

## Ag L3-NEXAFS of Electrodeposited Silver on Au(111)

Osamu ENDO<sup>1\*</sup>, Masashi NAKAMURA<sup>2</sup>

<sup>1</sup>Department of Organic and Polymer Materials Chemistry, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

<sup>2</sup>Department of Applied Chemistry and biotechnology, Faculty of Engineering, Chiba University, Inage-ku, Chiba 263-8522, Japan

### Introduction

Thin film growth of hetero metals on solid surfaces is an important topic in material science, electrochemistry and catalysis. Silver has a similar lattice constant to gold (Au 0.4079 nm, Ag 0.4086 nm), hence, a silver thin film on a gold surface is a proper system for heteroepitaxy. At the early stage of the electrochemical deposition on Au(111), silver forms a monolayer and a bilayer film with the same lattice constant as the substrate[1]. Since these processes occur at more positive potentials than the bulk equilibrium one, it is called as underpotential deposition (UPD).

Although the geometrical structure of the deposited films is almost equivalent to that of the bulk Ag(111), the UPD bilayer silver (Ag(UPD2)/Au(111)) exhibits a specific electrochemical response against the chlorine containing solution. The Ag(111) electrode undergoes a surface chlorination at a negative potential than the bulk AgCl formation. In contrast, chlorine on Ag(UPD2)/Au(111) forms only an overlayer at these potentials. In this study, we have measured Ag L3-near edge X-ray absorption fine structure (Ag L3-NEXAFS) spectra of Ag(UPD2)/Au(111) to elucidate the origin of the difference.

### Experimental

Ag L3-NEXAFS spectra were measured at BL-11B with a fluorescence detection mode using silicon drift detector. A disk of Au(111) electrode was cleaned with a flame annealing and quenched with Milli-Q water. After silver was deposited on the surface in the 1 mM AgNO<sub>3</sub> + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, the Au(111) electrode was transferred into an another solution containing 10 mM NaCl + 0.5 M NaOH, covered with a proper amount of chlorine, rinsed with Milli-Q water, and carried to a measurement chamber. All the spectra were taken with the normal incidence.

### Results and Discussion

A black line in Fig. 1 shows a normalized Ag L3-NEXAFS spectrum of Ag(UPD2)/Au(111) covered with a saturation amount of chlorine. Several peaks observed for the bulk Ag (blue line) are smeared out in the Ag UPD2 as indicated by the arrows. Since d-channel dominates in the Ag L3-NEXAFS[2], it is supposed that the structure

of the conduction band with a d-component is different in the Ag UPD2 from that in the bulk Ag. A red line in Fig. 1 displays chlorinated Ag UPD2/Au(111), which was emersed at a potential positive enough for the bulk AgCl formation. The spectral curve from the absorption edge to about 15 eV above exists in an intermediate region between that of the bulk AgCl(green line) and the Ag UPD2. Hence, it is deduced that the second layer in the Ag UPD2 undergoes chlorination, and the first layer in contact with the Au(111) surface possesses the metallic character.

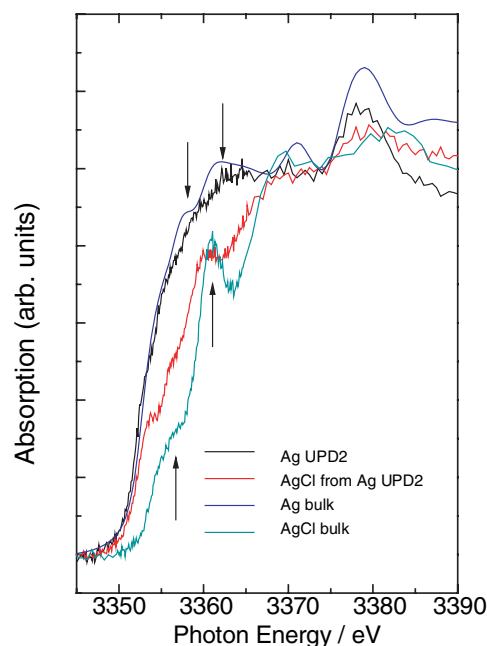


Figure 1. Ag L3-NEXAFS spectra of the Ag underpotentially deposited bilayer on the Au(111) electrode with a saturation amount of chlorine overlayer (black line), the AgCl formed from Ag UPD bilayer (red line), the bulk AgCl (blue line), and the bulk Ag (green line).

### References

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- [2] W. Drube et al., *Phys. Rev. B* 58, 6871 (1998).

\* oendo@cc.tuat.ac.jp