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Optical second harmonic spectroscopy of the Au(100) 5x20 surface

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Abstracts

We have performed SH spectroscopy on the reconstructed Au(100) 5x20 surface. We have found a broad SH intensity continuum for the SH photon energy from $2\eta\omega = 2.2$ to 4.2eV. Between the photon energies $2\eta\omega = 3.7$ and 4.2eV, the SH intensity in the *s*-in/*p*-out (*s*-polarized input and *p*-polarized output) polarization configuration is stronger than that in *p*-in/*p*-out polarization configuration, but the former signal disappeared when the surface was exposed to air. Surface electronic states are suggested to contribute to the SH response in this photon energy region.

Pacs Codes: 78.68.+m; 42.65.Ky

Key words: optical second harmonic spectroscopy; Au(100); reconstructed surface; electronic level

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1. Introduction

Some transition metals show surface reconstruction in order to reduce their surface energy [1,2]. The detailed mechanism of the surface reconstruction has not been clarified yet and it has been a research topic of many researchers. In surface reconstruction of transition metals, the involvement of *d*-electronic states near the band gap energy region is suggested [2]. This also means that the reconstruction should have a large effect **on the surface *d*-electronic states**. Hence, the information on the electronic states on the reconstructed surface will serve as a great help in clarifying the mechanism of the surface reconstruction. In the present paper as a first step to clarify the mechanism of the surface reconstruction, we have measured the electronic spectra of a typical reconstructed noble metal surface Au(100) 5x20 by optical second harmonic (SH) spectroscopy.

Optical second harmonic (SH) spectroscopy is a useful method to investigate selectively the surface electronic states of centrosymmetric media, with the energy resolution of a laser-driven coherent light source. In optical second harmonic generation (SHG) the light beam with twice the frequency of the exciting field is radiated and the output intensity is enhanced when one or two photon resonance takes place. By using SHG we can expect to detect the *d*-electronic states involved in the surface reconstruction. For example, according to Murphy et al [3] and Kitahara et al [4], SH intensity observed from the Al and Au crystalline surfaces depends strongly on the azimuthal angle and the face index of the sample

surface. This is nothing but a response of d-electronic states because *s*-, and *p*-electrons described by the "jellium" model [3, 7, 8] will not show the azimuthal and face index dependence in the SH intensity. Sharp resonance peaks in SH intensity spectra were observed for Ag(110) by Urbach et al [5] and for the glass/Au interface by Tanaka et al [6]. This is also the response of the d-electronic states because s-, and p-electrons described by the "jellium" model show a very broad energy spectrum.[reference お願い]

To our knowledge no spectroscopic measurement of SH intensity from the reconstructed metal surfaces has yet been carried out, although measurements of SH intensity from such surfaces as a function of the azimuthal angle has already been performed at a fixed photon energy [9,10]. Our sample selection is motivated by the facts that the Au(100) 5x20 reconstructed surface takes on a stable and interesting hexagonal close-packed arrangement at room temperature [2,11] and its surface preparation procedure is well known [12]. Spectroscopic SH measurements for Ag(110) [5], **Ag(111) [13]**, Cu(111) [14], **Al(111) [15]** single crystal surfaces have already been done, but these surfaces do not show reconstruction.

2. Experiment

A mechanically polished Au(100) disk (Surface Preparation Laboratory, 99.999%) was thermally annealed at 650°C by flash heating and sputtered by Ar^+ ion of 0.5keV for 30min in

a UHV chamber with the base pressure of $2x10^{-8}$ Pa. After 5 times repetition of this procedure, we obtained a surface giving Reflection High Energy Electron Diffraction (RHEED) diagram in the $[1\bar{1}0]$ direction as shown in Fig. 1. The surface was free of contamination, as was checked by Auger Electron Spectroscopy. In Fig. 1 the streak interval in the lateral direction, namely in each of the n/20 rows indicated in the figure, shows the 5 times structure of this surface. The interval of streaks along the longitudinal direction, namely between 1/5 and 4/20, shows the 20 times structure [16].

The SH spectroscopy of the Au(100) 5x20 surface was carried out in the UHV chamber at room temperature. The optical excitation and observation was done through two glass windows attached to the chamber. The light source of the fundamental frequency was an optical parametric oscillator (OPO) pumped by a frequency-tripled Q-switched Nd:YAG laser. The spectral band width of the OPO output was ~20meV, the pulse duration time was ~3nsec, and the repetition rate was 10Hz. The *p*- or *s*-polarized excitation beam at the fundamental frequency was directed onto the sample at the angle of incidence of 45° and the reflected *p*-polarized SH light was passed through a monochromator and was detected by a photomultiplier. The plane of incidence was parallel to the [110] direction on the Au(100) surface. A fraction of the incident laser light was split off from the excitation beam and was directed onto a reference sample [a GaAs(100) wafer] and the reflected SH light from it was used to correct for the laser-intensity fluctuation. In order to calibrate the signal intensity,

α-SiO_2(0001) was used as a reference sample.

3. Results and discussion

The SH intensity from the Au(100) 5x20 reconstructed surface as a function of the SH photon energy is shown in Fig. 2. In *p*-in/*p*-out polarization configuration we see a broad background SH intensity continuum **from $2\eta\omega$ = 2.3 to 4.2 eV** and three peaks on it at $2\eta\omega$ = 2.4eV, 2.7eV, and 3.2eV. In *s*-in/*p*-out polarization configuration we see a gradual rise in SH intensity above the photon energy $2\eta\omega$ = 3.0eV. Compared with the SH spectra of Au thin films by Kitahara et al with SH intensity peaks of width ~0.2eV[4], the widths of the observed SH intensity continua in Fig. 2 are much broader. In the following, we will discuss the origins of the observed **structures** in Fig. 2 and the origin of the broadness of the SH intensity continuum in s-in/p-out polarization configuration.

First, we discuss the origin of the rise in SH intensity from $2\eta\omega$ = 3.0eV in *s*-in/*p*-out polarization configuration represented by open circles in Fig. 2. In the same photon energy region the SH intensity in *p*-in/*p*-out polarization configuration decreases as a function of the photon energy as represented by filled circles. These results indicate that the electronic states excited in this photon energy region are different between these two polarization configurations.

In order to check whether the signals observed in Fig. 2 are attributed to surface

electronic states, we have measured the ratio of the SH intensity in *s*-in/*p*-out polarization configuration to that in *p*-in/*p*-out polarization configuration (*Isp*/*Ipp*) in vacuum and in air in the same UHV chamber as shown in Fig. 3. The vertical axis in Fig. 3 is the ratio of the SH intensity *Isp*/*Ipp*. According to Fig. 3, the SH intensity in vacuum in *s*-in/*p*-out polarization configuration is much stronger than that in *p*-in/*p*-out polarization configuration for SH photon energy above 3.75eV, while this inequality is reversed in air. This result indicates that the surface states involved in the SH light radiation in *s*-in/*p*-out polarization configuration has disappeared by the exposure of the surface to air. The incident electric field exciting this surface electronic states was parallel to the [110] direction.

The rise in SH intensity observed in *s*-in/*p*-out polarization configuration cannot be assigned to the resonance of the image state, because SHG from the image state is reported to be observed in *p*-in/*p*-out polarization configuration [17]. According to the band structure calculated by Eibler et al [18], there are an occupied bulk *d*-state at 2.2 eV below the Fermi level and an unoccupied surface *s*-state at 2.2 eV above the Fermi level at $\overline{X}$ point in the surface Brilloiun zone of the Au(100) 1x1 structure. Combination of these states gives a maximum of the joint density of states (JDOS) at $2\eta\omega = 4.4$eV, so the observed resonance in SH intensity in *s*-in/*p*-out polarization configuration in Fig. 2 may be due to the transition between these two electronic states. However, because the structure assumed in their calculation (1x1) is different from that studied in the present experiment (5x20), this

assignment is a tentative one.

There are two candidate origins of the polarization dependence of SH intensity in the energy region above 3.7eV in Fig. 2. One is the interference between different surface nonlinear susceptibility elements $\chi^{(2)}_S$ of this Au(100) 5x20 surface. For p-in/p-out polarization configuration $\chi^{(2)}_{S333}$, $\chi^{(2)}_{S311}$, and $\chi^{(2)}_{S113}$ elements contribute to the SHG, while for s-in/p-out polarization configuration only $\chi^{(2)}_{S311}$ element contributes. Here 1 and 3 indicates [110] and [001] directions on the Au(100) surface, respectively. The intensity I_{sp} can be larger than I_{pp}, when the contributions from $\chi^{(2)}_{S333}$, $\chi^{(2)}_{S311}$, and $\chi^{(2)}_{S113}$ makes negative interference. The other origin is the anisotropy of the surface electronic states on the reconstructed surface [9], but the viability of this candidate cannot be examined at present because our sample holder does not have a rotation mechanism around its surface normal.

The width of the SH intensity structure observed in *s*-in/*p*-out polarization configuration in Fig. 2 is more than 1eV, while that observed for Au thin films on NaCl(100) by Kitahara et al [4] and Cu(111) by Ishida [14] et al were around 0.2eV. The broadness of the structure might be attributed to the dispersion of the surface electronic states induced by the 5x20 reconstruction. In the above discussion, the rise in SH intensity above $2\eta\omega =$ 3.0eV was tentatively assigned to the resonant transition from the occupied bulk *d*-state to the unoccupied surface *s*-state. When surface reconstruction occurs, the inter-atomic distances at the surface will be reduced, and the interaction between *d*-electrons localized around the Au

atoms increases and gives rise to the dispersion of the *d*-electronic states in the surface layer **[2, 19, 20]**. This dispersion in the band structure increases the energy spread in the JDOS of surface electrons. Then the observed SH structure might be broadened because the SH intensity is proportional to the JDOS of the resonant electronic states.

The origin of the broad continuum of SH intensity **from $2\eta\omega$ = 2.3 to 4.2 eV** observed in *p*-in/*p*-out polarization configuration in Fig. 2 is not clear. As for the three peaks superposed on this continuum, the following candidate origins are possible. First, there are two candidate origins of the SH intensity peak at $2\eta\omega$ = 2.4eV. One is the enhancement of the local electric field by surface plasmon excitation [4] and the other is the drastic change of the imaginary part of the dielectric constant of Au near 2.4eV [21]. The latter should have an effect on the SH intensity through the Fresnel factors. As for the peak around $2\eta\omega$ = 2.7eV, SH response might originate from the electronic states of the hexagonal structure on the Au(100) 5x20 surface. This suggestion is due to the fact that a SH intensity peak around $2\eta\omega$ = 2.7eV was observed for a Au thin film consisting mainly of (111) or hexagonal faces [4, 22]. The peak at $2\eta\omega$ = 3.2eV in Fig. 2 might originate from **the electronic states of the second layer [2] or those of some unreconstructed domains on the topmost layer [23].** This suggestion is motivated by the fact that a SH intensity peak around $2\eta\omega$ = 3.2eV was observed for a Au thin film consisting mainly of (100) faces [4].

4. Conclusion

We have carried out SH spectroscopy of the Au(100) 5x20 surface. We have found a rise in SH intensity above $2\eta\omega = 3.0$eV in *s*-in/*p*-out polarization configuration. This SHG diminished when surface was exposed to air. This result indicates that the surface states are involved in the SH response in *s*-in/*p*-out polarization configuration. This SH intensity structure was suggested to be broadened by the reconstruction of the Au(100) surface.

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Figure Captions

Fig. 1 RHEED diagram of the Au(100) 5x20 surface. The plane of incidence of the electron beam is parallel to the $[1\bar{1}0]$ direction. We follow the notation in Ref. [16] for the indices of the streaks.

Fig. 2 SH intensity as a function of the SH photon energy from the Au(100) 5x20 structure for *p*-in/*p*-out polarization configuration (filled circles) and for *s*-in/*p*-out polarization configuration (open circles). The plane of incidence of the excitation beam is parallel to the $[1\bar{1}0]$ direction. **The solid lines are guide to the eyes.**

Fig. 3 Ratio of the SH intensity (*Isp*/*Ipp*) as a function of the SH photon energy measured in vacuum (open circles) and in air (filled triangle). **The solid lines are guide to the eyes.**

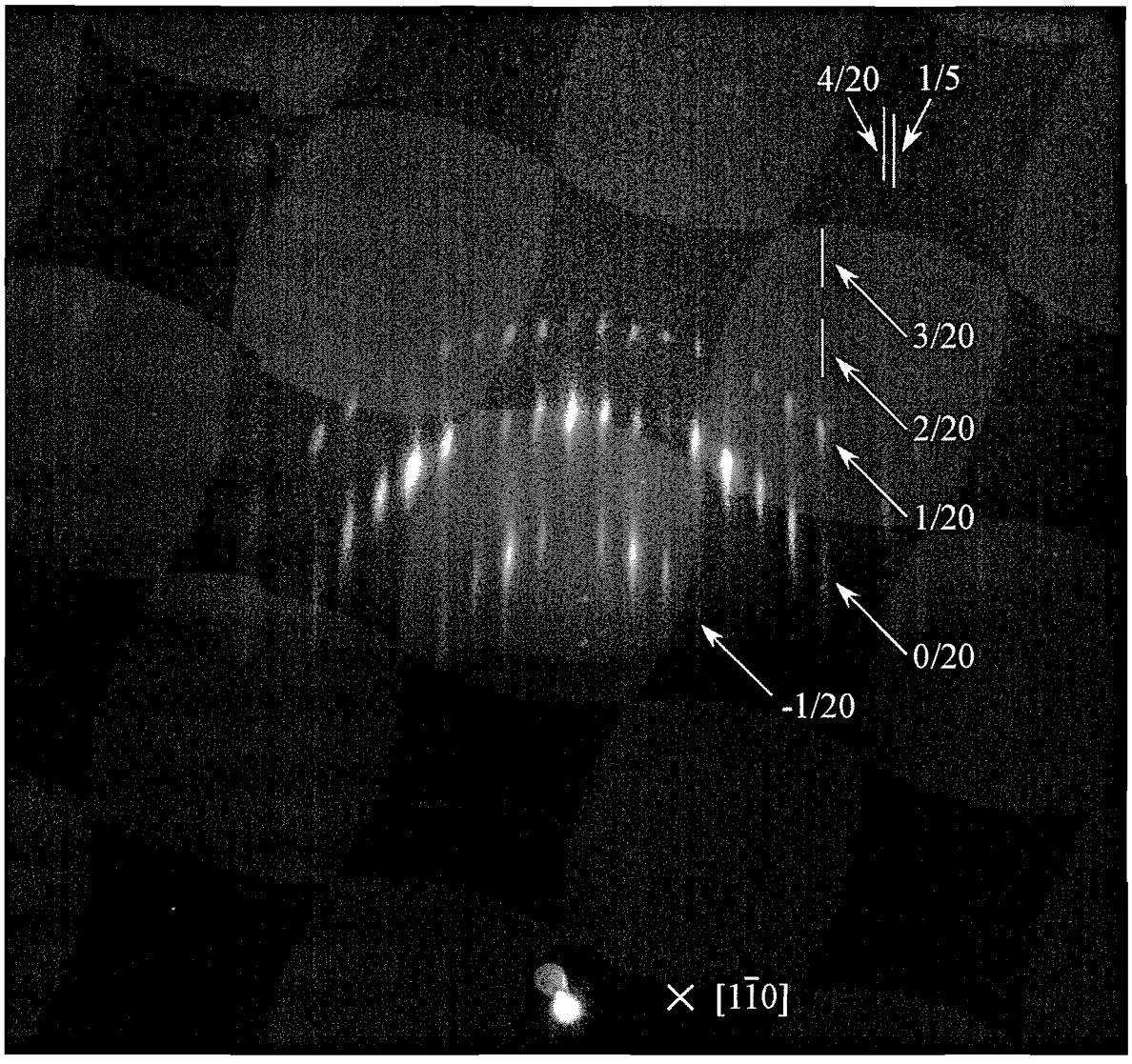

Figure 1 Iwai et al

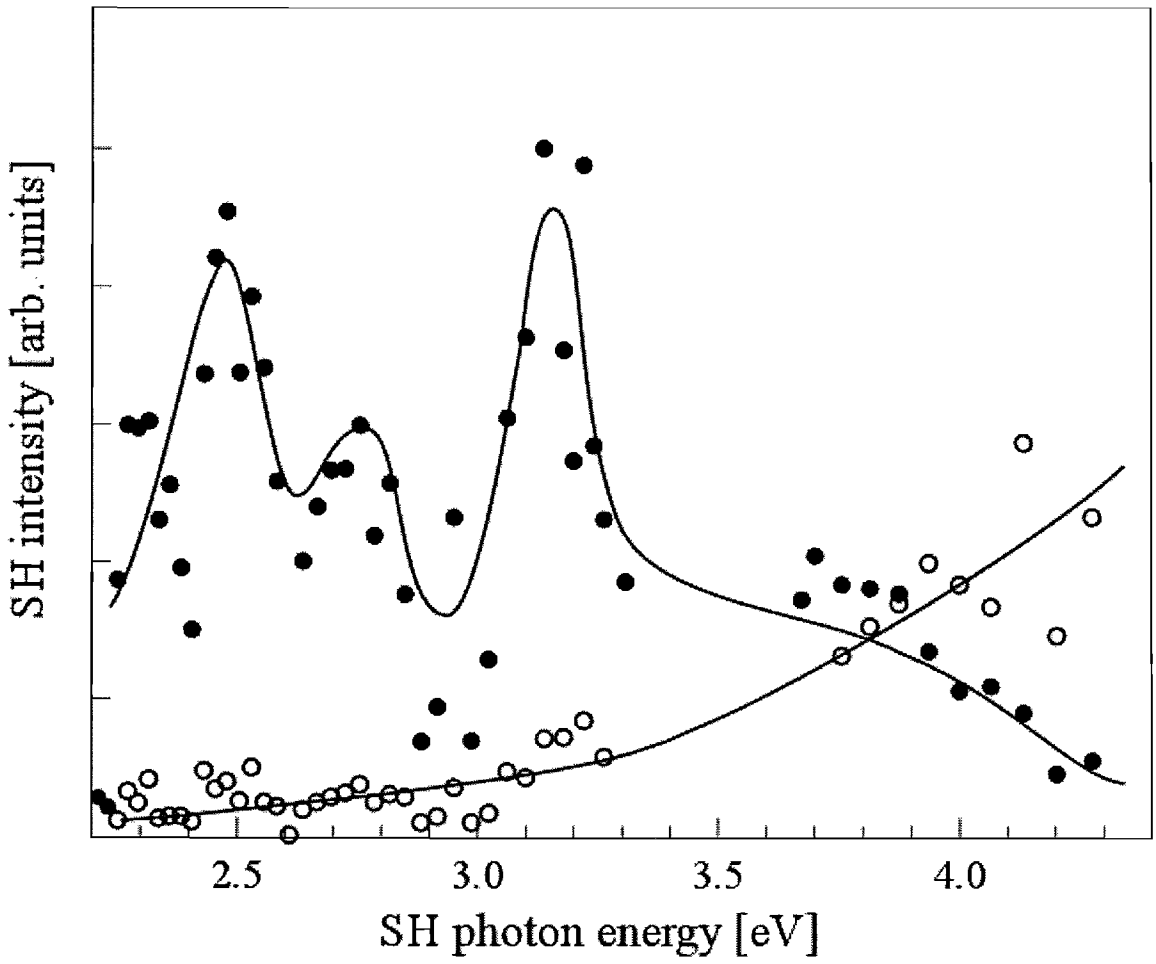

Figure 2 Iwai et al

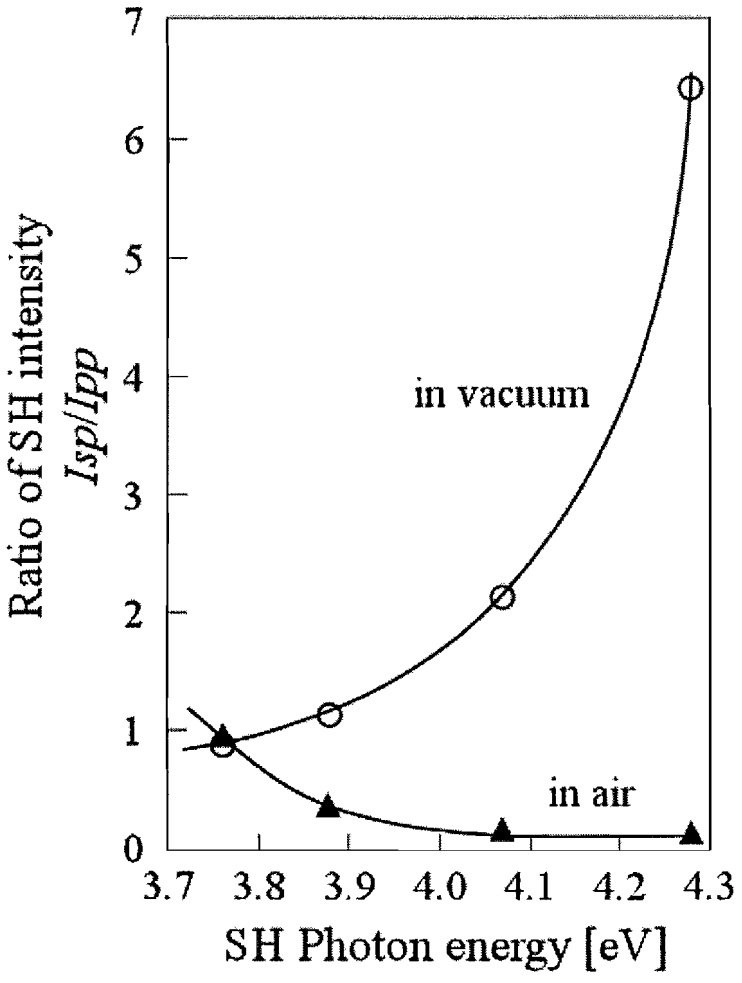

Figure 3 Iwai et al