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Adsorption of Pd Deposited on Ag (100) Surface

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Abstract : PdAg(100) ordered surface alloys have been prepared by e-beam evaporation technique *in-situ* in UHV and were investigated using normal incidence *x*-ray standing wave method with wiggler radiation. The Pd deposited preferably occupies 4 fold hollow site on Ag(100) surface. Ordered alloys could be prepared upto about 25% Pd composition and for the alloys of higher Pd concentrations, long range order disappears due to the strong disorder induced by Pd in Ag (100) crystal. In the ordered alloys a short range ordered phase of Ag c(2X2) develops for Pd coverages above 1.5 ML.

Keywords: X-ray Standing Waves, adsorption, Coherent fraction and position, surface structure

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1. Introduction

Pd-Ag alloy system possesses fcc structure and offers a prototype system for theoretical studies due to negligible volume effects on alloying. Surface alloy formation and inter diffu-sion of Pd was observed when Pd was deposited on Ag (100) kept at elevated temperatures. [1-3] Surface alloys were also formed on Ag (110) surface by depositing Pd.[4, 5] In these studies it was observed that Pd depletes into the Ag(100) surface. Pd is more stable in the sub-surface layers than on the top surface of Ag(100) since the Pd has higher surface energy compared to Ag.[6] Pd deposited on Ag surface can deplete and intermix with Ag and forms alloys in a wider composition range. Interesting aspect about Pd on Ag(100) surface is that the Pd intermixing in the sub-surface region upto about 50ºA which provides a way to prepare continuous range of ordered Pd*x*Ag1¡*x* surface alloys.

2. Experiment

PdAg(100) ordered surface alloys have been prepared *in-situ* in $1.0X10^{9}$ Torr pressure in the preparation chamber of THE-XPS machine at BW2 beamline, HASYLAB/DESY, Germany by e-beam evaporation of Pd onto clean Ag(100) surface. Various compositions of surface alloys were prepared by evaporating 0.5, 1.5, 2.0, 2.5 and 3.0 ML equivalents of Pd. Prior to Pd deposition, Ag(100) surface was cleaned by sputtering with 1.0 keV argon ions followed by an annealing at 450^{0}C. Pd depositions were carried out keeping the substrate Ag crystal at 250^{0}C and were investigated using high normal incidence X-ray standing wave (NIXSW) techniques. Ag(200) reflection at 3034.8 eV was used for NIXSW measurements.

3. Results

Figure 1 shows the NIXSW data of 0.5 ML and 1.5 ML Pd coverages on Ag(100). Both position and fraction of Ag substrate which was represented by TEY, exhibited high values indicating a well ordered substrate crystal. TEY is representative of the bulk Ag crystal and the effect of small amount of Pd is insignificant on the structure of the bulk Ag crystal. Therefore, F_C (89%) and P_C (97%) actually correspond to the bulk Ag crystal. Interestingly, Pd $3d_{5/2}$ yield (Fig. 1(b)) which represents the adsorption characteristics of Pd on Ag (100) surface also exhibits high coherent parameters, with fraction 87% and position 96%. These values suggest that Pd on Ag(100) possesses single adsorption site and the inter layer spacing of Ag-Pd is nearly same as that of Ag-Ag. Figure 2 shows the possible adsorption sites on Ag (100) crystal. Most stable adsorption site is the four fold hollow site (H4). The Ag-Pd distance obtained using this geometry is 2.86 A^{0}, which is in close agreement with the sum of the metallic radii of Ag (1.44 A^{0}) and Pd (1.37 A^{0}) indicating the formation of PdAg(100) surface alloy.

As the Pd is known to be more stable in the subsurface region, intermixing of Pd and Ag take place upto few layers below the surface and forms alloy with Ag. When the Pd coverage increased to 1.5 ML, substrate coherent position exhibited only a nominal change from 97% to 96%(Fig. 1 (c)) suggesting that the substrate structure remains unchanged at this coverage. Decrease in coherent fraction 83% can be due to intermixing and disorder induced by Pd. The coherent fraction of Pd, drastically came down (Fig. 1 (d)) due to intermixing and disorder. Due to multiple site occupancy coherent position of Pd decreased to 89%. Shape of the total electron yield curve remains the same. Coherent position of the TEY

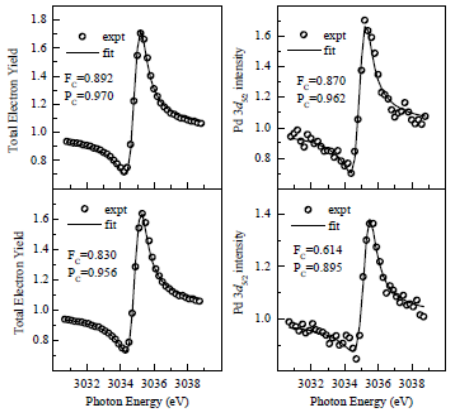

FIG. 1: (a) Total Electron Yield and (b) Pd $3d_{5/2}$ intensity of of 0.5 ML Pd on Ag(100) (c) Total Electron Yield and (d) Pd $3d_{5/2}$ intensity of 1.5 ML Pd on Ag (100).

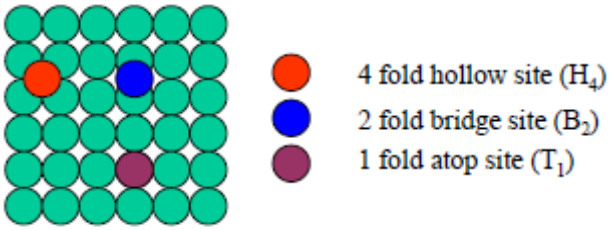

FIG. 2: Adsorption sites on 100 surface

came down to about 90% for 2.5 ML Pd coverage. Strikingly, Pd $3d_{5/2}$ yield exhibits a drastic change in shape and coherent parameter values. Coherent position drops down to 75% for 2.0 ML coverage and to 62% for 2.5 ML coverage indicating possibly the gradual development of new structural phase with Pd coverage. Interestingly, LEED pattern showed p(1*X*1) for all coverages. However, background in the LEED pattern gradually increased with coverage of Pd. This new phase was not observed in LEED pattern suggesting that the newly developing phase does not possess long range order.

4. Discussion

Adsorbate induced surface reconstruction of Ag crystal surface has been extensively studied by both experimentally and theoretically.[10{14] On Ag

(100) surface, a missing row re- construction c(2x2) was observed upon oxygen or bromine adsorption [10, 11]. Top surface of the Pd/Ag(100) system is terminated by Ag p(1x1). Pd depletes few layers below into the Ag crystal by site exchange mechanism.[1] and forms PdAg alloy. As the coverage increased, Pd can deplete much deeper into Ag crystal. This was observed in our XSW measurements as the reduction in the coherent fraction of the total electron yield. Interestingly, for all the coverages, a p(1x1) LEED pattern observed through the XSW measurements indicated the development of the new Ag c(2x2). This new phase does not possess long range order and it was not observed in the LEED. Ag c(2x2) phase was also observed in (100) surface of AgPd alloys[6]. Initial Pd deposition upto about 1.5 ML forms a substitutional alloy with Ag p(1x1) un-reconstructed Ag crystal. As the coverage increases, reconstructed Ag c(2x2) regions gradually develop. These regions stay below the unreconstructed Ag plane by an amount $0.7A^0$[6]. Pd atom can take H_4 hollow site in plane with the Ag c(2x2) region. This region seems to be growing from 2.0 ML coverage onwards. Drastic decrease in coherent position of in the XSW data is due to the development of these regions along with the long range ordered p(1x1)Ag-Pd alloy.

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