

Pd registry on Ag (111): X-ray standing wave study

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Abstract : Normal incidence x-ray standing wave (NIXSW) has been formed inside the Ag crystal normal to the Ag(111) planes by making x-rays of energy 2629.4 eV normally incident on the crystal surface. The standing wave field extends above the surface of the crystal with the periodicity of the <111> planes of the Ag crystal. Pd photoelectron signal detected with the standing wave field exhibits modulations depending on the adsorption site of the Pd on Ag(111) surface. From the coherent position of the Pd photoelectron yield, the Pd height above the crystal surface has been determined and was found to be three fold hollow site. The shape of the Pd signal exhibits drastic changes due to intermixing with energy when thickness is increased gradually.

Keywords : X-ray standing waves, Metallic alloys, Bragg Reflection

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1. Introduction

Metal atoms deposited on a dissimilar metal surface pose fundamental challenges in condensed matter physics. The surface and interface properties of the bilayer system are primarily decided by the adsorption site of the adsorbate. The study of adsorbate structure is of prime concern for catalysis, corrosion and many surface related phenomena. Pd deposited on Ag surface can deplete and intermix with Ag into the Ag due to higher surface energy of Pd compared to Ag and forms alloys in a wider composition range [1,2]. Pd-Ag alloy system possesses fcc structure and offers a prototype system for theoretical studies due to negligible volume effects on alloying. Pd and Ag are known to be completely miscible in their bulk form which provides an opportunity to prepare continuous Pd_xAg_{1-x} random bulk alloys [3]. Surface alloy formation and inter diffusion of Pd was observed when Pd was deposited on Ag (100) kept at elevated temperatures [4,5,6]. Surface alloys were also formed on Ag (110) surface by depositing Pd [2,7]. 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[1]. Pd deposited on Ag surface can deplete and intermix with Ag and forms alloys in a wider composition range. Steiner *et. al.* measured core level shifts for random bulk alloys of Pd_xAg_{1-x}, prepared using arc melting technique. CLS of Pd showed a change of sign at about x=35% and the CLS of Ag did not exhibit such sign change. This interesting behavior of experimentally observed CLS in Pd-Ag system was explained using first principle calculations within the complete screening picture which includes both initial and final state effects [8,9,10].

Though, there are numerous investigations, studying PdAg random bulk alloys, but the ordered PdAg alloys are not well explored. We have prepared PdAg(111) ordered alloys by evaporating Pd onto Ag(111) surface to investigate the structural and electronic properties in detail. Since the lattice matching is good between Pd and Ag crystals, substrate induced strain on the surface alloy is negligible and this provides a feasible way to study the well ordered PdAg surface alloys. Another interesting aspect about Pd on Ag(111) surface is that the Pd intermixing in the sub-surface region upto about 50Å which provides a way to prepare continuous range of ordered Pd_xAg_{1-x} surface alloys.

2. Experiment

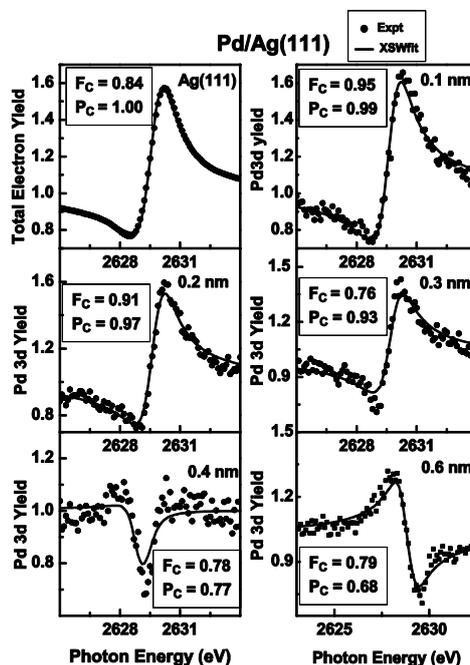
Pd has been deposited on clean Ag(111) surface in 1.0×10^{-9} Torr pressure in the preparation chamber of THE-XPS machine at BW2 beamline at HASYLAB/DESY by e-beam evaporation method. Pd thickness has been varied from 0.1 to 0.6 nm. Prepared thin films have been investigated using normal incidence X-ray standing wave (NIXSW) technique. Ag(111) reflection at 2629.4 eV was used for NIXSW measurements. We have used Pd 3d_{5/2} photoelectron signal for obtaining Pd adsorption characteristics and the total electron yield (TEY) signal for substrate Ag structure.

3. Results and Discussion

Figure below shows the modulation of total electron yield (TEY) and Pd 3d_{5/2} intensity when photon energy is scanned through the Ag(111) Bragg reflection energy for normal incidence (2629.4 eV). For small Pd coverages (upto 0.3 nm) TEY and Pd 3d_{5/2} intensity exhibit qualitatively similar modulation with photon energy indicating same adsorption site of Pd on Ag(111) surface. The coherent fraction (F_C) drops down gradually from 0.95 to 0.78 when Pd coverage increases from 0.1 to 0.3 nm. Pd layer has the same periodicity as that of Ag(111) for small coverages. The intensity modulation of Pd 3d_{5/2} changes drastically from that of TEY for 0.4 and 0.6 nm Pd coverages. As Pd mixes with Ag, a structural reconstruction of the surface alloy region takes place at these

coverages and thus the position of Pd comes down to about 70%. Pd adsorption site changes from three fold hollow site to bridge site after 0.3 nm coverage.

Figure: Total Electron Yield and Pd 3d_{5/2} intensity across the Bragg reflection of Ag(111) energy at normal incidence for various Pd coverages.



Conclusion

Normal incidence X-ray standing wave technique is used to obtain the adsorption characteristics of the Pd deposition on clean Ag(111) surface. Pd goes into three fold hollow site for low coverages. At higher coverages it occupies bridge site due to the change of surface structure of the substrate Ag due to intermixing of Pd upto few nm.

References

- [1] P.T. Wouda, M. Schmid, B.E. Nieuwenhuys, P. Varga, Surf. Sci. 417, 292 (1998)
- [2] C. Massobrio, F. Patthey, H.-V. Roy, and W.-D. Schneider, Phys. Rev.B 52, 2063 (1995)
- [3] P. Steiner and S. Hüfner, Acta Metall. **29**, 1885 (1981)
- [4] F. Patthey, C. Massobrio and W.-D. Schneider, Phys. Rev. B **53**,13146 (1996).
- [5] D. A. Arena, R. A. Bartynski, R. A. Nayak, A. H. Weiss, S, L.Hulbert and M. Weinert, Phys. Rev. Lett. **91**, 176403 (2003).

- [6] R. L. Fink, C. A. Ballentine, J. L. Erskine, and J. A. Araya-Pochet, *Phys. Rev. B* **41**, 10175 (1990).
- [7] K. C. Prince and V. Chab, *J. Electron Spectroscop. and Relat. Phenomen.* **52**, 61 (1990).
- [8] I. A. Abrikosov, W. Olovsson, and B. Johansson, *Phys. Rev. Lett.* **87**, 176403 (2001).
- [9] W. Olovsson, I. A. Abrikosov, and B. Johansson, *J. Electron Spectroscop. Relat. Phenom.* **127**, 65 (2002).
- [10] W. Olovsson, L. Bech, T. H. Anderson, Z. Li, S. V. Hoffmann, B. Johansson, I. A. Abrikosov, and J. Onsgaard, *Phys. Rev. B* **72**, 075444 (2005).