# Oscillation of the optical second-harmonic generation intensity during Ag thin film growth on a Si(111)7×7 surface

H. Hirayama,* T. Kawata, and K. Takayanagi
*Department of Materials Science and Engineering, Tokyo Institute of Technology 4259 Nagatsuda, Midori-ku, Yokohama 226-8502, Japan*

(Received 10 May 2001; published 26 October 2001)

The optical second harmonic generation (SHG) intensity demonstrated clear oscillations during Ag thin film growth on an Si(111)7×7 surface at room temperature. The first intensity peak appeared at two monolayer (ML) for 1.20, 1.30, and 1.40 eV pump photon energies, and the second peak shifted to a lower coverage side with increases in the excitation photon energy. The SHG spectra and atomic force microscope images indicated that the first peak was due to local field enhancement by the plasmon confined in isolated Ag islands. The second peak was caused by resonance with the quantized electronic states confined in the flat Ag thin film.

DOI: 10.1103/PhysRevB.64.195415 PACS number(s): 78.66.−w, 73.20.At, 73.20.Mf

## I. INTRODUCTION

Optical second harmonic generation (SHG) has gained attention as a powerful tool for *in situ* monitoring of thin film growth processes because it eliminates the needs for vacuum, a quick response in the time domain, and sensitivity to the surface and interface in SHG measurements.[1] The SHG intensity is quadratically proportional to the incident pump light intensity. Thus, growth of the film modifies the SHG intensity by enhancing the local electric field. Enhancement of the SHG intensity has been previously reported with nucleation of three-dimensional islands[2,3] due to light field enhancement by local plasmons confined in the small islands. Enhancement of the SHG intensity by resonant transition with the quantum well states confined in planar thin films grown layer-by-layer was also recently reported.[4–6] In general, both the local field enhancement and resonance of the quantum well states could influence the SHG intensity during the growth of thin films with morphological changes. However, only one of the two origins was investigated in previous studies on the correlation of the SHG intensity with the thin film growth process. In this study, we combine SHG and atomic force microscope (AFM) observations for Ag thin film growth on an Si(111)7×7 surface at room temperature to demonstrate that both local field enhancement with island nucleation and resonance with quantum well states in a flat film contribute to changes in the SHG intensity.

Ag film grows in the Stranski-Krastanov mode on an Si(111)7×7 surface at room temperature in the initial growth stage. A scanning tunneling microscope (STM) study indicated that a two-dimensional wetting layer is completed at ~0.7 ML, and three-dimensional Ag islands then start to nucleate.[7] However, large islands with flat surfaces have been observed in ultrahigh vacuum secondary electron microscope (FE-SEM) images at coverages above ~10 ML.[8] Quantum well states in flat Ag thin films have also been reported for coverages above 5 ML in an ultraviolet photoemission (UPS) study.[9] SHG intensity changes with Ag film growth on an Si(111)7×7 surface were recently reported by Pedersen *et al.* for Ag coverage up to 25 ML. They observed an oscillation of the SHG intensity with coverages at several fixed pump photon energies. Peaks in the SHG intensity were very recently attributed to resonance with the quantum well states.[5,10] However, the initial change of the SHG intensity could not be explained by the quantum well resonance. Local field enhancement was cited as the reason for the unexplained initial change of the SHG intensity, but the details were not studied. Our study complements that of Pedersen *et al.*[4,8] In this study, we concentrate on coverage up to ~10 ML, where the growth mode changes from three-dimensional small island nucleation to flat layer growth, and investigate the changes in the SHG intensity in more detail. A combination of the SHG intensity measurements with several fixed pump photon energies, the SHG spectrum measurements at several fixed coverages, and an atomic force microscope (AFM) measurement revealed that the first SHG intensity peak was due to local field enhancement, while the following peaks were due to resonance to the quantum well states in the flat Ag layers.

## II. EXPERIMENT

Details of the experiments have been described elsewhere.[11] Briefly, experiments were performed in an ultrahigh vacuum chamber 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. Si(111) samples were thermally cleaned in the chamber. The surface cleanliness was confirmed by observing a sharp 7×7 RHEED pattern. SHG was caused by a pulsed laser beam from an optical parametric oscillation (OPO) system excited by a *Q* switched YAG laser. The SH signal was separated from the pump light by color filters and was detected by a photomultiplier tube (PMT). The SHG intensity was calibrated by considering the wavelength dependence of the transmittance of the color filters and the sensitivity of the PMT. The quadratic dependence of the SHG intensity on the pump beam intensity was also considered. The sample was irradiated at 45° from the surface normal by a *P*-polarized pump laser beam. The *P*-polarized component of the SHG light was detected. The polarization vector was parallel to the $[01\bar{1}]$ direction at the Si(111) surface. The SHG intensity was measured at 1.20,

 

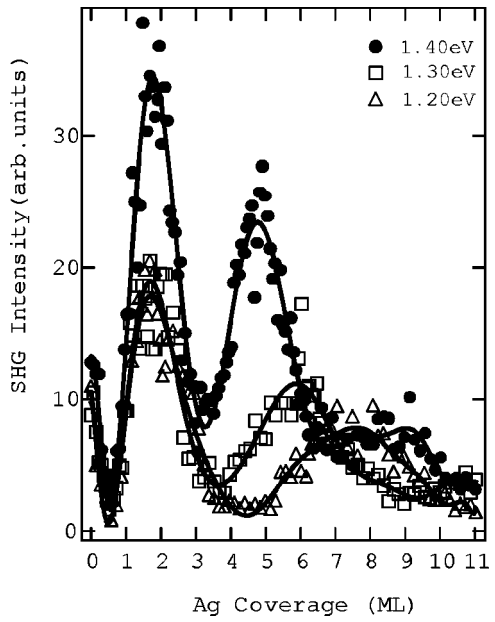


FIG. 1. The SHG intensity oscillation with an increase in Ag coverage. The results for 1.20, 1.30, and 1.40 eV pump photon excitations are indicated by triangles, squares, and dots. The solid lines are the least square fits of the data.

1.30, and 1.40 eV pump beams during Ag growth on an Si(111)7×7 surface at room temperature. The SHG spectrum was also measured at several coverages in a pump beam range between 1.05 and 1.60 eV. The Ag coverage was determined by the deposition time under the assumption that the Ag-induced $\sqrt{3}\times\sqrt{3}$ reconstruction was completed at 1 monolayer (ML).[12] The growth rate of the Ag film was 0.25 ML/min. The surface morphology of the grown film was observed *ex situ* by an atomic force microscope (AFM) in contact mode.

## III. RESULTS

Figure 1 shows the coverage dependence of the SHG intensity at 1.20, 1.30, and 1.40 eV pump photon energies. The SHG intensity initially decreased with the coverage in the submonolayer regime at all pump photon energies. The intensity then increased and exhibited the first peak at 2ML. The intensity was twice a great in the 1.40 eV pump beam as in the 1.30 and 1.20 eV pump beams. However, the position of the first peak was independent of the pump photon energy. In contrast to the first peak, the second peak position was dependent on the pump photon energy. The second peak appeared at 4, 6, and 8 ML for 1.40, 1.30, and 1.20 eV pump photon energies. The intensity of the second peak decreased with decreases in the pump photon energy.

Figure 2 shows the SHG spectra taken at 1.9 (a), 3.7 (b), 5.2 (c), and 7.5ML (d). Arrows in the figure indicate the 1.20, 1.30, and 1.40 eV pump photon energy positions at which the SHG intensity oscillations were observed in Fig. 1. Figures 2(a) and 2(b) were taken at the coverage of the first peak and the subsequent valley in Fig. 1. Figure 2(c) was taken at the

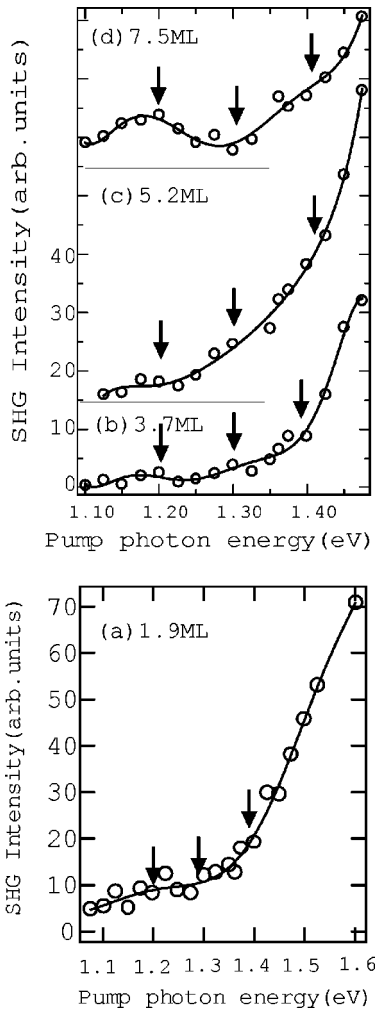


FIG. 2. SHG spectrum taken at Ag coverages of (a) 1.9ML, (b) 3.7ML, (c) 5.2ML, and (d) 7.5ML. Arrows indicate the pump photon energies of 1.20, 1.30, and 1.40 eV used for the measurements in Fig. 1. The zero signal lines are indicated by fine horizontal lines in (c) and (d).

coverage of the second peak in the 1.30 eV pump photon energy. This coverage also corresponds to the high and low coverage side tails of the second peak in the 1.40 and 1.20 eV pump beams. Figure 2(d) was taken at the coverage of the second peak at the 1.20 eV pump photon energy. At this coverage, the SHG intensity of the second peak was sufficiently reduced at the 1.30 and 1.40 eV pump photon energies in Fig. 1. The spectral shape of Fig. 2(a) is similar to that of (b), though the spectrum (b) intensity is relatively less than that of (a). The SHG intensity in Fig. 2(c) is relatively greater at around 1.4 eV compared with spectra (a) and (b), suggesting that a small peak was embedded at ~1.4 eV in the slope from the higher energy side. A clear peak is observed at 1.20 eV in Fig. 2(d), while the intensity is reduced at ~1.30 and 1.40 eV relative to spectra (a) and (b).

Figure 3 shows AFM images of the Ag films grown on the Si(111)7×7 surface. Figures 3(a), 3(b), and 3(c) were taken at the coverages at the upward tail, the maximum, and the downward tail of the first peak in Fig. 1. Figure 3(d) was taken at the coverage of the valley following the first peak.

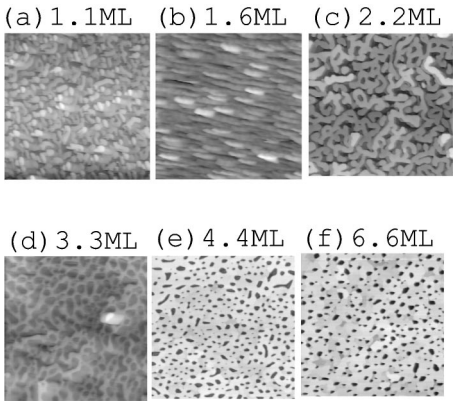


FIG. 3. AFM images of Ag films grown on an Si(111)7×7 surface at room temperature. The image size was 1×1 $\mu$m. The Ag coverage is indicated in the figures.

Figure 3(e) was taken at the coverage of the second peak in the 1.40 eV pump beam. This coverage also corresponds to the valley following the first peak in the 1.30 and 1.20 eV pump beams. Figure 3(f) was taken at the coverage of the second peak in the 1.20 eV pump beam. These AFM images demonstrate that the Ag atoms initially nucleate into three-dimensional islands. The islands then coarsen into a network. Finally, the surface of the film had the same contrast in most areas except for small dark regions in AFM images. It means that the surface morphology changes to flat, though the surface includes many holes. In comparison with Fig. 1, the first peak was found to appear in the growth stage of the small island nucleation. The second peak was found to appear in the second stage where the islands coalesced and formed a film with flat surface morphology.

## IV. DISCUSSION

The positions of our second peaks in Fig. 1 are consistent with the positions of the first clear peaks in Pedersen's recently published results.[5] The first peaks were identified at ~5 ML in the 1.40 eV pump beam and at ~7 ML in the 1.17 eV pump beam in the SHG intensity oscillation in their report. However, the change in the SHG intensity differed in the small coverage region up to 3 ML. Our results are characteristic in that the SHG intensity initially decreased and then the first peak appeared clearly at 2 ML, independent of the pump photon energy. In Pedersen's results, the SHG intensity increased from zero toward a small peak at 1 ML and an intense shoulder at 4 ML before the clear peak at 7 ML in a 1.17 eV pump beam. The SHG intensity initially decreased in their 1.40 eV pump energy, had a minimum at 2 ML, and then increased to a clear peak at 5 ML. These discrepancies may be caused by a difference in the growth rate, which influences the island nucleation, though no description of the rate was found in the previous report.

The pump photon energy dependence of the *S*-polarized SHG intensity from an Si(111)7×7 surface has been reported by several groups.[11,13–16] In the SHG spectrum, the Si(111)7×7 surface exhibited peaks at 1.15, 1.35, and 1.7 eV pump photon energies due to a two-photon transition from the occupied back bond state to the empty adatom state (S3-U1), a one-photon transition from the occupied rest atom state to the empty adatom state (S2-U1) of the 7×7 dimer-adatom-stacking (DAS) fault surface reconstruction, and the two-photon resonance to the $E_0'$ transition in the strained near-surface layers.[11,14] The assignments of the 1.15 and 1.35 eV peaks are convincing because these surface dangling bond-related peaks are quenched by exposure to oxygen[13,14,17–19] and hydrogen.[15,20] Only the $E_0'$ transition was observed as a distinct peak in the spectrum in a *P*-polarized SHG intensity.[16,21] However, the S2-U1 transition has been reported to cause a broad resonance at ~1.30 eV and to contribute to the intensity at the long tail of the peak at ~1.7 eV in the *P*-polarized SHG spectrum.[16] In our previous study on the *S*-polarized SHG spectrum, the peak due to the S2-U1 transition was observed to decrease with coverage in the submonolayer regime in Ag deposition on an Si(111)7×7 surface because of the saturation of the surface dangling bonds by Ag atoms.[11] Thus, an initial decrease of the SHG intensity is reasonable at pump photon energies of 1.20, 1.30, and 1.40 eV close to the broad S2-U1 resonance.

AFM images indicated that the film was not continuous but consisted of three-dimensional Ag islands at around the first peak in Fig. 1. The two-dimensional quantum well does not expand in such an assembly of three-dimensional Ag islands. Therefore, the first peak is not due to resonance with the quantum well states in the Ag film, but to local field enhancement in the Ag small islands. The light field can couple with the plasmon due to the breaking of $k_{//}$ conservation at the surface with small islands, and can then enhance the local field. The SHG intensity increases through the enhancement of the local field.[22] The number of nucleated small islands increased with the coverage in the initial stage of the Ag thin film growth. However, the islands later decreased to form a continuous flat film, and the number of islands decreased. This change in the number of islands caused the first peak in the initial stage of the thin Ag film growth.

In surface enhanced Raman scattering (SERS), the local field has been reported to be enhanced by several orders when the pump beam photon energy hits the local plasma resonance precisely.[23] The increase of our first SHG peak was not substantial, probably because the pump photon energies of 1.20, 1.30, and 1.40 eV were far from the local plasma resonance. The resonant energy depends on the shape of the Ag island.[24–26] In the simplest sphere shape of depolarization factor $A=1/3$, the resonant energy is calculated to be 2.20 eV using Eq. (1) in Ref. 26 for a Drude type dielectric function with an Ag bulk plasma frequency of 3.84 eV. The resonant energy differs for a more complicated shape, but is still expected to be higher than our scanning range of the photon energy of the spectrum in Fig. 2. Thus, no local plasmon resonant peak was observed in the spectrum. However, the local plasmon resonance has a broad tailing of ~0.6 eV in the full width of the half maximum (FWHM).[24]

Thus, our pump photon energies are expected to be on the edge of the lower energy side tail of the local plasma resonance in the initial growth stage. This agrees with the spectral shapes in Figs. 2(a) and 2(b). The increase (decrease) of the number of islands increases (decreases) the intensity at the tail. However, this change does not depend on the pump photon energy. We presume that this is the reason for the pump photon energy independence of the first peak. This is also consistent with the spectral change in Figs. 2(a) and 2(b).

In addition to the local plasmon resonance, a two-photon resonance with the $E_0'$ transition in the strained subsurface Si layers at $\sim 1.7$ eV (Refs. 16, 21) could increase the SHG at the high-energy side in our SHG spectrum. The $E_0'$ resonance has been reported to shift by $\sim 0.1$ eV with a change of the strain due to a heterolayer growth on the Si substrate.[11,27] The direction of the shift depends on the sign of the change of the strain. A redshift is expected in the Ag deposition on an Si substrate.[11] This shift may increase the SHG intensity on its lower energy side, but the direction of the shift does not reverse in the course of the Ag thin film growth. Thus, it does not produce a peak in the coverage-dependent change of the SHG intensity and is ruled out as the reason for the first peak in Fig. 1. The strain resonance remains in all stages of Ag thin film growth; therefore the tail of the local plasmon resonance with the low-energy side was superimposed on the strain resonance in the initial stage of growth. The contribution of the local plasmon tail first increased in the initial stage and then decreased to cause the first peak in Fig. 1. The local plasmon contribution disappeared in the latter stage, but the strain resonance remained. The increase in the SHG intensity at the high-energy side in Figs. 2(c) and 2(d) is regarded to be due to this residual strain resonance.

In contrast to the first peak, the excitation energy-dependent shift and flat surface morphology of Ag films support the hypothesis that the second peak is caused by SHG resonance with the quantum well states confined in the Ag films. The shift of the peak to the large coverage side with decreases in the pump photon energy agrees with the tendency of the quantum well state to become shallower with the thickness of the Ag thin film. Our results indicate that the quantum well states evolved in the Ag films of coverages above $\sim 4$ ML. This is consistent with the UPS study[9] and a linear optical reflectance spectroscopic study on an Si(001) surface, which indicated that Ag film suddenly has a metallic nature at a coverage of 3.4 ML.[28] The clear peak at 1.20 eV in Fig. 2(d) and the peak suggested to be embedded at 1.40 eV in Fig. 2(c) also support resonance with the quantum well state. Pedersen *et al.*[10] recently theoretically studied the contribution of the quantum well states in an Ag film on an Si(111) surface to the SHG. They calculated the SHG by the electronic transition from the occupied quantum well states of an Ag film to the quasifree empty states coupled to an Si conduction band continuum as a function of the Ag film thickness. Several transitions were included simultaneously in a film of specific thickness because of the broadness of the empty states. The resonant peak was predicted to appear at 7 and 5 ML for 1.17 and 1.40 eV excitations in the theory. This is consistent with our results.

## V. SUMMARY

In summary, we studied SHG intensity oscillation in detail during Ag film growth on an Si(111)$7\times7$ surface. The first peak appeared at 2 ML, and was independent of the pump photon energy. Based on the independence of the pump photon energy and the SHG spectra and the AFM images of the three-dimensional Ag islands, we concluded that this peak was due to local plasmon resonance in the Ag islands. The second peak shifted to a lower coverage with increases in the pump photon energy. The peak position agreed with theoretical values. The pump photon energy shift and the AFM images of the flat surface morphology of the Ag film support the supposition that the peak is caused by resonance with the quantum well states in the Ag film. This study demonstrated that coverage-dependent oscillation of the SHG intensity can provide information about both island nucleation and flat layer film growth.

*Correspondence author; Email: hirayama@materia.titech.ac.jp

[1] Y. Jiang, P. T. Wilson, M. C. Downer, C. W. White, and S. P. Withrow, Appl. Phys. Lett. **78**, 766 (2001).
[2] F. R. Aussenegg, A. Leitner, and H. Gold, Appl. Phys. A: Mater. Sci. Process. **60**, 97 (1995).
[3] G. T. Boyd, Th. Rasing, J. R. R. Leite, and Y. R. Shen, Phys. Rev. B **30**, 519 (1984).
[4] A. Kirilyuk, Th. Rasing, R. Megy, and P. Beauvillain, Phys. Rev. Lett. **77**, 4608 (1996).
[5] T. G. Pedersen, K. Pedersen, and T. B. Kristensen, Phys. Rev. B **60**, R13 997 (1999).
[6] K. Pedersen, T. G. Pedersen, T. B. Kristensen, and P. Morgen, Appl. Phys. B: Lasers Opt. **68**, 637 (1999).
[7] H. Hirayama, H. Okamoto, and K. Takayanagi, Phys. Rev. B **60**, 14 260 (1999).
[8] Y. Gotoh, S. Ino, and H. Komatsu, J. Cryst. Growth **56**, 498 (1982).
[9] A. L. Wachs, A. P. Shapiro, T. C. Hsieeh, and T.-C. Chiang, Phys. Rev. B **33**, 1460 (1986).
[10] T. G. Pedersen, K. Pedersen, and T. B. Kristensen, Phys. Rev. B **61**, 10 255 (2000).
[11] H. Hirayama, T. Komizo, T. Kawata, and K. Takayanagi, Phys. Rev. B **63**, 155 413 (2001).
[12] T. Takahashi and S. Nakatani, Surf. Sci. **282**, 17 (1993).
[13] K. Pedersen and P. Morgen, Phys. Rev. B **52**, R2277 (1995).
[14] T. Suzuki, Phys. Rev. B **61**, R5117 (2000).
[15] U. Hofer, Appl. Phys. A: Mater. Sci. Process. **63**, 533 (1996).
[16] K. Pedersen and P. Morgan, Surf. Sci. **377-379**, 393 (1997).
[17] K. Pedersen and P. Morgen, Phys. Rev. B **53**, 9544 (1996).
[18] H. W. K. Tom, X. D. Zhu, Y. R. Shen, and G. A. Somorjai, Surf. Sci. **167**, 1675 (1987).
[19] P. Batrau, K. L. Kompa, and U. Hofer, Phys. Rev. B **49**, 14 070 (1994).
[20] G. A. Reider and U. Hofer, J. Chem. Phys. **94**, 4080 (1991).
[21] W. H. Daum, H.-J. Krause, U. Reichel, and H. Ibach, Phys. Rev. Lett. **71**, 1234 (1993).

[22] C. K. Chen, T. F. Heinz, D. Ricard, and Y. R. Shen, Phys. Rev. B **27**, 1965 (1983).
[23] M. Kerker, D.-S. Wang, and H. Chew, Appl. Opt. **19**, 3373 (1980).
[24] A. Wokaum, J. P. Gordon, and P. F. Liao, Phys. Rev. Lett. **48**, 957 (1982).
[25] G. T. Boyd, Th. Rasing, J. R. R. Leite, and Y. R. Shen, Phys. Rev. B **30**, 519 (1984).
[26] P. F. Liao, J. G. Bergman, D. S. Chemla, A. Wokaum, J. Melengailis, A. M. Hawryluk, and N. P. Economou, Chem. Phys. Lett. **82**, 355 (1981).
[27] C. Mayer, G. Lupke, U. Emmerich, F. Wolter, H. Kurtz, C. H. Bjorkman, and G. Lukovsky, Phys. Rev. Lett. **74**, 3001 (1995).
[28] Y. Borensztein, R. Alameh, and M. Roy, Phys. Rev. B **48**, 14 737 (1993).