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Optical second harmonic generation spectrum of Ag/Si(111) reconstructed surfaces

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Optical second harmonic generation (SHG) spectra were measured at Ag/Si(111) reconstructed surfaces; the excitation photon energy ranged from 1.0 to 1.7 eV. The Si(111) surface exhibited two peaks resonant to the transition between the surface states of the 7×7 reconstruction at 1.15 and 1.35 eV. These peaks disappeared in the Ag deposition at room temperature with the completion of the Ag-induced 1×1 surface structure. Instead, the E_0' transition peak red-shifted to appear at 1.6 eV. The peaks of the 7×7 reconstruction disappeared at 0.5 monolayers in the deposition at 400 °C, and two new peaks then grew at 1.15 and 1.45 eV with the appearance of the Ag-induced $\sqrt{3}\times\sqrt{3}$ reconstruction. The peak at 1.15 eV was reasonably assumed to be the transition from the free-electron-like surface state to the surface Umklapp empty state of the $\sqrt{3}\times\sqrt{3}$-Ag reconstruction. The intense peak at 1.45 eV was tentatively assigned to the multipole plasmon excitation at the Si(111) $\sqrt{3}\times\sqrt{3}$-Ag reconstructed surface with a metallic nature.

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I. INTRODUCTION

Reconstructions of a Si surface as 7×7 and $\sqrt{3}\times\sqrt{3}$ have been reported to be maintained at the interface between a thick Ag film and Si(111) substrate.[1,2] In addition, a close correlation between the interface reconstruction and Schottky barrier height (SBH) of the interface has been identified.[3,4] An investigation into the characteristic electronic states of these interface reconstructions is of great interest. Unfortunately, conventional electron spectroscopy cannot approach interfaces buried under thick metal films. However, light can penetrate the film, and reach the buried interface. Optical second harmonic generation (SHG) in particular is sensitive to the electronic excitations at the surface and interface of centrosymmetric crystals like Si.[5] Thus SHG is expected to be a useful tool for characterizing buried interface states.

SHG intensity has been monitored at several excitation beam energies *in situ* during Ag deposition up to 25 monolayers (ML's) at Si(111) surfaces by Pedersen *et al.*[6,7] They observed a coverage-dependent change of the SHG intensity. However, the change was concluded to be caused by the formation of Ag islands to enhance the local plasmon excitation and the resonance to the quantum well states confined in the Ag films. Although a different Ag coverage dependence of the SHG intensity has been observed on Si(111) 7×7, $\sqrt{3}\times\sqrt{3}$, and 1×1-H surfaces, the variance is attributed to differences in the growth modes. No interface state-related excitation was reported in their studies. One reason that interface excitation has not been observed is that the SHG has been measured at a fixed excitation beam energy. The interface excitation is expected to be detected as peaks at the energy resonant to the interface excitation in a spectrum of SHG intensity obtained by varying the excitation beam energy. However, the resonance to the quantum well state of an Ag film will overlap the interface-related peaks and make the assignment somewhat complicated for a thick Ag film on an Si(111) surface. Thus we investigated the SHG spectrum of Si(111) 7×7-Ag, $\sqrt{3}\times\sqrt{3}$-Ag, and 1×1-Ag reconstructed surfaces in this study as a first step in examining the possibility of SHG spectrum measurement to monitor interface excitation. The characteristic peaks of the 7×7 reconstruction disappeared in the submonolayer Ag deposition on the Si(111) surface, while new peaks appeared in accordance with Ag-induced changes of the surface reconstruction. A close correlation between the SHG spectrum and the electronic states of Ag-induced reconstructions at Si(111) was clearly demonstrated in this study.

II. EXPERIMENT

The experiments were performed in an ultrahigh vacuum apparatus with a base pressure of 5×10^{-9} Pa. The apparatus was equipped with reflection high-energy electron diffraction (RHEED), low-energy electron diffraction-Auger electron spectroscopy (LEED-AES), and an Ag Knudsen cell with a shutter. An 8×9-mm^2, sample was cut from an *n*-type Si(111) wafer. The sample was loaded into the UHV apparatus after being rinsed in a chemical solutions and was flashed up to 1200 °C to expose a clean surface. The cleanliness of the surface was confirmed by observing sharp RHEED spots on the 7×7 reconstruction. Ag was deposited at 400 °C and at room temperature on the Si(111) 7×7 surface to cause $\sqrt{3}\times\sqrt{3}$-Ag and 1×1-Ag reconstruction.[8] The Ag coverage was determined by AES under the assumption that the $\sqrt{3}\times\sqrt{3}$-Ag reconstruction was completed at one monolayer (ML).[9]

The sample was illuminated by a pulsed laser beam from an optical parametric oscillation/amplifier (OPO) system pumped by a *Q*-switched Nd:YAG laser. A 10-nsec laser pulse was supplied with a repetition rate of 10 Hz.The wavelength of the beam could be changed within a range of 1.05–1.70 eV (729–1180 nm). The pulse energy changed depending on the wavelength, but was in the range of 2–8 mJ in a 6-mmϕ spot. The laser beam was introduced to the sample in the UHV apparatus through a quartz window from a near surface-normal direction (the off-normal angle was 1.5°). The beam was polarized along the $[01\overline{1}]$ direction of the Si(111) surface. The SHG signal was separated from the fundamental beam by the combination of color filters in the specular reflected beam. The filters blocked the fundamental beam but penetrated the beam in a narrow wavelength range around the SH component. The $[\overline{211}]$ polarized component of the SHG signal was detected with a polarizer. The gated SHG signal applied to the excitation laser pulse was detected by a photomultiplier tube (PMT) and was averaged over 128 laser shots by a digital storage oscilloscope. A successful separation of the SHG signal from the fundamental beam was confirmed by observing that the SHG signal showed azimuthal rotation angle dependence, as expected in theory.[10] The SHG intensity was calibrated by dividing the detected signal intensity by the transmittance of the color filters, and the sensitivity of the PMT at each SH wavelength. The quadratic dependence of the SHG intensity to the excitation beam was also considered. The excitation pulse energy was checked at every wavelength every time by a power meter.

Two types of experiments were performed in this study. One experiment was an *in situ* measurement of the SHG intensity during the Ag deposition with the excitation wavelength fixed at 1064 nm (1.17 eV). The coverage dependence of the SHG intensity was measured in detail with respect to the change of the surface reconstruction induced by submonolayer Ag atoms both at room temperature and at 400 °C. The surface reconstruction was monitored by RHEED during and after the Ag deposition. This measurement corresponded to the recent study by Pedersen *et al.*[6,7] in which the change of SHG intensity was measured up to a coverage of 25 ML's with respect to the number of Ag layers deposited on the Si(111) surfaces. The second experiment was the SHG spectrum measurement. Since this measurement took time, the spectra were taken only for several coverages in both the room-temperature and 400 °C depositions. The surface structures were not changed by lowering the substrate temperature from 400 °C to room temperature. Thus all the spectra were measured at room temperature to prevent thermal desorption of Ag atoms during the measurement.

III. RESULTS

The 7×7 RHEED spots of the clean Si(111) surface became faint at 0.25 ML, and almost disappeared at around 0.5 ML in the room temperature deposition. No spots other than the 1×1-Ag structure were observed in further deposition. In the 400 °C deposition, the 7×7 spots became faint at 0.25 ML as well as in the room-temperature deposition. However, the spots of the $\sqrt{3}\times\sqrt{3}$- Ag reconstruction started to appear at ~0.5 ML. The $\sqrt{3}\times\sqrt{3}$ diffraction became intense with the coverage, and the $\sqrt{3}\times\sqrt{3}$ reconstruction was completed at ~1.0 ML.[8]

Figure 1 shows the results of the *in situ* measurement of the SHG intensity excited by a 1.17-eV photon energy laser beam. The SH intensities in the room-temperature and 400 °C depositions are indicated by dots and circles. The SHG intensity initially decreased with the coverage in both the room-temperature and 400 °C depositions. However, the SHG intensity did not change in further depositions and remained at a low level in the room-temperature deposition, while it recovered to a higher level in the 400 °C deposition. Lowering the substrate temperature from 400 °C to room temperature did not change the RHEED pattern, but the SHG intensity increased by several times (not shown). Thus the high SHG intensity in the 400 °C deposition was not due to the high substrate temperature, but was essential to the $\sqrt{3}\times\sqrt{3}$-Ag reconstruction.

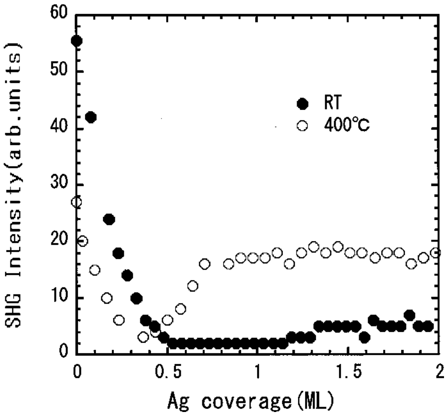

FIG. 1. Ag coverage dependence of the SHG intensity from the Ag/Si(111) surfaces. The SHG intensity was measured *in situ* with the fixed excitation photon energy at 1.17 eV. The dots and circles indicate the SHG signal measured for room-temperature and 400 °C depositions.

Figure 2 shows the SHG spectrum of the Ag/Si(111) surfaces. The spectra obtained in the 400 °C deposition and in the room-temperature deposition are shown in the left and right columns. The spectra were obtained at 0, 0.25, 0.50, 0.75, and 1.00 ML coverage. Note that the bottom panels in the left and right column show the same spectrum of the Si(111) 7×7 clean surface at different magnifications. Furthermore, the spectra at 0, 0.25, and 0.50 ML in the left column are magnified by a factor of 2 with respect to those at 0.75 and 1.00 ML. Consequently, the maximum intensity in the SHG spectrum of the $\sqrt{3}\times\sqrt{3}$-Ag reconstructed surface (top panel in the left column) was roughly six times larger than that of the Si(111) 7×7 surface. The maximum intensity of the 1×1-Ag surface (top panel in the right column) was 1/3 that of the Si(111) 7×7 surface.

The spectrum of the Si(111) 7×7 surface (the bottom panel in the right column) contained two peaks at excitation photon energies of 1.15 and 1.35 eV. In addition to these peaks, a small increase of the SHG intensity was observed at ~1.7 eV. Since the region above 1.7 eV could not be reached in our optical system, no obvious peak was detected at ~1.7 eV. However, a peak has been reported at ~1.7 eV in previous studies on the SHG spectrum from Si(111) 7×7 surfaces in a wider energy range.[11–14] Thus we regard the increase of the SHG intensity as a trace of the peak at ~1.7 eV. For the peak intensity dependence on the combination of the polarized directions of the excitation and the resulting SHG light,[14] the *P*-polarized excitation has been reported to exhibit only a small peak at ~1.7 eV in the *S*-polarized SHG signal. Since our optics were Pin-Sout, we

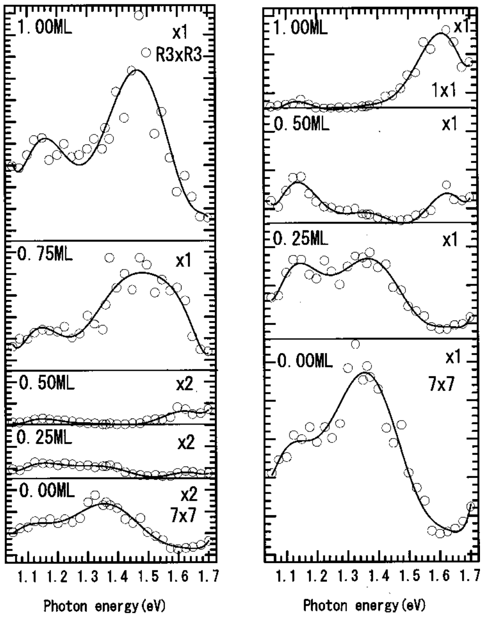

FIG. 2. The SHG spectrum of the Ag/Si(111) surfaces. The spectra obtained in the 400 °C deposition and in the room-temperature deposition are shown in the left and right columns. Circles: data. Solid line: least-square fit of the data. The coverage is indicated in each panel. Note that the bottom panels in the left and right columns show the same spectrum of the Si(111) 7×7 clean surface with different magnifications. In the left column, the spectrum of 0, 0.25, and 0.50 ML are magnified by a factor of 2 with respect to those at 0.75 and 1.00 ML.

attribute the small increase to the trace of the peak at ~1.7 eV.

The peaks at 1.15 and 1.35 eV disappeared at 0.50 ML in the 400 °C deposition (the left column). The peak at 1.7 eV red-shifted to ~1.6 eV. At coverages above 0.5 ML, where the $\sqrt{3}\times\sqrt{3}$-Ag reconstruction started to appear, two new peaks grew at 1.15 and 1.45 eV. The evolution of the peak at 1.45 eV was particularly outstanding. The peak at ~1.6 eV was not distinct at 0.75 and 1.00 ML. It may be involved under the shoulder of the intense peak at 1.45 eV, but this has not been clarified.

The peaks at 1.15 and 1.35 eV of the Si(111) 7×7 surface were reduced in the room-temperature deposition. We found the reducing rate of the peak at 1.35 eV to be clearly faster than that at 1.15 eV. The peak at 1.7 eV red-shifted to 1.6 eV with the coverage as well as in the 400 °C deposition. However, no new peak appeared at coverage above 0.5 ML.

The coverage dependence of the SHG intensity at 1.17-eV excitation (Fig. 1) is consistent with the change of the SHG spectrum shown in Fig. 2. Figure 2 indicates that the SHG intensity initially reduced from the intensity at 1.17 eV, and then recovered in the 400 °C deposition, while it reduced monotonically in the room-temperature deposition, as shown in Fig. 1.

IV. DISCUSSION

The SHG spectrum at the Si(111) 7×7 surface has recently been reported by several groups.[11–14] Our result is consistent with these previous studies, in which peaks were observed at ~1.2, ~1.4, and ~1.7 eV. Since the peak at ~1.7 eV is not reduced with the oxygen adsorption,[11] it has been attributed to the band transition in the strained subsurface Si layers, as described later. The peaks at ~1.2 and ~1.4 eV have been attributed to the transition with the surface states of Si(111) 7×7, since these peaks decrease with the oxygen adsorption.[11,12] Based on the energy levels of the occupied and empty surface states of Si(111) 7×7,[15,16] the peak at ~1.4 eV has been designated as a one-photon transition between the occupied rest atom (S_2) state to the empty adatom (U_1) state. However, the assignment of the peak at ~1.2 eV is controversial. Pedersen and Morgen designated the peak as the transition from S_2 to the lower edge of the broad U_1 state band,[11] while Suzuki assigned the peak to the two-photon transition between the occupied back bond (S_3) state to the U_1 state.[12] In this study, the two peaks were found to reduce at different rates with the Ag coverage. The different reducing rates indicate that the two peaks have different origins. Thus we support that the peak at 1.15 eV was a S_3-U_1 two-photon transition. This designation is consistent with the results of our STM study.[17] STM images have shown that the long-range ordering of 7×7 dimer-adatom-stacking fault (DAS) reconstruction[18] is preserved in a room temperature deposition even after the 1-ML Ag deposition, though the adatom and rest atom sites of the surface are already covered by the Ag wetting layer. Therefore it is reasonable to assume that the peak at 1.35 eV with the rest atom state is quenched faster than the peak at 1.15 eV with the back bond state.

The spectrum changed in a different way in the Ag deposition depending on the substrate temperature as shown in Fig. 2. We obtained the spectra of the 400 °C deposition at room temperature by cooling the substrate after a small increase of the coverage. Thus the difference in the SHG spectrum is related to a difference in the electronic states of the $\sqrt{3}\times\sqrt{3}$-Ag structure in the 400 °C deposition and the 1×1-Ag structure in the room-temperature-deposition.

The peaks in the SHG spectrum of the Si(111) $\sqrt{3}\times\sqrt{3}$-Ag are related to the transition with the characteristic surface electronic states of this surface reconstruction. Although one of the two characteristic peaks of the $\sqrt{3}\times\sqrt{3}$-Ag reconstruction appeared at the same energy as the S_3-U_1 transition of the Si(111) 7×7 surface (1.15 eV), it was regarded to have originated from the intrinsic transition of the $\sqrt{3}\times\sqrt{3}$-Ag surface because $\sqrt{3}\times\sqrt{3}$-Ag reconstruction[9] has a completely different framework from DAS reconstruction.[18] Angle-resolved ultraviolet photoelectron spectroscopy (AR-UPS) studies have revealed three occupied surface states (S'_1, S'_2, S'_3) at the Si(111) $\sqrt{3}\times\sqrt{3}$-Ag surface.[19,20] S'_1 was located at ~-0.3 eV and had a free-electron-like upward dispersion at around $\bar{\Gamma}$, whereas S'_2 and S'_3 were degenerated at -1.4 eV at $\bar{K}$. Only one distinct surface state (U') has been observed at $+1.9$ eV above Fermi level by inverse photoemission spectroscopy (IPS).[16] U' was designated as a surface Umklapp of the Si empty state at $\bar{K}$ to $\bar{\Gamma}$. Judging from the energy difference and $k_{\parallel}$ conservation, we attributed the peak at 1.15 eV at the $\sqrt{3}\times\sqrt{3}$-Ag reconstructed surface to the two-photon transition between the S_1' and $-U'$ states (energy difference $\sim$2.2 eV). In addition to these surface states, the valence band can also contribute to the SHG in the surface layers, which lacks inversion symmetry. However, no suitable valance band was found at the $\sqrt{3}\times\sqrt{3}$-Ag surface in the theoretically calculated band structure.[21]

In an unpolarized AR-UPS study, the S_1' state was observed clearly only under the electric vector parallel to the surface.[20] Therefore the transition from the S_1' state could be excited strongly in our SHG measurement with the excitation beam polarized parallel to the surface. Recent theoretical calculation indicated that the S_1' state has an Ag-Si bonding characteristic.[21] Since the Ag-Si bond directs along $\{11\bar{2}\}$, the S_1' state is regarded to have even parity with the $[11\bar{2}]$ mirror plane. The Umklapped U' state at $\bar{\Gamma}$ also has even parity with the $[11\bar{2}]$ mirror plane. The SHG was excited in this study by the electric field polarized along $[1\bar{1}0]$ (which is perpendicular to the $[2\bar{1}\bar{1}]$ mirror plane). Thus the optical transition matrix is nonzero in the one-photon process between the states of different parity with the $[2\bar{1}\bar{1}]$ mirror plane, and in the two-photon process between the states with the same parity.[22] In this case, the above assignment of the two-photon transition between S_1' and U' state is reasonable.

The intense peak at 1.45 eV has no suitable transition between the characteristic states of the $\sqrt{3}\times\sqrt{3}$-Ag reconstruction. Judging from its strong intensity, we tentatively attribute this peak to plasmon excitation. The Si(111) $\sqrt{3}\times\sqrt{3}$-Ag surface is regarded to have a metallic nature in respect to the free-electron-like dispersion of the S_1' surface state.[19,20] The Na overlayer makes surfaces metallic similar to the Si(111) $\sqrt{3}\times\sqrt{3}$-Ag surface. A theoretical study demonstrated that this Na overlayer shows plasmon peaks at $0.8\omega_p$ and ω_p, where ω_p is the bulk Na plasmon.[23] The multipole plasmon at $0.8\omega_p$ in particular has been shown to cause a strong peak in SHG at the excitation photon energy of $0.4\omega_p$.[24,25] The multipole plasmon peak was expected to appear at 1.51 eV ($0.4\omega_p$) in our case of the Si(111) $\sqrt{3}\times\sqrt{3}$-Ag surface, assuming that ω_p is 3.78 eV (the bulk plasmon value). This estimation is satisfactorily close to the observed peak position at 1.45 eV. In respect to the peak position and intensity, the peak at 1.45 eV can be attributed to multipole plasmon excitation at the metallic Si(111) $\sqrt{3}\times\sqrt{3}$-Ag surface.

The problem here is whether the surface parallel electric field of our normal incident laser beam can excite the multipole plasmon. A time-dependent density-functional approach has indicated that the multipole plasmon excitation is a result of dynamic screening of the surface normal electric field at the edge of the jellium surface.[24,25] The strong resonance enhancement of SHG has in fact been found at an excitation photon energy of $0.4\omega_p$ at metal surfaces in an SHG experiment with a *p*-polarized off-normal incident laser beam.[25,26] However, the surface parallel electric field does not couple to the multipole plasmon excitation within the framework of a jellium model where the anisotropic response in SHG is neglected.[27] The surface parallel electric field does couples, however, with the surface normal electric field through its anisotropic response at the Si(111) surface. In this study, we observed an SHG signal with the surface parallel electric vector along $[2\bar{1}\bar{1}]$(x-axis) excited by a laser beam with the surface parallel electric vector along $[01\bar{1}]$(y-axis). The second order nonlinear polarization along $[2\bar{1}\bar{1}]$ is described by the following equation for normal incident beam geometry:[10]

$$P_x^{2\omega}\sim(\chi_{xxx}^{2\omega}\cos^2\phi+\chi_{xyy}^{2\omega}\sin^2\phi+\chi_{xyx}^{2\omega}\sin 2\phi)E^2.$$

$\chi^{2\omega}$s are the nonlinear susceptibility components, ϕ is the angle between the incident electric field vector E and the x axis. $\phi=90°$ in our experimental setup, and the response came from anisotropic tensor component $\chi_{xyy}^{2\omega}$. This anisotropic response is understood in the bond model[5] as the sum of the nonlinear polarization at each surface bond along $\{2\bar{1}\bar{1}\}$ directions. The surface bond does not lie in the (111) plane here, and it has a surface normal component. Thus the surface parallel electric field can couple with the surface normal excitation at the Si(111) surface via polarization of the surface bond. Therefore our electric field can couple with the multipole plasmon.[28]

The multipole plasmon peak became sharper and blue-shifted with the coverage in electron energy-loss spectroscopy of Na and K overlayer formation on Al(111).[29] This is in contrast to the peak at 1.45 eV not shifting for 0.75–1.0-ML coverage at the $\sqrt{3}\times\sqrt{3}$-Ag surface. Theoretical works have indicated that the blue-shift and sharpening of the peak are due to a reduction of the coupling between the collective mode and one particle excitation.[23,29] The alkali atoms distributed uniformly in the overlayer and their distance reduced gradually with the coverage. The overlap of the electron orbital with the coverage enhances the metallic nature of the overlayer and causes a peak shift. However, Ag atoms demonstrated perfect $\sqrt{3}\times\sqrt{3}$-Ag reconstruction locally on the Si(111) surface even at a small coverage. The local domain of the $\sqrt{3}\times\sqrt{3}$-Ag reconstruction extended with the coverage and finally covered all of the surface at 1.0 ML. We deduced that the local $\sqrt{3}\times\sqrt{3}$-Ag domain formation is the reason why the peak did not shift at 1.45 eV.

The SHG spectrum of an Si(111) 1×1-Ag surface is characterized by a single peak at $\sim$1.6–1.7 eV. This feature has been commonly observed in the SHG spectrum at molecule-adsorbed Si surfaces and SiO_2/Si interfaces.[11,14,30,31] The peak was attributed in these previous cases to the bulk band transition since the intrinsic surface states of the Si surface had been quenched. The peak has since been assigned to be due to the E_0' transition in the strained subsurface layers that lacks the inversion symmetry for the SHG excited by the surface parallel electric field.[31] The Si(111) 1×1-Ag surface is similar to SiO_2/Si interfaces in that the dangling bonds of the Si surface are passivated. Thus we also attributed the peak to the E_0' transition in the subsurface Si layers. The peak position has been observed to shift at SiO_2/Si interfaces depending on the film thickness and the film growth condition.[30–32] Some previous studies have determined the vertical tensile strain to be the cause of the red-shift.[30,31] Ag film has been reported to accumulate tensile strain in the (111) plane at the epitaxial Ag/Si(111) interface.[33] Assuming volume conservation in the deformation, the in-plane tensile strain in the Ag film causes a vertical tensile strain in the Si layer. This is qualitatively consistent with the redshift of the peak with the Ag coverage. However, a recent study indicated that the change in the surface local electric field, not the strain, is the primary origin of the peak shift.[32] In that case, a charge redistribution due to the quenching of the dangling bonds may be the main reason for the redshift of the peak.

Finally, we compare the present results with previous studies on the SHG from thick Ag film on an Si(111) surface.[6,7] A change of the SHG intensity has been reported in coverage up to 25 ML's with the excitation beam fixed at 1.17, 1.40, 1.70, and 2.34 eV in the room-temperature deposition of Ag film on an Si(111) 7×7 surface.[7] The oscillatory behavior with the film thickness has been attributed successfully to the resonance of the transition from the quantum well states localized in the Ag film at each excitation photon energy. Our results suggest that the E_0' interface SHG should also be observed at $\sim$1.6 eV. However, it is difficult to judge whether the E_0' interface SHG was detected in the previous data, though the excitation energy at 1.70 eV was close to E_0' transition and a relatively larger SHG intensity was recorded at this excitation photon energy. The thickness dependence of the SHG intensity has also been measured for thick Ag film at 1.17 eV on Si(111) 7×7 and $\sqrt{3}\times\sqrt{3}$-Ag surfaces.[6] In this study, the thickness dependences were found to differ depending on the starting surface structure, though the oscillatory behavior was not as obvious as in the study cited above.[7] The starting surface dependence was related to a difference in the growth mode of the Ag film. The quantized states in the Ag film and enhancement of the field by the localized plasmon in three-dimensional Ag islands have been suggested as the origins of the coverage dependence of the SHG intensity. However, this local plasmon in Ag islands is not the same as the plasmon of the $\sqrt{3}\times\sqrt{3}$-Ag surface discussed in this study. Further studies with a full spectrum measurement for a thick Ag/Si(111) system are necessary to examine whether the electronic states at a buried interface can be detected by SHG.

V. SUMMARY

The SHG spectrum was measured at Si(111) 7×7, $\sqrt{3}\times\sqrt{3}$-Ag, and 1×1-Ag surfaces. The SHG spectrum exhibited features characteristic of the surface electronic states of these surfaces. The peaks at 1.15 and 1.35 eV of the 7×7 reconstruction reduced in the Ag deposition. Based on their different reducing rates, these peaks were designated as a S_3-U_1 two-photon transition and S_2-U_1 one-photon transition of the 7×7 reconstruction. Two intense peaks were observed at 1.15 eV and 1.45 eV at the Si(111) $\sqrt{3}\times\sqrt{3}$-Ag surface. These were attributed to the two-photon transition from the free-electron-like S_1' state to the surface Umklapp U' state, and the multipole plasmon resonance at the $\sqrt{3}\times\sqrt{3}$-Ag reconstructed metallic surface. The dangling bond-related peaks disappeared at the Si(111) 1×1-Ag surface, and only the peak due to the E_0' transition at the strained surface layers was observed. These results demonstrated the possibility of using SHG spectrum measurements to detect characteristic electronic states localized at the surface.

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be given by the experiment with the off-normal, *p*-polarized excitation beam. However, this was not conducted because of the geometrical restriction in our vacuum chamber.

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