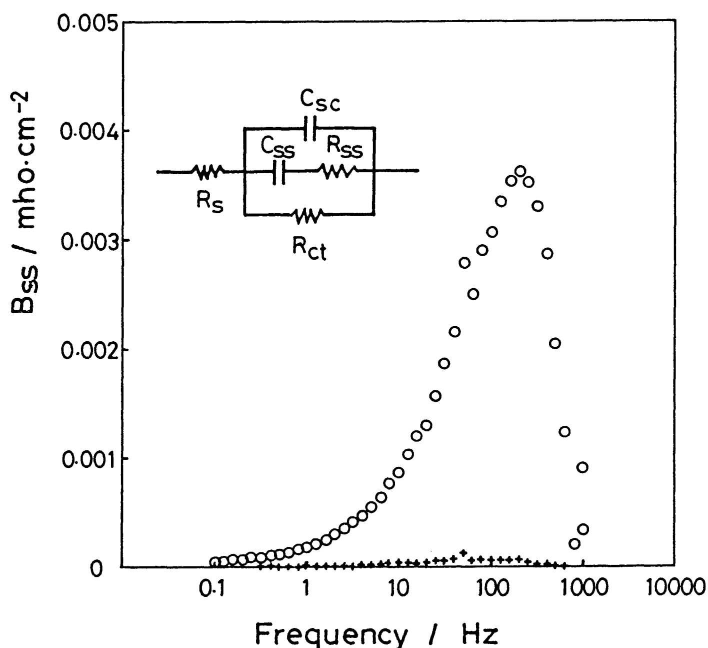

Fig. 3. Frequency dependence of the imaginary part of the admittance due to surface states analysed by using the equivalent circuit shown as inset where R_s is the bulk resistance, C_{sc} is the space charge capacitance, R_{ct} is the charge transfer resistance, C_{ss} is the surface state capacitance and R_{ss} is the surface state resistance.
+: naked p-GaAs. o: Ru^{+++} treated p-GaAs. -0.9 V vs. Ag/AgCl.

and the capacitance thus obtained gives good linear Mott-Schottky plots. Heller proposed the removal of surface states at n-GaAs by the Ru^{+++} treatment[16] while Butler and Ginley reported the introduction of the states at p-GaP by the same treatment.[17] The present results support the latter. In the case of p-InP, the Ru^{+++} treatment increased the photoelectrochemical hydrogen evolution reaction rate quite significantly[18] contrary to the present results at p-GaAs and this is the first time that the negative effect of the Ru^{+++} treatment on the photoelectrochemical kinetics is reported. One possible reason for the opposite effect of Ru^{+++} treatment on the photoelectrochemical H.E.R. kinetics at p-InP and that at p-GaAs could to be as follows. It is known that GaAs and InP represent two different limiting cases as far as the essential aspects of surface and interface recombination are concerned.[19] According to the unified model for interface states by Spicer *et al.*,[20] surface states are expected to be introduced by a wide variety of metal adsorbents near the conduction-band minimum at InP and near midgap at GaAs, respectively. Since the surface recombination is most effective when the recombination centers are located at midgap, surface recombination velocity at GaAs is considered to be faster than that at InP. Thus, the Ru^{+++} treatment increases both H.E.R. rate and recombination velocity at p-GaAs but more dominantly the latter process, resulting in the decrease in the photocurrent and the increase in the dark current. On the other hand, the increase of the recombination velocity at p-InP by the Ru^{+++} treatment is not so significant that the photocurrent increases because of the catalytic activity increase.

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9) n-GaAs samples used for this study were doped with Si ($4.2\text{-}8.0 \times 10^{18}$ cm^{-3}). Ohmic contacts to the n-GaAs electrodes were made by using In-Ga alloy. Etching was carried out in a HNO_3-HCl (1L1) solution.
10) The Ru^{+++} treatment of the electrodes was carried out by dipping GaAs electrodes for 2 min in a solution containing 0.10 M HNO_3 and 0.01 M of unhydrous $RuCl_3$ (Wako Pure Chemicals Co. Ltd.). The Ru^{+++} treated electrodes were subsequently rinsed thoroughly with purified water prior to experiment. XPS measurements of Ru^{+++} treated p-GaAs suggest ruthenium existed as Ru(0) on GaAs surface.
11) The flat band potential of n-GaAs was not shifted by the Ru^{+++} treatment.
12) Three types of the p-GaAs samples were used for the experiments. 1. Zn doped (1.09×10^{19} cm^{-3}); 2. Zn doped (2.35×10^{18} cm^{-3}); 3. Cd doped (2.3×10^{17} cm^{-3}). Ohmic contacts to the p-GaAs electrodes were made by using In-Zn alloy. Etching was carried out in a HNO_3-HCl (1:1) solution.
13) A 500W Xe lamp (Ushio Denki Co. Ltd., UXL-500D-0) with a heat absorbing filter (Toshiba Co. Ltd., IRA-20) was used as a light source. Pulsed light (1 s illumination and 10 s in dark) was provided by using an electro-magnetic shutter (Copal Co. Ltd., EMS No.0) which was controlled by a personal computer (Nippon Electric Co. Ltd., PC-8801).
14) A frequency analyser (NF Electronic Instruments, Ltd., S-5720) controlled by a PC-8801 personal computer via GP-IB interface was used for the impedance measurements.
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