12

INTERACTION OF WATER AND HYDROGEN WITH Pd(111) SINGLE CRYSTAL STUDIED BY TDS AND $\triangle \Phi$

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I. INTRODUCTION

Interaction of water and hydrogen with the nearnoble metals(Pt, Pd) and Ni has been extensively studied over the last decade. It is found that water is adsorbed non-dissociatively on Pt and Pd surfaces. On Ni surface, however, H_2O is adsorbed molecularly at low temperature but subsequent heating to T> 200 K causes dissociation of some of the adsorbed H_2O. The dissociated H eventually desorbs as H_2 and the OH groups thus formed on the surface recombine at higher T to form H_2O and adsorbed O. It is believed H_2O is adsorbed on metal surface through the lone pair of oxygen atom and decreased the work function of metal.

In this study we examined the types and strengthes of adsorbed H_2 and H_2O on the Pd(111) single crystal by the work function change($\triangle \Phi$) and thermal desorption spectroscopy(TDS) under UHV conditions.

II. EXPERIMENTAL

Pd(111) crystal(8mm diameter, 2mm thickness) was spot-welded via two 0.25mm tantalum wires to the toungsten rods cooled by liquid nitrogen. The clean surface was prepared by a repeated cycles of Ar^+ ion sputtering(2 keV, $2\mu A/cm^2$) and annealing at elevated temperature(1023 K). The temperature was controlled by PID controller and the exposure was controlled by molecular leak valve. H_2 and H_2O wewe detected by QMS(VG, Monitorr). We measured the work function change using the contact potential difference(CPD) method(error range= ±1mV).

III. RESULTS AND DISCUSSION

1. TDS and $\triangle \Phi$ of H_2 on clean Pd(111)

Fig.1 shows the thermal desorption spectra of H_2 on Pd(111). The surface was exposed to different coverages of the H_2 at a sample temperature of 250 K. Large exposures result in the shift of peak maximum to the lower temperature. Different from Pd(110) having $\alpha_1, \alpha_2, \beta_1, \beta_2$ states, the Pd(111) have only two α_1 and β_2 states. Fig.2 shows the work function change associated with a TD spectra containing only β_2 peak. The desorption of β_2 state begin to appears at 300 K and causes $\triangle \Phi$ decrease(about 180mV). Fig.3 shows the relationship between $\triangle \Phi$ and coverage(θ) for H_2 adsorption. At the coverage of 0.4L the β_2 state begin to saturate and the curve of $\triangle \Phi$ versus coverage(θ) become flat. This means that the monolayer of surface covered with H_2 and begin to form multilayer above 0.4L.

2. TDS and $\triangle \Phi$ of D_2O on clean Pd(111)

Fig.4 shows the thermal desorption spectra of H_2O on Pd(111). At the large exposures the new peak appears at ~150 K. Fig.5 shows the work function change associated with a TD spectra containing C_1 and A_2 peak. The desorption of C_1 and A_2 state causes $\triangle \Phi$

increase. The work function increase during desorption clearly shows an inflection point which separates the two stages of desorption. The desorption of A_2 state makes much more change than the desorption of C_1, and it can be assigned the A_2 state as monolayer state and the C_1 state as ice layer adsorbed on the monolayer of H_2O.

IV. CONCLUSION

The hydrogen adsorbed in the β_2 state(300K– 350K) increased $\triangle \Phi$ of Pd(about +180mV). Above 0.4L the surface become saturated with H_2.

The adsorbed H_2O molecule form A_2, C_1 state and decreased $\triangle \Phi$ of Pd(about –600mV) through lone pair electron of oxygen.
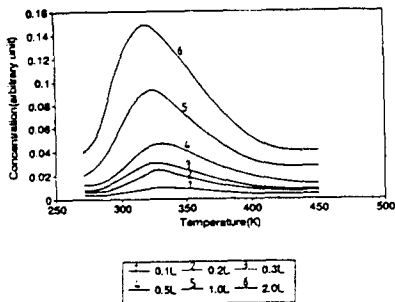

Fig.1 Thermal desorption spectra of H_2/Pd(111). The adsorption was performed for various exposures at T=250K. The various desorption states are marked in the figure. The heating rate was 2 K/s.
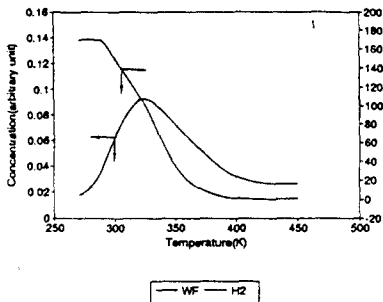

Fig.2 Correlation of thermal desorption and $\Delta \theta$. The Pd(111) surface was exposed to 1.0 L H_2 at 250 K. The heating rate was 2K/s.
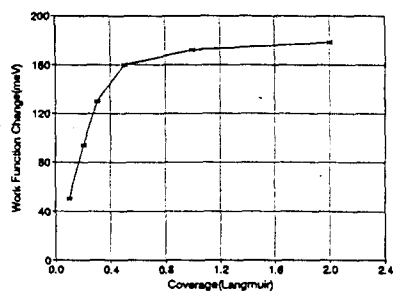

Fig.3 Work function change on Pd(111) surface as a function of hydrogen exposure at 270 K.
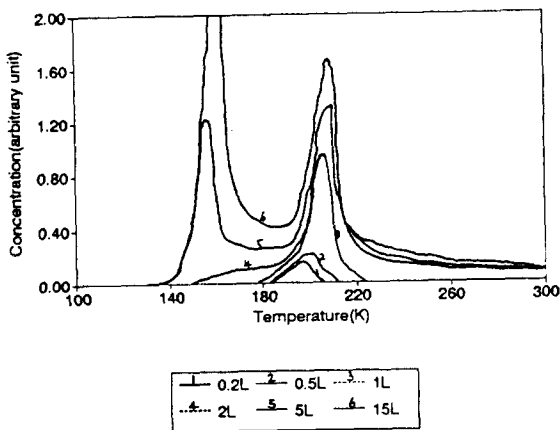

Fig.4 Thermal desorption spectra of H_2O/Pd(111). The adsorption was performed for various exposures at T=100K. The various desorption states are marked in the figure. The heating rate was 2 K/s.
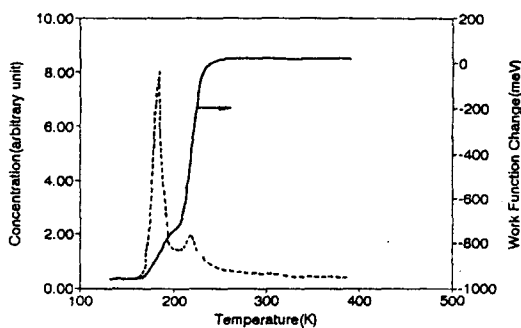

Fig.5 Correlation of thermal desorption and $\Delta \theta$. The Pd(111) surface was exposed to 30 L H_2O at 100 K. The heating rate was 2K/s.