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Author(s)	Iwai, T.; Mizutani, G.
Citation	Physical Review B, 72(23): 233406-1-233406-4
Issue Date	2005
Type	Journal Article
Text version	publisher
URL	http://hdl.handle.net/10119/4021
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Description	

Optical second harmonic spectroscopy of reconstructed Au(100) and (111) surfaces

T. Iwai and G. Mizutani*

School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi-shi, Ishikawa 923-1292, Japan

(Received 28 April 2005; revised manuscript received 2 September 2005; published 19 December 2005)

We have performed optical second harmonic (SH) spectroscopy of Au(100) 5×20 and Au(111) $\sqrt{3} \times 23$ surfaces, in order to gain an insight into the formation mechanism of electronic states of reconstructed surfaces. The SH intensity spectra measured in the p -in/ p -out (p -polarized input and p -polarized output) polarization configuration showed peaks near $2\hbar\omega=2.4$ and 2.8 eV for both the Au(100) and (111) reconstructed surfaces, while a peak at $2\hbar\omega=3.2$ eV was observed only for the Au(100) reconstructed surface. The SH intensity peaks near $2\hbar\omega=2.8$ eV are attributed to an electronic transition in the hexagonal structures at the top layers of the two surfaces.

DOI: [10.1103/PhysRevB.72.233406](https://doi.org/10.1103/PhysRevB.72.233406)

PACS number(s): 78.68.+m, 78.66.Bz, 73.20.At, 42.65.Ky

It has been known that the surfaces of some noble metals such as platinum and gold reconstruct in order to reduce their surface energy. The detailed mechanism of this surface reconstruction has not been clarified and has been the topic of many research programs.¹⁻⁸ It has been suggested that d -electronic states near the band gap energy region are involved in the surface reconstruction of noble metals. For example, theoretical calculations have found that the top layer of Au(100) has a stronger tendency to go to a more compact arrangement than that of Ag(100), and that this is mainly due to a stronger participation of the Au d orbitals in the bonding than those of Ag.⁵ Hence, an advanced study of the electronic spectra of reconstructed surfaces will clarify the interaction between the surface lattice and d -electronic states and the mechanism of surface reconstruction.

We have been carrying out optical second harmonic (SH) spectroscopy on Au films^{9,10} and a Au(100) single crystal surface¹¹ in order to study the d -electronic states of these noble metal surfaces. Optical second harmonic generation (SHG) offers information on surface electronic states, since it is allowed only at surfaces for centrosymmetric media.¹² In many of the former studies, the SH response of metal surfaces was discussed using the “jellium” model.^{13,14} In this model, the contribution of free electron gas to the SH response is considered. Introducing a finite corrugation of the effective potential of positive ion cores at the crystal surface, this model predicts correctly the Schockley and image potential surface states.^{15,16}

However, our recent investigations of the SH response of Au surfaces have revealed that the d electrons can make a large contribution. The peak energy in the SH intensity spectra in the d - to s,p -electronic transition region of Au crystalline surfaces depends strongly on the face index on the sample surface⁹ so that the optical transition is suggested to involve the surface d -electronic states. In our previous study we carried out SH spectroscopy on the Au(100) 5×20 reconstructed surface and observed three intensity peaks at $2\hbar\omega=2.4$, 2.8, and 3.2 eV.¹¹ The SH intensity peak at $2\hbar\omega=2.8$ eV was tentatively attributed to a resonant transition from d - to s,p -electronic states with hexagonal structure⁶ formed in the 5×20 reconstructed domain, while that at 3.2 eV was tentatively attributed to a resonance of fourfold

symmetric electronic states formed in the second layer.¹⁷

A part of our main interest in the present paper is to ascertain if these SH intensity peaks at $2\hbar\omega=2.8$ eV and 3.2 eV can also be observed on the Au(111) reconstructed surface. The Au(100) and (111) reconstructed surfaces have structures consisting of (100) and (111) bulk crystals covered by similar hexagonal topmost monolayers. If the electronic states are formed independently in the topmost layer and in the second layer, and the SH intensity peak at $2\hbar\omega=3.2$ eV originates from the fourfold symmetric electronic states in the second layer, the peak at 3.2 eV will not be observed on the Au(111) surface. On the other hand, if the peak at 2.8 eV originates from the hexagonal structure, it will be seen for both the surfaces. In the present paper, in order to check these points and also to examine the effect of the surface atomic arrangement upon the electronic structure, we have carried out a comparative study of the SH spectra of Au(111) $\sqrt{3} \times 23$ and (100) 5×20 reconstructed surfaces. In our results, we did not observe the peak at $2\hbar\omega=3.2$ eV for the Au(111) surface, but observed peaks at 2.8 eV for both the surfaces in the p -in/ p -out (p -polarized input and p -polarized output) polarization configuration. We also found an anisotropic rise in the SH intensity above $2\hbar\omega=3$ eV from the Au(100) reconstructed surface in the s -in/ p -out polarization configuration.

Mechanically polished Au(100) and (111) disks were thermally annealed at 650 °C by flash heating and sputtered by Ar⁺ ions of 0.5 keV for 30 min in an UHV chamber with a base pressure of 2×10^{-8} Pa. After five repetitions of this procedure, we obtained well-defined Au(100) 5×20 and Au(111) $\sqrt{3} \times 23$ reconstructed surfaces¹ with no contamination, as checked by reflection high energy electron diffraction (RHEED) and auger electron spectroscopy (AES). The SH spectroscopy of the Au reconstructed surfaces was carried out in an UHV chamber at room temperature. Optical excitation and observation were done through two glass windows attached to the chamber. The angle of incidence of the excitation beam at the fundamental frequency was 45°. The plane of incidence was parallel to the $[0\bar{1}1]$ and $[1\bar{1}\bar{2}]$ directions on the Au(100) and (111) surfaces, respectively. The experimental setup for the SH intensity measurement was described in our previous paper.¹⁸

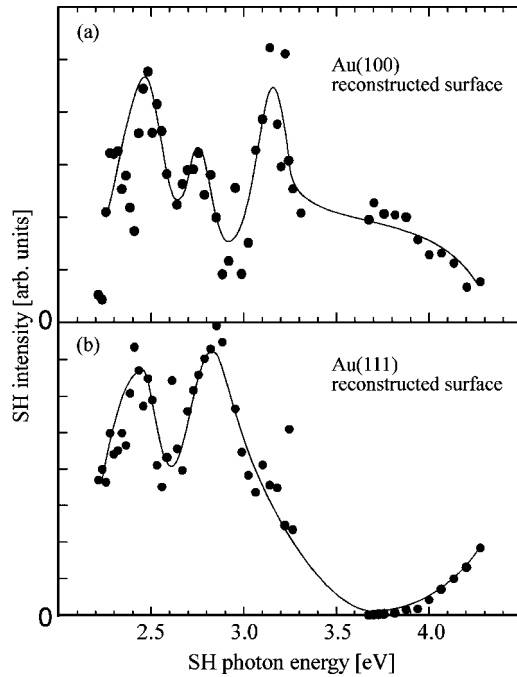


FIG. 1. SH intensity spectra of (a) the Au(100) 5×20 and (b) the Au(111) $\sqrt{3} \times 23$ reconstructed surfaces, measured in the p -in/ p -out polarization configuration. The plane of incidence in (a) and (b) was parallel to the $[0\bar{1}1]$ and $[11\bar{2}]$ direction, respectively. The solid lines are guides for the eyes.

The SH intensity spectra from the Au(100) 5×20 and Au(111) $\sqrt{3} \times 23$ reconstructed surfaces are shown in Fig. 1 as a function of the SH photon energy measured in the p -in/ p -out polarization configuration. Those in the s -in/ p -out polarization configuration are shown in Fig. 2. In the SH intensity spectra measured in the p -in/ p -out polarization configuration (Fig. 1), the peaks at $2\hbar\omega=2.4$ and 2.8 eV are observed for both Au(100) 5×20 and Au(111) $\sqrt{3} \times 23$ reconstructed surfaces, while that at $2\hbar\omega=3.2$ eV is observed only

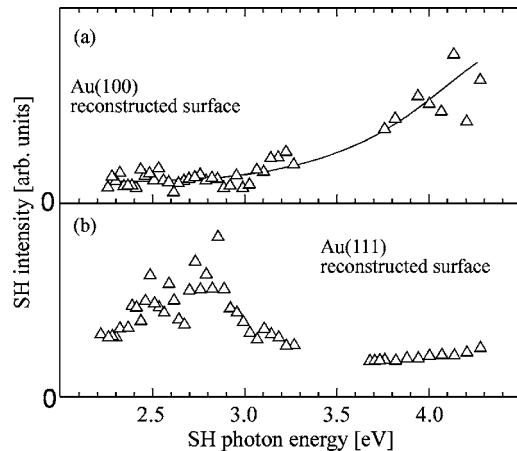


FIG. 2. SH intensity spectra of (a) the Au(100) 5×20 and (b) the Au(111) $\sqrt{3} \times 23$ reconstructed surfaces, measured in the s -in/ p -out polarization configuration. The plane of incidence in (a) and (b) was parallel to the $[0\bar{1}1]$ and $[11\bar{2}]$ direction. The solid line is a guide for the eyes.

for the Au(100) 5×20 reconstructed surface. In the SH intensity spectrum measured in the s -in/ p -out polarization configuration (Fig. 2), a rise in the SH intensity above $2\hbar\omega=3.2$ eV is observed for the Au(100) 5×20 reconstructed surface, while a broad band around $2\hbar\omega=2.7$ eV is observed for the Au(111) $\sqrt{3} \times 23$ reconstructed surface. In the following we analyze these SH intensity spectra and discuss the origin of the observed structures.

The SH intensity peak at $2\hbar\omega=2.4$ eV was observed both for Au(100) and (111) reconstructed surfaces, so it may be attributed to the electronic states common to these reconstructed surfaces. There are two possible origins of these SH intensity peaks.¹¹ One is the enhancement of the local electric field by surface plasmon excitation and the other is the resonance of the electronic states in the bulk. The former prediction stems from the fact that the surface plasmon energy of Au is located around 2.4 eV. Similar peaks assigned to the resonance of surface plasmon were observed at this photon energy in the SH spectra of Au thin films on NaCl(100)⁹ and Au particles.¹⁹ The latter prediction stems from the fact that the optical absorption edge of bulk d -electronic states of gold is located around 2.5 eV.²⁰ Two-photon resonance of SH radiation will be possible around this photon energy region.

The SH intensity peak at $2\hbar\omega=2.8$ eV was also observed for both Au(100) and (111) reconstructed surfaces, and it should again be attributed to the lattice structure or electronic states common to these two reconstructed surfaces. The structure common to these reconstructed surfaces is the hexagonal structure at the topmost layer. According to the band structure calculated by Takeuchi *et al.*⁶ there is an occupied surface d -electronic state at 1.5 eV below the Fermi level and an unoccupied surface s,p state at 1.3 eV above the Fermi level at \bar{M} point in the surface Brillouin zone of the Au(111) reconstructed surface. The combination of these states gives a maximum joint density of states (JDOS) at $2\hbar\omega=2.8$ eV, so the resonance in SH intensity observed in Fig. 1 is attributed to the transition between these two electronic states. SH intensity peaks around $2\hbar\omega=2.8$ eV have already been observed for a Au thin film consisting mainly of (111) faces by Kitahara *et al.*⁹ and a glass/Au(111) interface by Tanaka *et al.*¹⁰

The SH intensity peak at $2\hbar\omega=3.2$ eV was observed only for the Au(100) reconstructed surface and not for the Au(111) surface. Thus the peak should be attributed to the electronic states characteristic of the Au(100) reconstructed surface. The structure existing only on the Au(100) reconstructed surface in our study is the (100) 1×1 structure with fourfold symmetry in the unreconstructed domain on the topmost layer or in the second layer. According to the band structure calculated by Eibler *et al.*,¹⁷ there is an occupied p state at 1 eV below the Fermi level and an unoccupied surface s state at 2.2 eV above the Fermi level at \bar{X} point in the surface Brillouin zone of the Au(100) 1×1 structure. The combination of these states gives a maximum JDOS at $2\hbar\omega=3.2$ eV so the observed resonance in the SH intensity in the p -in/ p -out polarization configuration in Fig. 1 may be due to the transition between these two electronic states. The SH intensity peak around $2\hbar\omega=3.2$ eV has been observed

for a Au thin film consisting mainly of (100) faces by Kitahara *et al.*⁹ However, the area of the fourfold structure on the topmost layer should be smaller than that of the hexagonal structure on the single crystal (100) surface²¹ because the latter is the more stable on the (100) surface without defects. If we consider the fact that the SH intensity of the peak is stronger at $2\hbar\omega=3.2$ eV than at $2\hbar\omega=2.8$ eV, it is not appropriate to assign the former peak to the electronic states formed by the fourfold structure on the topmost layer. Instead, it should be attributed to the electronic states formed by the fourfold structure in the second layer. Later we will discuss whether surface electronic states are stable in the second layer of metal crystals.

A rise in SH intensity above $2\hbar\omega=3$ eV was observed for the Au(100) reconstructed surface in the *s*-in/*p*-out polarization configuration, as shown in Fig. 2(a). In the same photon energy region, the SH intensity in the *p*-in/*p*-out polarization configuration decreases as a function of the photon energy, as seen in Fig. 1(a). This rise in SH intensity could be assigned to a resonance of an image state because the image state on Au(100) surface is located at 4.5 eV above the Fermi level.²² However, it has been reported by Ishida *et al.* that the image state on the Cu(111) surface gives a SH signal in the *p*-in/*p*-out polarization configuration.²³ Since we do not see a rise in the SH intensity in this energy region in the *p*-in/*p*-out polarization configuration in Fig. 1(a), this assignment is not acceptable.

In order to determine whether the signals observed in Fig. 2(a) are attributable to surface electronic levels, we measured the SH intensity in the two polarization configurations in vacuum and in air in the same UHV chamber. The SH intensity in vacuum in the *s*-in/*p*-out polarization configuration was much stronger than that in the *p*-in/*p*-out polarization configuration for the SH photon energy above 3.75 eV, while this inequality was reversed in air. This result indicates that there are surface electronic levels sensitive to air exposure and that the signal in Fig. 2(a) was due to these levels.

Here we also note that this sensitivity of the SH signal to air exposure was not observed when the sample was rotated by 90° around its surface normal. Namely, there is an anisotropy of the surface electronic states created by the surface reconstruction. Friedrich *et al.* have reported that there is an imbalance between the areas of two equivalent 5×20 reconstructed domains on Au(100) at a macroscopic scale.²⁴ Our experimental result may indicate predominant formation of one reconstructed domain in the probed area. As for the structures seen in Fig. 2(b) below $2\hbar\omega=3.2$ eV, we could not obtain enough signal-to-noise ratio for spectral shape analysis and the clarification of its origin is our future problem.

It is noteworthy that similar SH intensity spectra were observed for the Au(100) and (111) reconstructed surfaces below $2\hbar\omega=3$ eV in the *p*-in/*p*-out polarization configuration, as seen in Fig. 1. By surface reconstruction, the arrangement of the atoms in the topmost layer changes so as to smooth the electronic wave function at the surface. As a result, a hexagonal structure similar to the one at the unreconstructed (111) surface is formed at the topmost layer of the (100) surface.⁵ In the bulk (100) plane of gold, each Au

atom has four atoms at the nearest neighbor distance, 2.89 Å, and four atoms at the second nearest neighbor distance, 4.08 Å. As for the topmost hexagonal plane of reconstructed Au(100), each Au atom has six atoms at the nearest neighbor distance, nearly equal to 2.89 Å. Accordingly, the atomic density of the hexagonally reconstructed topmost layer of the Au(100) surface is 15% higher than that of the second layer of the nearly fourfold structure. Such a large difference in the atomic density may give rise to electronic states localized in each of the two layers.

For heteroepitaxially grown metallic monolayers on single crystal metal surfaces, the electronic states localized in the overlayers and the top substrate layers have been reported.^{25–28} Wesner *et al.*²⁵ and Memmel *et al.*²⁶ reported that localized electronic states occur in a monolayer of sodium on Ni(110) and a monolayer of Pd on Co(0001), respectively. Dutton *et al.*²⁷ have reported that the $n=1$ image state of Cu(111) is stable in the presence of one monolayer of C₆₀. Frank *et al.*²⁸ reported that the Λ_1 intrinsic surface-state band of Cu(111) is found to persist in the presence of the Ni overlayer without changing its binding energy or dispersion. Similarly, two electronic states localized in the topmost layer and in the second layer might be expected to exist on the Au(100) reconstructed surface in our case, if we regard the first and the second layers of this surface as different materials because they have different two-dimensional atomic densities.

The rise in the SH intensity in higher energy regions observed for the Au(100) reconstructed surface in the *s*-in/*p*-out polarization configuration in Fig. 2(a) disappeared when the sample was rotated by 90° around its surface normal. If the hexagonal structure alone is responsible for this rise in the SH intensity, the rise should also have been observed for the Au(111) reconstructed surface. If the fourfold structure alone is responsible for this rise, the spectrum should not change when the sample is rotated by 90° around its surface normal. Therefore, the rise in the intensity should not be attributed to the electronic states localized in one of the two structures, but should be attributed to those at the interface between them. Since one of the two equivalent 5×20 structures might have been dominant in the probed region, the observed anisotropy in the SH spectrum might have been caused by the way the hexagonal structure was stacked on the fourfold bulk layer.

In summary, we have carried out SH spectroscopy on the Au(100) 5×20 and (111) $\sqrt{3} \times 23$ reconstructed surfaces. SH intensity peaks at $2\hbar\omega=2.8$ eV were observed for both the Au(100) and (111) reconstructed surfaces in the *p*-in/*p*-out polarization configuration and are attributed to the electronic states formed by the hexagonal structure common to these surfaces. The SH intensity peak at $2\hbar\omega=3.2$ eV was observed only for the Au(100) reconstructed surface and may reflect the electronic states formed by the fourfold structure located in the second layer. The rise in the SH intensity above $2\hbar\omega=3$ eV was observed in the *s*-in/*p*-out polarization configuration and it diminished with the exposure of the surface to air, indicating that surface electronic states are involved in this photon energy.

*Email address: mizutani@jaist.ac.jp

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