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***In situ* structural study on underpotential deposition of Ag on Au(111)
electrode using surface X-ray scattering technique**

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Abstract

In situ surface X-ray scattering (SXS) measurements were carried out to study the structure of a Ag layer on a Au(111) electrode formed by underpotential deposition (UPD) in sulfuric acid solution. Specular rod profiles showed that a monolayer of Ag was formed at a potential between the second and third UPD peaks, and a bilayer of Ag was formed at a potential between the third UPD peak and bulk deposition. Non-specular rod profiles demonstrated that electrochemically deposited Ag atoms both in the first and second layers were situated at the three-fold hollow cubic closest packing (ccp) site of the underlying Au and Ag layers, respectively.

Keywords: In situ Surface X-ray Scattering (SXS) , Underpotential Deposition (UPD), Ag on Au(111)

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1. Introduction

The deposition of metal on a foreign metal substrate is one of the most important processes not only for fundamental surface science but also for various industrial applications such as electronics, catalysis, sensors, and surface finishing. Although gas phase processes such as vacuum deposition are commonly employed to form metal layers [1], liquid phase processes such as electrochemical deposition should be more economical and convenient than the growth in an ultra-high vacuum (UHV) because they do not require the expensive UHV equipment. The electrochemical deposition of metals has been extensively studied for a long time but structural investigation of the deposits in atomic resolution became possible only recently after Clavilier's method [2], by which single crystals can be rather easily prepared, and several *in situ* surface characterization techniques such as scanning tunneling microscopy (STM), atomic force microscopy (AFM) and surface X-ray scattering (SXS) techniques became available [3-13].

Metals can be deposited on a foreign substrate at potentials more positive than the reversible potential of the bulk phase if the interaction between the deposited metal and the substrate is stronger than that between the deposited metal itself. This process is called underpotential deposition (UPD) and only the first monolayer can be deposited by UPD in most cases as is easily understandable. The UPD process has been one of the central issues of surface electrochemistry in the last decade [13].

Electrochemical deposition including UPD of Ag on Au(111) is one of the most well studied systems. Many peaks in the cyclic voltammogram (CV) in the UPD region suggest that rather complicated processes are involved. Two or three major current peaks with a number of smaller peaks corresponding to UPD have been observed. Furthermore, the CVs reported by various groups are not necessarily the same and some of the peaks are very small or missing in some cases particularly at the evaporated gold electrode, maybe because the quality of the surface was not high. To clarify the details of each process, a wide variety of techniques such as STM [14-19], AFM [20,21], electrochemical quartz crystal microbalance (EQCM) [22], second harmonic generation (SHG) [23], UHV techniques such as low energy electron diffraction (LEED) [21,24], surface extended X-ray absorption fine structure

(EXAFS) using X-ray from a synchrotron radiation source [25], and X-ray diffraction (XRD) using a conventional laboratory X-ray source [26,27] have been applied. STM measurements in a sulfuric acid solution showed an ordered (bi)sulfate adlayer with the $(\sqrt{3} \times \sqrt{7})R19.1^\circ$ structure [19] and the Ag UPD layer with the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure [14,15,19] in the potential region more positive and negative, respectively, than the first UPD peak. The UPD layer with the (1×1) structure was observed just before the bulk deposition was started [14,15,23]. Some groups also found compressed (3×3) , (5×5) , and/or (6×6) structures before the (1×1) structure was formed [19-21,23,24,26].

There is still some controversy on the structure of the UPD layer just before the bulk deposition is started because the total charge of the UPD peaks, $380 \mu\text{C cm}^{-2}$, are more than that of the monolayer, $222 \mu\text{C cm}^{-2}$, but less than that of the bilayers. It has been generally believed that a UPD Ag monolayer is formed just before the bulk deposition is started as the (1×1) structure was observed [14,15] and the excess charge is due to the bulk deposition and the desorption of adsorbed sulfate and/or bisulfate anions during the UPD process [14,15,22]. Recently, however, Exlandiu et al. proposed that the Ag UPD bilayer and not a monolayer is formed on Au(111) before the bulk deposition and the smaller charge originates from the difference in the potential of zero charge (pzc) between Au and Ag [19]. Most of the techniques mentioned above are not suitable to address the question whether a monolayer or a bilayer of Ag is formed. STM, AFM, and LEED can provide structural information only about the top surface layer. Furthermore, the spatial resolutions of STM and AFM are only on the order of \AA , which is much less than the required resolution, 0.1\AA , to discuss the detailed structure of the deposited layer.

SXS should be the most suitable method to determine the precise structure of the UPD Ag layer as it can provide not only the two-dimensional but also the three-dimensional structural information about the interfaces with a very high resolution *in situ* [10,11,28,29]. In this study, we investigated the UPD process of Ag on a Au(111) electrode surface using the *in situ* SXS technique and demonstrated that initially a complete monolayer and then a bilayer, both with a (1×1) structure, were formed just before the bulk deposition started.

2. Experimental

2.1 Materials A Au(111) single crystal disk (diameter: 10 mm, thickness: 5 mm) was purchased from the Surface Preparation Laboratory (Netherlands). The Au(111) disk was electrochemically etched in a solution containing 0.1 M HClO₄ and 5 mM NaCl [30] then annealed at 850 °C for 10 h under an Ar atmosphere in the electric furnace (Denken, KDF S-70). Ultrapure reagent grade H₂SO₄ and HClO₄ and reagent grade Ag₂SO₄ and NaCl were purchased from Wako Pure Chemicals and were used without further purification. Water was purified using a Milli-Q system (Yamato, WQ-500). Ultrapure N₂ (99.9995 %) and Ar (99.999 %) were purchased from Air Water. The Ag and Pt wires (diameter: 0.5 mm, 99.99 %) used as the reference and counter electrodes, respectively, were purchased from Nilaco. A 6.0 μm thick Mylar film (Chemplex, D) was used as the window of the spectroelectrochemical cell, which was specially designed for the *in situ* SXS measurements and was made of Kel-F [31].

2.2 Electrochemical and *in situ* SXS Measurements Both the CV and *in situ* SXS measurements were carried out in the spectroelectrochemical cell. The electrode potential was controlled by a potentiostat/galvanostat (Hokuto Denko, HA-151) and an external potential was provided by a function generator (Hokuto Denko, HB-111). The CV was recorded on an X-Y recorder (Graphtech, WX1200). The Pt and Ag wires were used as the counter and reference electrodes, respectively. Prior to each measurement the Au(111) disk was flame annealed using a Bunsen burner and slowly cooled in air. It was then transferred to the spectroelectrochemical cell with the surface being covered with a drop of pure water to avoid any surface contamination. The electrolyte solution containing 50 mM H₂SO₄ and 1 mM Ag₂SO₄ was deaerated by passing the ultrapure N₂ gas into the solution for more than 30 min prior to the injection into the cell. The potential of the Au(111) electrode was kept at 620 mV (vs. Ag/Ag⁺), which was more positive than the potential of any UPD peak. Only the (111) face was in contact with the electrolyte solution during the CV measurements and the electrochemical deposition of a controlled amount of Ag for the *in situ* SXS measurements. The real surface area was determined from the charge needed for the reduction of the surface gold oxide [32].

The *in situ* SXS measurement was carried out in the following sequence. The electrode potential was scanned from +620 mV in the negative direction at a scan rate of 5 mV s⁻¹ and the potential scan was stopped either at +50 mV or at +10 mV, where no current was observed, then the electrode surface was pushed to the Mylar window. The thickness of the electrolyte layer between the electrode and the window was estimated to be ca. 30 μm. The thin layer configuration has advantages not only in avoiding X-ray scattering by the solution but also in preventing further Ag deposition and/or dissolution. The cell was turned over and mounted on a six-circle diffractometer (HUBER, 5020) installed on a bending-magnet beamline BL4C at the Photon Factory. The X-ray was monochromated by the Si(111) double crystal system and focused by a Rh-coated bent mirror. The beam size of the incident X-ray was 0.2 mm (vertical) × 0.2 – 0.5 mm (horizontal), which was adjusted by a slit which was placed in front of the sample. A wavelength of 1.100 Å was selected to avoid any fluorescence from the Au substrate. All the measurements were carried out in such a mode that the incoming and outgoing angles with respect to the sample surface were equal. At each measuring point, a rocking scan of the ω axis was performed for a background subtraction and for the integration over the mosaic spread of the sample. A reciprocal coordinate system (H, K, L) with two components (H and K) lying parallel with the surface and the other one (L) along the surface normal was used in this study. Specular and non-specular rods were measured along the reciprocal rods perpendicular to the surface, i.e., in the L direction [28].

3. Results and Discussion

Figure 1 shows the CV of the Au(111) electrode measured in the solution containing 50 mM H₂SO₄ and 1mM Ag₂SO₄ in the potential region between +650 and 0 mV (vs. Ag/Ag⁺) at a scan rate of 5 mV s⁻¹. When the potential became more negative than 0 mV, a very large cathodic current due to the bulk deposition of Ag started to flow. The CVs reported by various groups are not necessarily the same and some of the peaks are very small or missing in some cases as mentioned before. The CV of the present study shown in Fig. 1 is very similar to the one obtained by Explandiu et al. [19] and the current peaks are very sharp and well resolved,

showing the very high quality of the electrode surface. Three dominant cathodic peaks were observed at 520 mV (C1), 130 mV (C2), and 30 mV (C3). These peaks were also observed in most of the previous studies and the positions of these peaks are in good agreement with the ones reported before [14,15,19-21,26]. In addition to these peaks, several small cathodic peaks were also observed at 500 mV (C1'), 330 mV (C4), 240 mV (C4'), and 100 mV (C2'). Anodic peaks (A1, A1', A4, A4', A2, A2', and A3) corresponding to these cathodic peaks were also observed. Peak C1' was observed and assigned as the first UPD peak together with peak C1 in most of the previous reports. Peaks C4 and C4' were often missing in the CVs previously reported. Peaks C2 and C2' and peak C3 were considered as the second and third UPD peaks, respectively [19]. The charges corresponding to the first, second and third UPD peaks were $100 \mu\text{C cm}^{-2}$, $60 \mu\text{C cm}^{-2}$, and $220 \mu\text{C cm}^{-2}$, respectively, and were exactly the same as those reported by Explanidui et al. [19]. Chen et al. suggested that peaks C4 and/or C4' were due to a commensurate-incommensurate transition [20]. There is still some controversy on the structure of the UPD layer just before the bulk deposition is started as to whether the monolayer or the bilayer is formed because the total charge of the UPD peaks, $380 \mu\text{C cm}^{-2}$, is more than that of the monolayer, $222 \mu\text{C cm}^{-2}$, but less than that of the bilayers. One reason for this confusion was due to the fact that peak C3 and the current due to the bulk deposition were often not well separated because of the low quality of the electrode surface but the results of Explanidui et al. and ours clearly showed that $380 \mu\text{C cm}^{-2}$ was only due to the UPD as peak C3 was well separated from the bulk deposition. It is, however, impossible to determine the origin of the charge discrepancy and, therefore, whether the monolayer or the bilayer is formed based only on the electrochemical data.

Figure 2(a) shows the specular rod profile measured at 50 mV that is between peaks C2' and C3, i.e., between the second and third UPD peaks. The charge passed before peak C3 was $160 \mu\text{C cm}^{-2}$ corresponding to 0.72 ML of Ag. Very deep dips were observed between the two adjacent bulk Bragg peaks. The rod profiles calculated for the ideally terminated Au(111) surface (- - -) and for the Ag monolayer on a Au(111) surface using the bulk atomic radii of Au and Ag under the assumption that Ag atoms are situated on the three-fold hollow site (—) are also shown in Fig. 2(a). The experimentally observed specular reflectivities (O) are

lower than those calculated for the ideally terminated Au(111) surface around dips, $L = 1.5$ and $L = 4.5$, by a factor of 10^2 but the experimentally observed rod profile matched very well with the solid line, i.e., the profile calculated for the Ag monolayer on the Au(111) surface. There are two three-fold hollow sites on the Au(111) surface, that is, the hexagonal closest packing (hcp) site and the cubic closest packing (ccp) site, but it is impossible to distinguish these two sites by the specular rod profile, because the specular rod profile contains the structural information only for the direction normal to the surface. To obtain information on the in-plane structure, the non-specular reflectivity of the (01) rod profile was also measured at 50 mV (O) and is shown in Fig. 2(b) together with the calculated profiles for the Ag monolayer on Au(111) with three possible adsorption sites, i.e., the ccp (—), hcp (- - -), and atop (— - —) sites. A calculation for the Ag atoms on the ccp hollow site gives the best fit to the observed non-specular reflectivity profile, indicating that the deposited Ag monolayer keeps the fcc stacking sequence of the Au(111) substrate. We also considered the incommensurate structure but the SXS data matched well with the commensurate structure as shown in Fig. 2(b). It is reasonable since the lattice constant of Ag bulk (4.086 Å) is almost the same as that of Au bulk (4.079 Å). These results clearly show that the deposited Ag formed a flat monolayer with Ag atoms situated on the three-fold ccp hollow site in this potential region.

Figure 3 shows the experimentally observed (O) (a) specular and (b) non-specular (01) rod profiles measured at 10 mV that is between peak C3, i.e., the third UPD peak, and the bulk deposition. The charge of the third UPD peak (C3) was $220 \mu\text{C cm}^{-2}$, which is exactly equal to that for the 1 ML deposition of Ag. The shape of these profiles are very much different from those shown in Fig. 2. While there is only one minimum between the two adjacent bulk Bragg peaks in Fig. 2, two minima and one maximum were observed between the two adjacent bulk Bragg peaks in Fig. 3. This type of rod profile suggests the formation of a bilayer [33]. Actually, the experimentally observed specular rod profile shown in Fig. 3(a) (O) is well represented by the profile calculated for the Ag bilayer on the Au(111) surface using the bulk atomic radii of Au and Ag with the assumption that Ag atoms are situated on the three-fold hollow site (—). The experimentally observed non-specular (01) rod profile

is also compared with the calculated profiles for the Ag bilayer on Au(111) with three possible adsorption sites for the Ag atoms of the second layer, i.e., ccp (—), hcp (- - -), and atop (— - —) sites of the first Ag layer whose Ag atoms were assumed to sit on the ccp site of Au(111) as at 50 mV. It is clear that the calculated curve for the ccp hollow site gives the best fit, indicating that the second Ag UPD layer also keeps the fcc stacking sequence of the Au(111) substrate. These results clearly show that the deposited Ag formed a flat bilayer with Ag atoms of the first layer situated on the three-fold ccp hollow site of Au(111) and those of the second layer sitting on the three-fold ccp hollow site of the first Ag layer.

It must be mentioned here that there were some deviations of the data points from the calculated curves. There may be a possibility that a small amount of other phases existed on the surface. To obtain more quantitative structural information, we need to carry out more rigorous fittings by varying the fitting parameters. Thus, the results obtained in this study should be treated as a first approximation.

4. Conclusions

The following conclusions were obtained by the present *in situ* surface X-ray scattering (SXS) study on the structure of the Ag UPD layer on the Au(111) electrode in sulfuric acid solution.

- 1 The formation of the Ag monolayer was completed at the potential between the second and the third UPD peaks and only $160 \mu\text{C cm}^{-2}$ corresponding to 0.72 ML of Ag was passed.
- 2 The bilayer of Ag was formed at the potential between the third UPD peak and bulk deposition.
- 3 Both the Ag UPD monolayer and bilayer keep the fcc stacking sequence of the Au(111) substrate. Thus, the Ag atoms of the monolayer as well as the first layer of the bilayer were situated on the three-fold ccp hollow site of Au(111) and those of the second layer of the bilayer were situated on the three-fold ccp hollow site of the first Ag layer.

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Figure Captions

Figure 1 Cyclic voltammogram of Au(111) measured in 0.05 M H₂SO₄ + 1 mM Ag₂SO₄ at a scan rate of 5 mV s⁻¹. Potential scan was started from 620 mV in the negative direction.

Figure 2 (a) The specular and (b) the non-specular rod profiles (O) measured at 50 mV. (a) The solid and dotted lines are the calculated curves for bare Au(111) and 1 ML Ag on Au(111), respectively. (b) Solid, dotted, and dot-dashed lines are calculated for the Ag adsorption on the ccp, hcp, and atop sites, respectively, of Au(111).

Figure 3 (a) The specular and (b) the non-specular rod profiles (O) measured at 10 mV. (a) Solid line is the calculated curve for 2 ML Ag on Au(111). (b) Solid, dotted, and dot-dashed lines are calculated for the Ag adsorption on the ccp, hcp, and atop sites, respectively, of the (1 × 1)-Ag on Au(111).

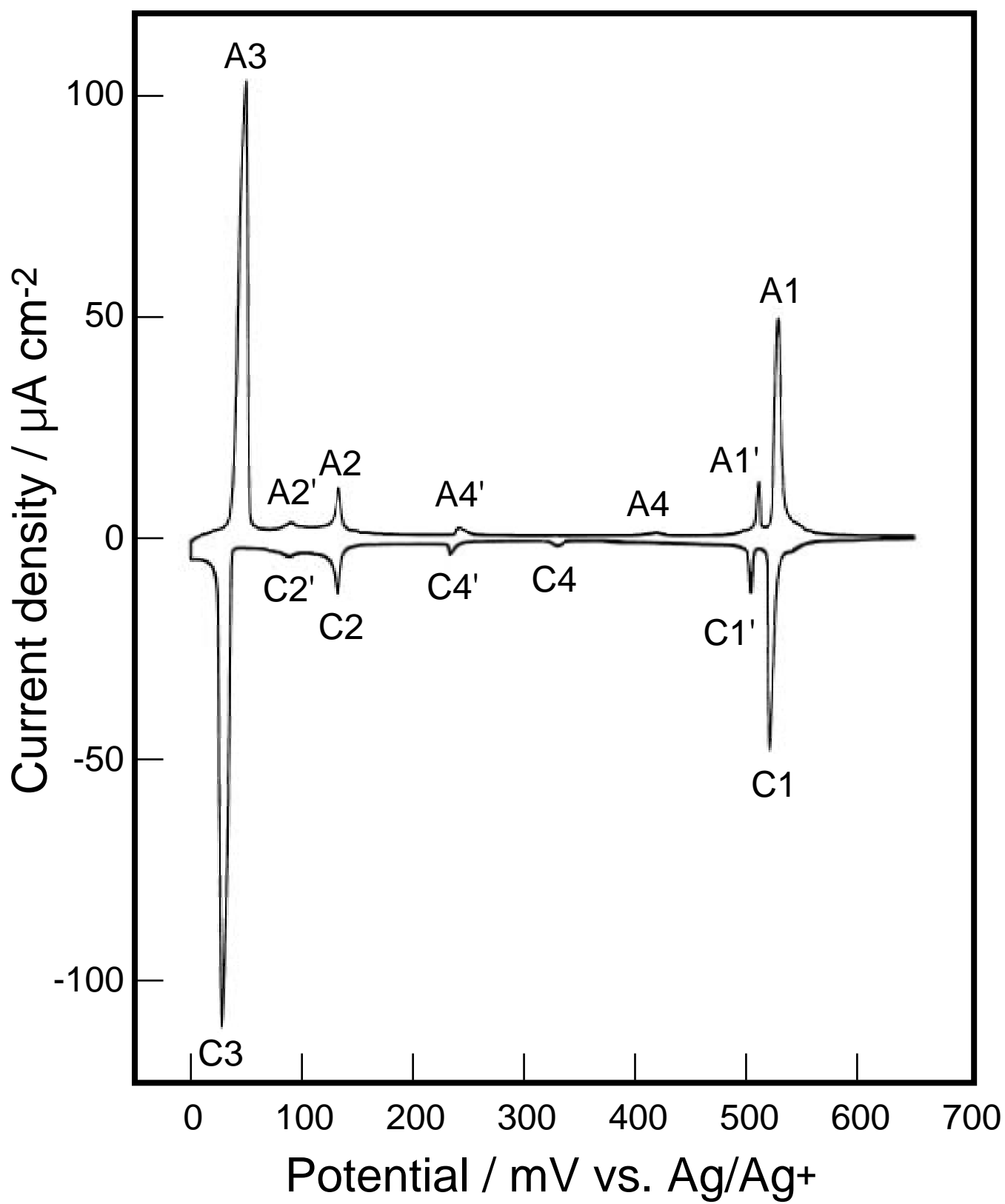


Figure 1
T. Kondo et al.

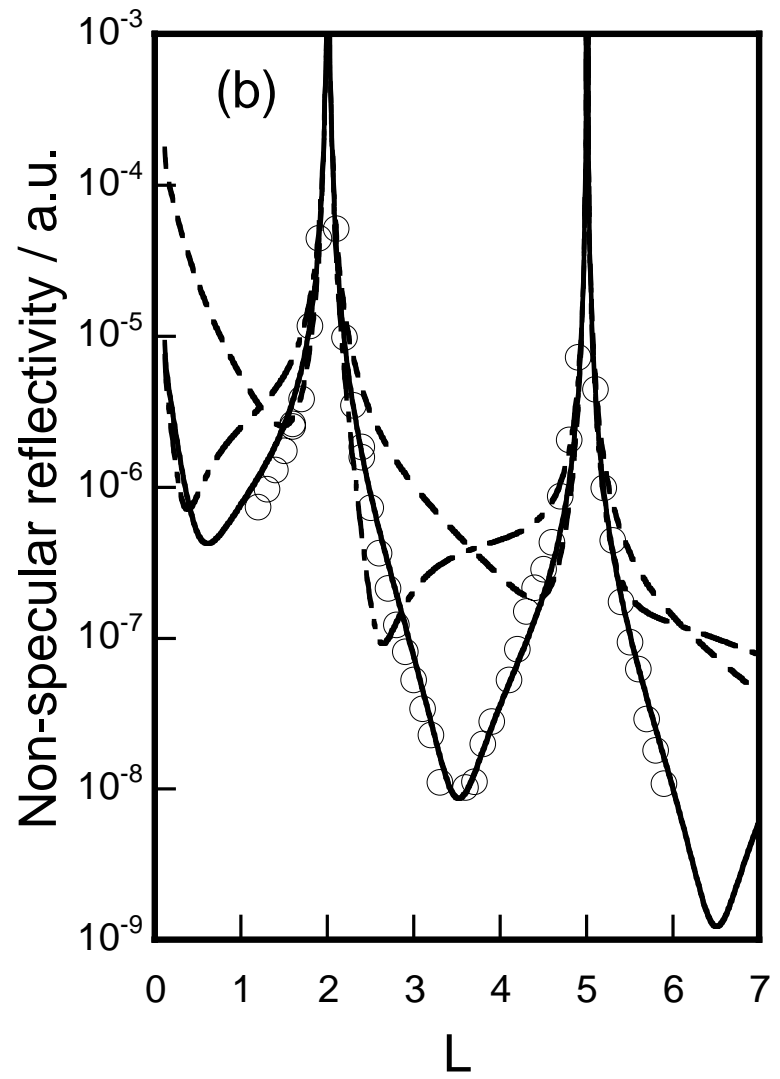
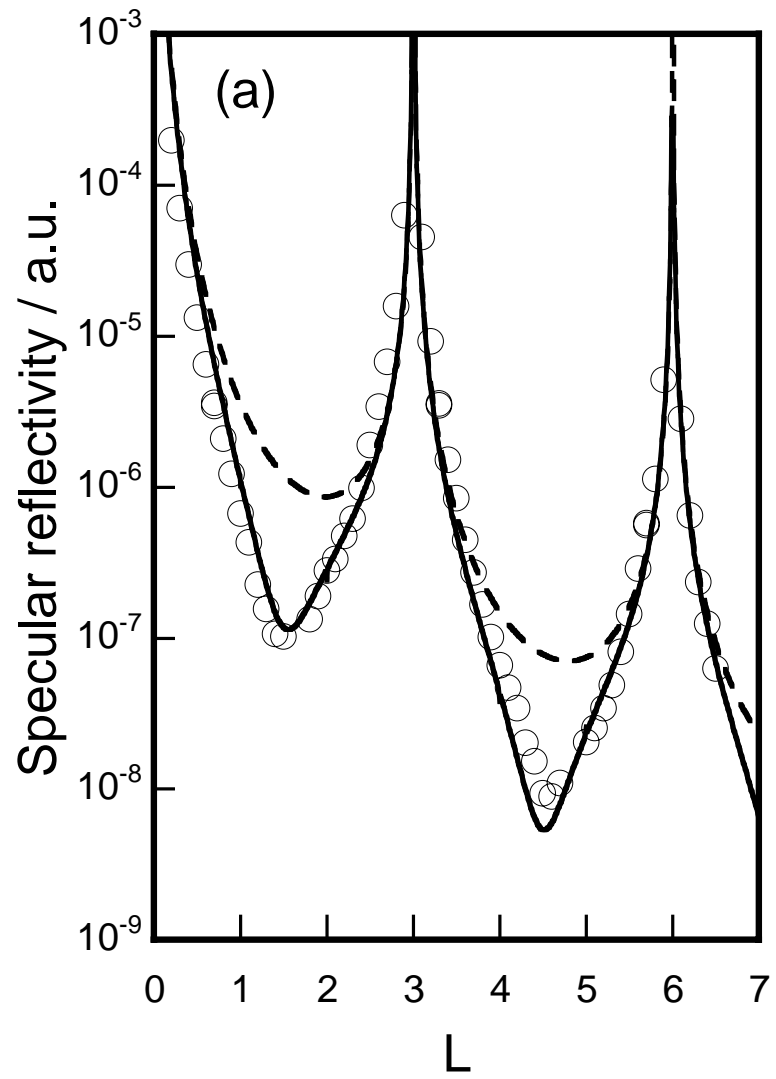


Fig. 2
T. Kondo et al.

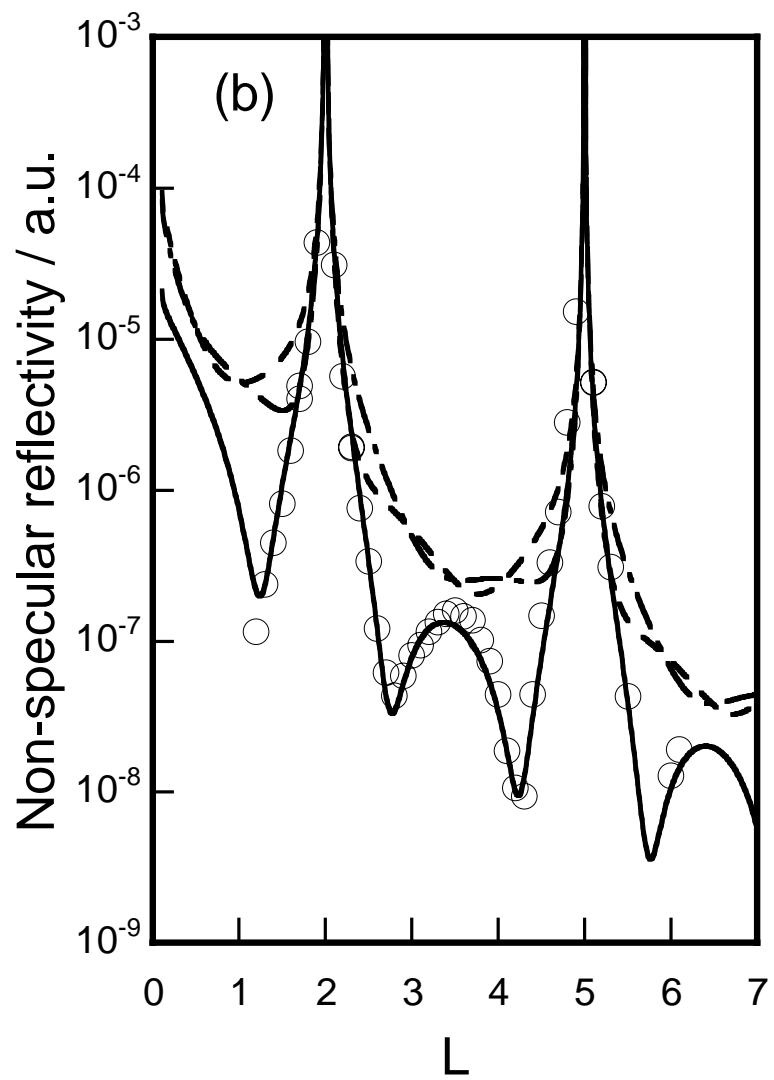
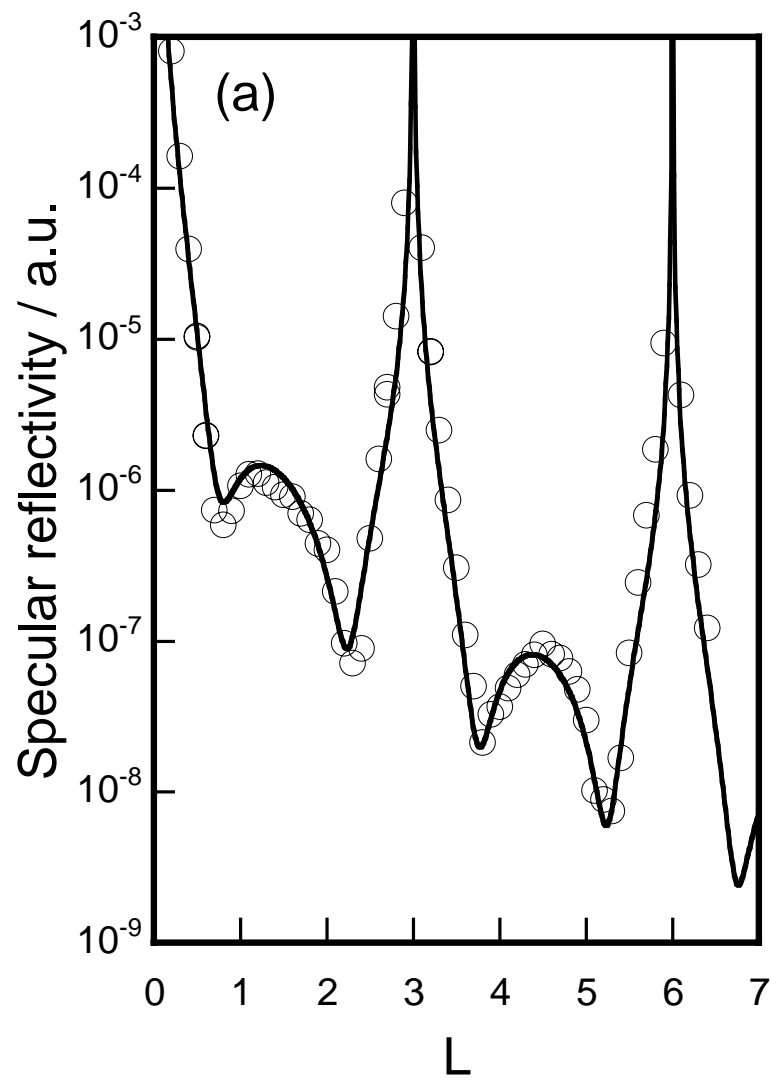


Fig. 3
T. Kondo et al.