

Resonant surface second harmonic generation from Au films on NaCl(100)

T. Kitahara, H. Tanaka, and Y. Nishioka

School of Materials Science, Japan Advanced Institute of Science and Technology Tatsunokuchi, Nomi-gun, Ishikawa 923-1292, Japan

G. Mizutani*

School of Materials Science, Japan Advanced Institute of Science and Technology Tatsunokuchi, Nomi-gun, Ishikawa 923-1292, Japan and "Fields and Reactions," PRESTO, Japan Science and Technology Corporation 4-1-8 Kawaguchishi-Honmachi, Saitama 332-0012, Japan

(Received 7 March 2001; revised manuscript received 2 July 2001; published 25 October 2001)

We have found that the resonance energy of optical second-harmonic (SH) generation from Au films on NaCl(100) depends strongly on the film thickness. The resonance peak of the SH intensity was found at $2\hbar\omega = 3.2$ eV for the island film of mean thickness 0.4 nm, while it appeared at $2\hbar\omega = 2.4$ eV for the continuous film of thickness 40 nm. We suggest that the SH intensity peak observed at $2\hbar\omega = 3.2$ eV originates from a resonant transition from occupied to unoccupied electronic levels of the (100) surface on top of the Au islands. The SH intensity peak observed at $2\hbar\omega = 2.4$ eV for the film thickness of 40 nm originates from the roughness-induced linear dielectric property of the film.

DOI: 10.1103/PhysRevB.64.193412

PACS number(s): 73.20.At, 42.65.Ky

I. INTRODUCTION

Optical second-harmonic (SH) spectroscopy has become a useful tool for investigating surface and interface electronic levels. However, there are still a lot of problems about how to relate SH spectra to the profiles of surface and interface electronic levels. Concerning smooth noble-metal surfaces the SH response is understood to originate either from the free-electron gas described by a "jellium" model¹ or from localized surface electronic levels.^{2,3} However, no systematic understanding of the relative importance of various sources contributing to the observed nonlinearity has yet been reached.

It has been pointed out that the SH response of surfaces of Ag(110),² polycrystalline Cu,³ and Cu(111)⁴ cannot be explained by the jellium model. For Ag(110) a SH intensity peak observed at $\hbar\omega \sim 1.7$ eV has been assigned to a resonance of a transition from occupied to unoccupied surface levels.² As for another important noble metal Au, we have observed a strong enhancement of SH intensity at $2\hbar\omega = 2.5$ and 5.0 eV from a glass-Au interface. We suggested that the SH enhancement arises from the resonance of an interband transition from an occupied *d* band to an unoccupied *s*, *p* band of a glass-polycrystalline Au(111) interface.⁵ Hohlfeld *et al.* reported that a similar peak observed near $2\hbar\omega = 5.0$ eV for a polycrystalline Au film is rather due to the structure of linear Fresnel factors.⁶ There has also been a SH observation by Pedersen *et al.* on a quantum-confinement effect of electrons in epitaxial Au films at coverage less than 45 ML.⁷ SH enhancement at $2\hbar\omega \sim 2.4$ eV is also observed for 4 nm diameter Au clusters embedded in an alumina matrix and the peak is assigned to the surface-plasmon resonance.⁸ However, no detailed SH spectroscopy has been performed on Au crystalline surfaces, although such measurement is necessary in order to clarify the character of the nonlinear response of localized *d* electrons systematically.

In this study, we have investigated how the face index of

Au surfaces influences the resonance energy of its surface-electronic states. For this purpose we have selected Au films deposited on NaCl(100). This selection is motivated by the fact that (100), (111) and polycrystalline surfaces of Au occur successively on NaCl(100) as the film thickness is increased.⁹ Namely, at the substrate temperature of 400 °C and for the mean film thickness less than 0.4 nm, films with (100) surfaces grow epitaxially on NaCl(100). When the thickness increases, the (111) surface component with random azimuthal orientation emerges. For the thickness of several tens of nanometers, the (111) surface component disappears and a polycrystalline component becomes dominant. Hence this sample is very convenient for the purpose of checking whether there is a change in the resonance energy as a function of the face index. However, we must take care of the fact that this film grows in the Volmer-Weber mode at low thicknesses.

II. EXPERIMENT

NaCl(100) surfaces were obtained by cleavage in air and Au thin films were evaporated on them with a metal evaporator by electron-bombardment heating (OMICRON EFM3) in an ultrahigh vacuum chamber with a base pressure of 3×10^{-10} Torr. The substrate temperature measured with a thermocouple attached to the sample holder was 400 °C and the deposition rate was ~ 0.1 nm/min. During the deposition the chamber pressure was around 5×10^{-9} Torr. The film thickness was monitored by a quartz-crystal microbalance. In order to obtain the nominal mean thickness, the measured thickness was multiplied by 0.6, the sticking probability of Au on NaCl at 400 °C.¹⁰ The surface structures of the deposited films were characterized by reflection high-energy electron diffraction (RHEED) and the surface morphology of the films was checked with an atomic-force microscope (AFM, Nanoscope III Digital Instruments) with spatial resolution of 1 nm. The linear reflection spectra of the film were also

measured in air, using a tungsten lamp as a light source and a monochromator (Jobin-Yvon HR-320).

The chamber is equipped with a tubulated viewport with a cylindrical quartz glass wall. For SH-generation (SHG) measurements the sample is transported into the cylindrical part of this viewport and the optical excitation and observation was done through the quartz glass wall. During the SHG measurements the sample was kept at room temperature.

The experimental setup for SHG measurements has been described elsewhere.⁵ The light source of the fundamental frequency was an optical parametric oscillator (Spectra Physics MOPO-730) driven by a frequency-tripled Q -switched Nd:YAG laser (Spectra Physics GCR-250), with a tunable wavelength in the visible and near-infrared regions. The spectral bandwidth of the laser beam was ~ 20 meV, the pulse duration time was ~ 3 nsec, and the repetition rate was 10 Hz. The p -polarized fundamental light was directed onto the sample at the angle of incidence of 45° and the reflected SH light of all polarizations from the sample was collected. The plane of incidence was parallel to the $[010]$ direction of the NaCl(100) substrate. A fraction of the incident laser light was split off from the beam and directed onto a reference sample [(a) GaAs(100) wafer] and the reflected SH light from it was used to correct for the laser-intensity fluctuations.

III. RESULTS AND DISCUSSION

In Fig. 1 we show AFM and RHEED images of the Au films deposited on NaCl(100) substrates with various thicknesses. Typically, NaCl(100) successfully cleaved gives smooth surface topography as shown in Fig. 1A(a) although we can also find step structures at other positions. The RHEED pattern of the cleaved NaCl(100) surface shows (00) , (20) , and $(2\bar{0})$ streaks as shown in Fig. 1B(a), indicating a smooth surface. For the Au film of mean thickness 0.4 nm, the AFM image [Fig. 1A(b)] shows isolated islands composed of small Au grains of height ~ 20 nm and diameter ~ 60 nm. The corresponding RHEED pattern shows distinct (100) spots of Au epitaxial component as are indicated by open triangles in Fig. 1B(b). The fact that the diffraction from the Au(100) structure is observed as spots and the streaks from the substrate is still seen indicates that the Au layer grows in three-dimensional islands, consistent with the observation by AFM [Fig. 1A(b)]. The other spots seen on the streaks are diffraction from the bulk NaCl induced by step structures. We have intentionally chosen the RHEED image including these spots to make the assignments of the spots from the Au film easier. For the Au film of the mean thickness 3.7 nm, the number of the islands observed by AFM is larger, but the sizes of the constituent grains are similar to those for the film of the mean thickness 0.4 nm [Fig. 1A(c)]. The corresponding RHEED pattern shows spots indicating the coexistence of Au(111) surfaces with random azimuthal orientation as are indicated by solid triangles in Fig. 1B(c). As a reference, RHEED spots expected from epitaxial Au(100) islands and the Au(111) polycrystalline domains with random azimuthal orientation on a NaCl(100) surface in the $[001]$ azimuth are shown schematically in Fig.

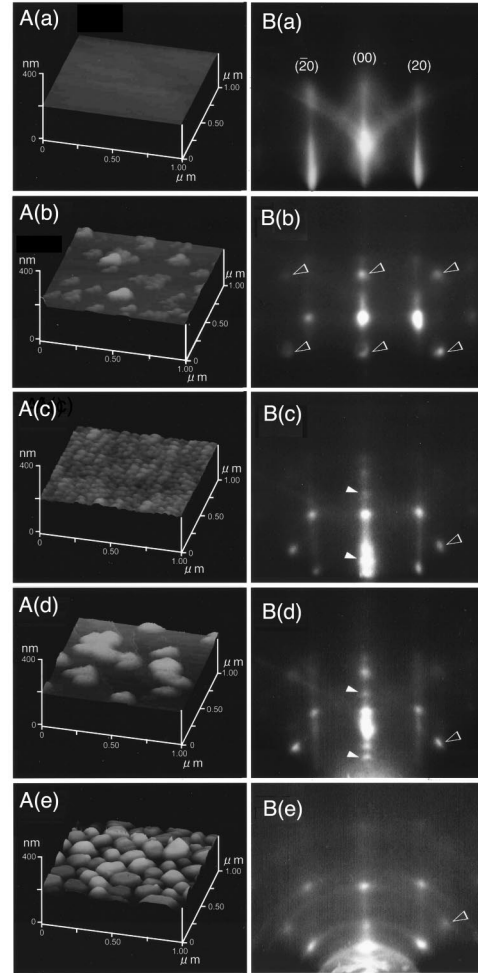


FIG. 1. AFM and RHEED images of the Au films deposited on NaCl(100) with various thicknesses. Panels (a)–(e) of part A are three-dimensional AFM images and panels (a)–(e) of part B are RHEED images. The mean thicknesses of the Au films are (a) 0 nm, (b) 0.4 nm, (c) 3.7 nm, (d) 6.0 nm, and (e) 40 nm. The RHEED patterns were taken in the $[001]$ azimuth and the energy of the incident electrons was 15 keV. Open triangles (∇) in the RHEED images indicate the spots from the epitaxial Au(100) structure. Solid triangles (\blacktriangledown) indicate the spots from the Au(111) structures with random azimuthal orientations.

2. For the Au film of the mean thickness 6.0 nm we see larger islands with the average height ~ 80 nm and diameter ~ 250 nm [Fig. 1A(d)], but the RHEED pattern [Fig. 1B(d)] looks similar to that from the film of mean thickness 3.7 nm [Fig. 1B(c)]. At the mean thickness 40 nm, the Au film is a continuous film with surface roughness as shown in Fig. 1A(e). On the corresponding RHEED pattern [Fig. 1B(e)], we can see strong Debye rings indicating a polycrystalline structure but very weak (100) spots, while the diffraction from the Au(111) surface component is not seen.

Figure 3 shows the SH intensity from Au thin films grown on NaCl(100) surfaces at various thicknesses as a function of the SH photon energy $2\hbar\omega$ for p -polarized excitation. The SH intensity from the substrate NaCl(100) is very weak in the whole spectral region, as shown in Fig. 3(a). The SH intensity spectra from Au films of mean thicknesses 0.4, 3.7,

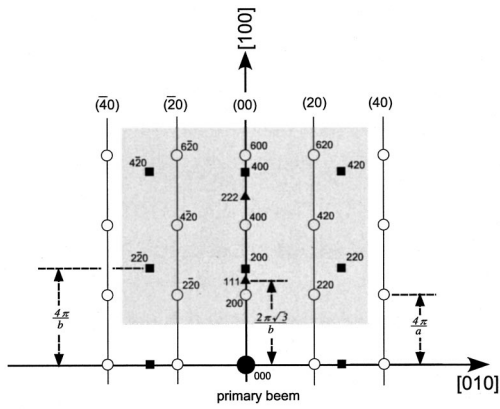


FIG. 2. Labeling of the RHEED spots from epitaxial Au(100) islands and the Au(111) polycrystalline domains with random azimuthal orientation on a NaCl(100) surface, seen in the [001] azimuth. Open circles (○), solid squares (■), and solid triangles (▲) indicate spots from the bulk NaCl structure, Au(100) surface structure, and Au(111) structures with random azimuthal orientations, respectively. The largest dot (●) indicates the direct spot of the primary electron beam. The hatched area indicates the field of view in the RHEED observation. a and b are the lattice constants of NaCl and Au, respectively.

6.0, 7.5, and 40 nm have peaks at $2\hbar\omega \sim 3.2$, 2.9, 2.5, 2.5, and 2.4 eV, respectively, as shown in Figs. 3(b)–3(f).

Here we discuss the origins of the SH intensity peaks in Fig. 3. There are several candidate origins of the observed SH intensity peaks. They are the roughness-induced effective linear dielectric property of the film,^{11–15} the “lightning-rod effect,”^{16,17} the quantum-confinement effects of free-electron gas,^{7,18} the resonant radiation from the bulk dipoles¹⁹ and higher-order multipoles,²⁰ and the resonance of surface-electronic levels.² The first two effects are related to the enhancement of the local electromagnetic field by the microscopic structures on the Au films. The others are associated with the enhancement of the nonlinear susceptibilities of the Au films themselves.¹⁹

First of all, we concentrate on the film of 40 nm thickness [Fig. 3(f)] and discuss the roughness-induced effective linear dielectric property of the film as a candidate origin of the SH intensity peak. The film of 40 nm thickness is a continuous film, but it has a considerable roughness on the surface as can be seen in Fig. 1A(e). In order to check the possibility of this candidate origin, we have measured linear reflectance spectra of the same films (not shown). For the Au film of mean thickness 40 nm, we have found a structure at 2.4 eV, the same energy as that of the SH intensity peak. It has been reported that change of dielectric property of Au occurs due to surface roughness or island structures.^{11,12} Mabuchi *et al.* have found a resonant absorption at 2.34 eV for Au particles with a diameter of 30 nm.¹³ Palpant *et al.* have also found a blueshift of the absorption resonance with decreasing cluster size, from 2.33 eV for size 3.7 nm to 2.52 eV for size 2.0 nm.¹⁵ Furthermore, Antoine *et al.* have found a SH intensity peak at $2\hbar\omega \sim 2.4$ eV from Au clusters of 4 nm diameters embedded in an alumina matrix and have suggested that surface-plasmon excitation is involved.⁸ Because the peak positions of the SH intensity and the linear reflectance of our

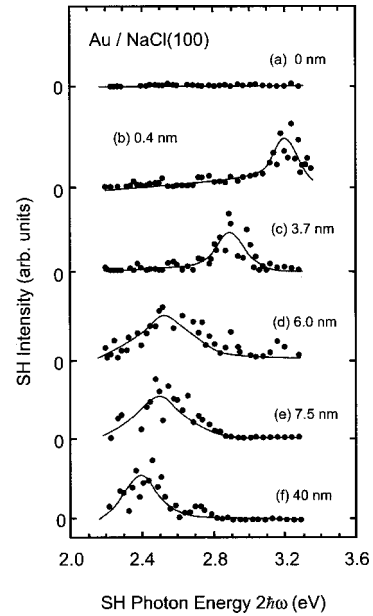


FIG. 3. The SH intensity as a function of the SH photon energy from Au thin films grown on NaCl(100) at various thicknesses. The solid curves are guides to the eyes. The relative magnitudes of the vertical scales of the six figures are arbitrary.

Au film of mean thickness 40 nm are roughly close to these energies, we infer that the peaks are caused by the roughness-induced effective linear dielectric property of the film.

On the other hand, the SH intensity peak at 3.2 eV for the mean thickness of 0.4 nm in Fig. 3(b) cannot be assigned to the roughness-induced effective linear dielectric property of the film. It might be possible that the energy of the roughness-induced linear dielectric structure shifts to the higher-energy side due to the size effect of the Au grains. However, the average height and diameter of the Au grains in the film of mean thickness 0.4 nm are 20 and 60 nm, respectively, and this size is not small enough for a size effect to occur.¹⁵

Lightning-rod effect¹⁶ is also possible if Au islands have sharp tops and it causes the shift of the surface-plasmonic resonance to the lower-energy side depending on the sharpness of the top of the islands.¹⁷ However, the shapes of Au islands in Figs. 1A(b)–1A(e) are rather oblate and do not change remarkably as a function of the film thickness. Thus the “lightning-rod effect” is not a major origin of the observed shift of the SH resonance.

The nonlinear response of free-electron gas¹⁸ at the surface described by the jellium model should not show such sharp peaks as those in Fig. 3, and the quantum-confinement effect of free electrons^{7,21} is not expected for the film of 0.4 nm thickness because the film is too thick (50 nm at maximum) and has a nonuniform thickness. The bulk higher-order multipole’s resonance cannot be the origin of the structure at 3.2 eV in SH intensity spectrum for the following reason: The bulk higher-order multipole’s effect²⁰ should have a resonance property similar to that of the bulk linear dielectric property, because they originate from the common electronic levels. Thus this resonance energy should not shift consider-

ably to the higher-energy side as in Fig. 3, because the sizes of the Au grains are rather too large as mentioned above for a size effect to occur. It is also said that SHG from dipoles are allowed for metallic nanoparticles of noncentrosymmetric shape.¹⁹ However, this SHG is observed for metallic particles with much smaller sizes (radius $R \leq 5.0$ nm) than those of the Au islands in this study. Thus, we can exclude this candidate also.

Now we are left with only the resonance of surface-electronic levels of Au(100) as a candidate origin of the peak at $2\hbar\omega = 3.2$ eV in Fig. 3(b). There have been several reports on the occupied and unoccupied surface states of Au(100).^{22,23} We can guess from them that resonant transition may occur at \bar{X} point for the present excitation-photon energy. Hence, we suggest that the peak at 3.2 eV in Fig. 3(b) can be assigned to the resonant transition between the surface-electronic levels of the Au(100) surface.

The origin of the SH intensity peaks at $2\hbar\omega = 2.9$ and 2.5 eV in Figs. 3(c), 3(d), and 3(e) for the mean film thickness 3.7, 6.0, and 7.5 nm may be twofold. The surfaces of these Au films are the mixture of an epitaxial Au(100) surface and Au(111) faces with random azimuthal orientation, as was found by the RHEED analysis. It has been reported that the SH intensity peak from the glass-polycrystalline Au(111) interface is located at 2.5 eV.⁵ Thus, it is likely that the resonant transition between the bands of the mixed surface of the Au(100) and Au(111) may be located between 2.5 and 3.2 eV. However, the peak energy $2\hbar\omega = 2.5$ eV in Figs. 3(d) and

3(e) is also close to the energy of the structure in the roughness-induced dielectric function, so it may also contribute to the enhancement of the SH intensity.

In conclusion we have obtained SH intensity spectra from Au films of various thicknesses grown on NaCl(100) in UHV. We have found several resonances of SH intensity and their resonance energy depends on the film thickness. We suggest that the peak at $2\hbar\omega = 2.4$ eV for the mean film thickness of 40 nm is caused by the roughness-induced effective linear dielectric property and that the peak at $2\hbar\omega = 3.2$ eV is due to a resonance of the interband transition of the Au(100) surface. As a next step, we plan to measure the azimuthal angle dependence of the SH intensity from the Au(100) surface, in order to check whether the d -electron character is found in the SH intensity response.

ACKNOWLEDGMENTS

The authors would like to thank Professor S. Ushioda of Tohoku University, Professor N. Otsuka, Professor M. Tomitori, Dr. H. Sano, and Dr. A. Sugawara of our Institute for valuable discussions, advice, and encouragement. They also acknowledge the contribution of H. Wakimoto at the early stage of this work and are grateful to H. Kita, E. Nakamura, and M. Uno of our Institute for their technical support. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture.

*Author to whom all correspondence should be addressed: Japan Advanced Institute of Science and Technology, Tatsunokuchi, Ishikawa 923-1292, Japan. FAX: +81-761-51-1149. Email address: mizutani@jaist.ac.jp

¹J. Rudnick and E. A. Stern, Phys. Rev. B **4**, 4274 (1971).

²L. E. Urbach, K. L. Percival, J. M. Hicks, E. W. Plummer, and H.-L. Dai, Phys. Rev. B **45**, 3769 (1992).

³G. Petrocelli, S. Martellucci, and R. Francini, Appl. Phys. A: Solids Surf. **56**, 263 (1993).

⁴H. W. K. Tom and G. D. Aumiller, Phys. Rev. B **33**, 8818 (1986).

⁵H. Tanaka, H. Wakimoto, T. Miyazaki, G. Mizutani, and S. Ushioda, Surf. Sci. **427–428**, 147 (1999).

⁶J. Hohlfield, S.-S. Wellershoff, J. Gdde, U. Conrad, V. Jhnke, and E. Matthias, Chem. Phys. **251**, 237 (2000).

⁷K. Pedersen, T. G. Pedersen, T. B. Kristensen, and P. Morgen, Appl. Phys. B: Lasers Opt. **68**, 637 (1999).

⁸R. Antoine, M. Pellarin, B. Palpant, M. Broyer, B. Prvel, P. Galletto, P. F. Brevet, and H. H. Girault, J. Appl. Phys. **84**, 4532 (1998).

⁹K. Mihama, H. Miyahara, and H. Aoe, J. Phys. Soc. Jpn. **23**, 785 (1967).

¹⁰T. Inuzuka and R. Ueda, J. Phys. Soc. Jpn. **25**, 1299 (1968).

¹¹D. E. Aspnes, E. Kinspron, and D. D. Bacon, Phys. Rev. B **21**, 3290 (1980).

¹²R. W. Wood, Philos. Mag. **4**, 396 (1902).

¹³M. Mabuchi, T. Takenaka, Y. Fujiyoshi, and N. Uyeda, Surf. Sci. **119**, 150 (1982).

¹⁴P.-M. Adam, S. Benrezzak, J. L. Bijeon, and P. Royer, J. Appl. Phys. **88**, 6919 (2000).

¹⁵B. Palpant, B. Prvel, J. Lerm, E. Cottancin, M. Pellarin, M. Treilleux, A. Perez, J. L. Vialle, and M. Broyer, Phys. Rev. B **57**, 1963 (1998).

¹⁶O. A. Aktsipetrov, I. M. Baranova, E. D. Mishina, and A. V. Petukhov, JETP Lett. **40**, 1012 (1984).

¹⁷J. Gersten and A. Nitzan, J. Chem. Phys. **73**, 3023 (1980).

¹⁸A. Liebsch and W. L. Schaich, Phys. Rev. B **40**, 5401 (1989).

¹⁹O. A. Aktsipetrov, I. M. Baranova, E. M. Dubinina, S. S. Elovikov, P. V. Elyutin, D. A. Esikov, A. A. Nikulin, and N. N. Forminykh, Phys. Lett. A **117**, 239 (1986).

²⁰J. E. Sipe, D. J. Moss, and H. M. van Driel, Phys. Rev. B **35**, 1129 (1987).

²¹A. Beckmann, M. Klaua, and K. Meinel, Phys. Rev. B **48**, 1844 (1993).

²²R. Eibler, H. Erschbaumer, C. Temnitschka, R. Podloucky, and A. J. Freeman, Surf. Sci. **280**, 398 (1993).

²³S. H. Liu, C. Hinnen, C. Nguyen van Juong, N. R. de Tacconi, and K. M. Ho, J. Electroanal. Chem. Interfacial Electrochem. **176**, 325 (1984).