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$M_{3,2}$ and $L_{3,2}$ XAFS of Au and Pt Nanoparticles on Porous Silicon

I. Coulthard, A. Bzowski, T.K. Sham, S.M. Heald* and M. Kuhn**

Department of Chemistry, University of Western Ontario, London, N6A 5B7, Canada

** Pacific Northwest Laboratory, Richland, WA, U.S.A.*

*** Physics Department, Tulane University, New Orleans, LA, U.S.A.*

Abstract: XAFS measurements at both the $M_{3,2}$ and $L_{3,2}$ edges of Pt and Au as well as scanning electron microscopy studies have been carried out for a series of porous silicon specimens onto which fine particles of Au and Pt with nanometre and tens of nanometre dimensions have been dispersed. A wet chemistry technique developed in our laboratory was used for the deposition. The Au XAFS clearly show that the Au deposits are essentially Au metal while the Pt deposits exhibit features that are noticeably different from that of metallic Pt. The $M_{3,2}$ and $L_{3,2}$ the XANES and their implications are discussed.

1. INTRODUCTION

Known best for its intense visible luminescence at room temperature, and its sponge-like nanostructure network and vast internal surface area [1], porous silicon, a material produced by electrochemically etching silicon, is also an effective reducing agent [2]. Noble metals can be reductively deposited onto porous silicon from aqueous solutions to form nanoscale sized clusters. These nanoparticle systems are very interesting in that they may display desirable electronic and chemical properties very different from those of the bulk materials [3].

We report some $M_{3,2}$ and $L_{3,2}$ -edge XANES measurements for Au and Pt nanoparticles on porous silicon. Both $L_{3,2}$ and $M_{3,2}$ edge XANES offer means for the characterization of 5d transition metals [4,5] with the former providing long range data for EXAFS analysis and the latter more suitable for surface and thin film studies. Emphasis is placed upon differences in the near-edge absorption features between the bulk material and the nanoparticles. The implications of this on d-charge distribution are noted.

2. EXPERIMENTAL

The porous silicon samples were prepared using methods described previously [2]. Both p- (B doped) and n- (As doped) wafers of (100) orientation were used. The samples were all prepared using a current density of 20 mA/cm² for 20 min. The deposition was carried out using aqueous solutions of Na[AuCl₄] and K₂[PtCl₆] respectively. The nominal coverage of the metals varies from submonolayer to monolayers and is determined by the active sites on the internal surface of porous silicon accessible to the metal complex ions [2]. Results reported here are from specimens with coverage of a couple of monolayers. SEM (Scanning Electron Microscopy) images were recorded utilizing a Hitachi S-4500 Field Emission Scanning Electron Microscope (FESEM) at an accelerated voltage of 5 keV. $M_{3,2}$ edge XANES experiments were carried out at the Double Crystal Monochromator soft x-ray beamline [6] of the Canadian Synchrotron Radiation Facility at the University of Madison-Wisconsin 800 MeV Synchrotron Radiation Center (SRC). $L_{3,2}$ edge XANES were recorded utilizing the X11A beamline of the National Synchrotron Light Source (NSLS) 2.5 GeV X-ray ring at Brookhaven National Laboratory. Both measurements were carried out in a total electron yield mode.

3. RESULTS AND DISCUSSION

Fig.1 shows an SEM image of an aggregate of small gold clusters on the surface of a porous silicon sample. The clusters are well defined and range in size from approximately 30 to 150 nm in diameter; scattered clusters with 10 nm size or smaller are also evident [7]. SEM images of platinum deposited onto porous silicon at the same magnification clearly show the presence of platinum, but no well-defined clusters and aggregates such as those found in Au can be identified. The clusters of Pt on porous silicon are obviously smaller than those of gold and have less tendency to aggregate. As a result, it is expected that differences in the XAFS of the clusters and the metal foils would be more pronounced in the platinum than in the gold as the gold clusters are larger and thus are more bulk-like.

Fig.2 shows the $L_{3,2}$ -edge XANES of gold on porous silicon (Au/n-PS) compared to that of the gold foil. The Au/n-PS system shows a slight decrease in the intensity just above the edge jump indicating that Au atom in this system, on average, is gaining d-charge with respect to the bulk material [8]. This may be due to the increase in gold surface atoms relative to the bulk (Au surface atoms constitute ~4% to ~13% of the total when particle size changes from 30 to 10 nm), surface reconstruction and smaller cluster size. It should be noted that the XANES for Au/PS and Au foil were recorded under same condition and are of high quality and that Au $L_{3,2}$ -edge XANES is very sensitive to changes involving Au 5d charge redistribution [8]. Surface gold is known to have a lower core level (4f) binding energy than bulk gold [9] which indicates that the surface gold atom gains d-charge relative to the bulk. The $L_{3,2}$ -edge

EXAFS of the Au/n-PS systems resembles that of the gold foil which indicates that apart from the size effect, the Au deposited on the porous silicon is essentially metallic gold. The same trend is observed in the $M_{3,2}$ -edge which is more surface sensitive [5]. Au/p-PS exhibits similar behaviour.

Fig 3. shows the $M_{3,2}$ -edge and $L_{3,2}$ -edge XANES for platinum on porous silicon (Pt/PS) compared to that of platinum foil. The Pt/PS system shows a significant increase in the intensity of the whiteline. The increase in the intensity of the $M_{3,2}$ -edge and $L_{3,2}$ -edge whitelines are accompanied by the appearance of a whiteline at the $M_{3,2}$ -edge and $L_{3,2}$ -edge that is absent in Pt metal. This observation indicates that the Pt atoms in the Pt/PS system on average is losing d-charge relative to bulk Pt metal. These results strongly suggest that Pt forms smaller clusters as suggested by the SEM and/or at least some of the surface atoms of the Pt clusters underwent a chemical change after reductive deposition. The latter change is likely oxidation of the surface atoms of the small Pt clusters to produce an oxide and/or a silicide. This is not unreasonable since of all the transition metals, platinum forms silicide under very mild conditions.[10]. We have also observed coverage dependence of the whiteline intensity (the smaller the coverage, the more intense the whiteline) in good accord with this notion. However, since beyond the whiteline the XANES and EXAFS of this system resembles that of the Pt foil it is evident that these surface atoms which have undergone a chemical change still represent a small fraction of the total platinum atoms on the porous silicon. More quantitative analysis of these results will be given elsewhere.

Fig. 1 SEM image of an aggregate of Au clusters on the surface of a p-type porous silicon sample

Fig. 2 Difference curve between L_3 of Au and Au on n-type porous silicon

4 SUMMARY AND CONCLUSION

We have reported some representative $L_{3,2}$ and $M_{3,2}$ XANES for nanoparticles of Pt and Au on porous silicon prepared by wet chemistry methods. Au tends to form larger clusters that aggregate whereas Pt forms smaller clusters that are more reactive and have less tendency to aggregate. The spectral results show that the gold particles are essentially metallic gold. This is unlike the platinum where it is likely that some chemical species are formed on the surface of the clusters.

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References

- [1]. L.T. Canham, Appl. Phys. Lett. **57** (1990) 1046.
- [2]. I. Coulthard, D.-T. Jiang, J.W. Lorimer, and T.K. Sham, Langmuir **9** (1993) 3441.
- [3]. H. Gleiter, Prog. Mater. Sci. **33**(4) (1989) 223.
- [4]. F.W. Lytle, Ber. Bunsenges Phys. Chem. **91** (1987) 1251.
- [5]. T.K. Sham, S.J. Naftel, and I. Coulthard, J. Appl. Phys. **79** (9), 1 May 1996, 7134.
- [6]. B.X. Yang, F.H. Middleton, B.G. Olsson, G.M. Bancroft, J.M. Chen, T.K. Sham, K.H. Tan, and D.J. Wallace, Rev. Sci. Instrum. **63** (1992) 1355.
- [7]. I. Coulthard, and T.K. Sham, XPS results to be published
- [8]. M. Kuhn and T.K. Sham, Phys. Rev. B **49** (1994) 1647.
- [9]. P.H. Citrin and G.K. Wertheim, Phys. Rev. B. **27** (1983) 3176.
- [10]. K.N. Tu, Silicides for Integrated Circuits: Materials Aspects, Symposium H, MRS 1995 Fall

Fig. 3 Difference curves of L_3 and M_3 of Pt and Pt on porous silicon