ABSTRACT

We have studied the electronic structure of polycrystalline PdH₀.₆ at 100K by means of photoelectron spectroscopy (XPS and UPS). In PdH₀.₆ as compared to Pd the 4d-band is shifted away from Eₚ and N(Eₚ) is considerably decreased. In contradiction to earlier investigations we do not observe a band at 5eV. However, we see weak emission at 8eV probably related with the hydrogen induced states or with chemisorbed hydrogen. The chemical shift of the 3d₅/₂ core level is very small (+0.15 ± 0.10eV). A weak additional peak at 5.5eV is found on Pd samples which have been exposed to O₂ at 600K.

INTRODUCTION

Pd dissolves at room temperature some hydrogen in the α-phase (PdH₀.₀₁) and forms at the equilibrium pressure of ≈10mbar the β-phase PdH₀.₆. At higher pressure the hydrogen content of the β-phase increases towards stoichiometric PdH.₁.

Many bandstructure calculations were performed for PdHₓ²⁻⁴. An overview on the different methods and the results was given recently by Switendick². All the calculations have the following features in common, which can be tested experimentally:
- The 4d-band of Pd is modified and shifted relatively to Eₚ. The density of states N(Eₚ) decreases from 1.1 states/eV unit cell for Pd to 0.25 states /eV unit cell in PdH.³.
- A new band is formed about 7eV below Eₚ. It is mainly derived
from s- and d-states of Pd. Its position shifts with the hydrogen concentration.

- A small charge transfer seems to occur.

The decrease of $N(E_F)$ is in good agreement with results from specific heat (cf. ref\(^3\)) and magnetic susceptibility measurements\(^5\).

The electronic structure of PdH\(_x\) and of hydrogen chemisorbed on Pd was investigated by several groups by means of photoelectron spectroscopy using X-rays (XPS) or UV radiation (UPS):

Eastman et al.\(^6\) evaporated Pd at $5 \times 10^{-6}$ Torr H\(_2\) onto a substrate at 350°C and exposed the film subsequently at room temperature to 170 Torr H\(_2\) for 30 min and analyzed it with UPS. An additional peak was detected at 5.4 eV and interpreted as the hydrogen induced band of β-phase Pd hydride. No decrease of $N(E_F)$ was observed. The analysis was probably made at room temperature in ultrahigh vacuum.

Antonangeli et al.\(^7\) analyzed electrolytically charged PdH\(_{0.6}\) with XPS. They observed additional states from 5.5 to 8 eV which they related to the hydrogen induced states. No variation of $N(E_F)$ was observed. The Pd 3d\(_{5/2}\) core level is shifted from 334.8 eV in Pd to 334.9 eV in PdH\(_{0.6}\). Again, sample temperature and hydrogen pressure during the analysis are not indicated.

Veal et al.\(^8\) and Gilberg et al.\(^9\) failed to see the hydrogen induced states of PdH\(_x\) by means of XPS and X-ray emission spectroscopy because the hydrogen escaped through the clean surface.

Demuth\(^10\) found a hydrogen induced peak at 6.5 eV for $1 \times 10^{-6}$ Torr-sec H\(_2\) chemisorbed on Pd(111) at 80K, in agreement with theory\(^11\), whereas Eberhardt et al.\(^12\) observed a similar peak at 7.9 eV on Pd(111) which was exposed to $2 \times 10^{-6}$ Torr sec H\(_2\) at 100K.

The discrepancies between the experimental results of different groups about the hydrogen induced states of PdH\(_x\) and between theory and experiment about $N(E_F)$ led us to the reinvestigation of PdH\(_x\) by means of XPS and UPS.

EXPERIMENTAL

The analysis was performed on a VG Escalab spectrometer using Mg Ka (1253 eV), He I (21.2 eV) and He II (40.8 eV) radiation. The analyzer was set to give a resolution of $=1.0$ eV for Mg Ka and 0.2 eV for He I,II. $E_F$ and the binding energy scale were calibrated on Au. Apart from the valence band we also investigated the Pd 3d\(_{5/2},3/2\) core levels. The photoemission was measured normal to the surface.