Title	Optical second-harmonic spectroscopy of Au nanowires
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Citation	Journal of Applied Physics, 95(9): 5002-5005
Issue Date	2004-05
Type	Journal Article
Text version	publisher
URL	http://hdl.handle.net/10119/3387
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Description	

Optical second-harmonic spectroscopy of Au nanowires

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We have measured the optical second-harmonic (SH) intensity spectra from an array of Au nanowires of average width 60 nm on a faceted NaCl(110) template. For the *s*-polarized input and *p*-polarized output polarization combination, the SH intensity with the incident field parallel to the nanowire axes was much stronger than that with the incident field perpendicular to the axes. The anisotropy is attributed to the anisotropic depolarization field in the Au nanowires. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1687991]

I. INTRODUCTION

Evaluating the distribution of electromagnetic field near nanostructured materials is an important subject for basic scientific research because it not only contributes to electromagnetic theory for nanoscaled objects, but also provides additional information on the optical properties of nanostructured materials. During the 1980s, electromagnetic field strength near noble metal particles was studied in an effort to elucidate the enhancement mechanism of surface-enhanced Raman scattering (SERS).[1,2] Although this problem has not been solved in a comprehensive manner, many researchers have agreed that the physical part of the mechanism of SERS on metal particles is described in the framework of resonant enhancement of the electric field by plasmon excitation.[2]

On the other hand, some studies have addressed the depolarization field created by nanostructures.[3] This aspect is another important consideration for understanding the optical properties of nanostructured materials. An incident electric field in the metal induces a so-called "depolarization field," which partially cancels the incident electric field in the material.[4] This effect occurs simultaneously with the aforementioned plasmon excitation. The effect in the case of small particles is described in a textbook,[5] and its role in optical second-harmonic generation (SHG) in asymmetrically aligned metal particles is dealt with by Sandrock *et al.*[6]

Generally, the dielectric properties of nanostructures are related to this effect,[3,7–9] but no clear demonstration exists of anisotropy of the depolarization field in anisotropic nanostructured materials. This article explores such explicit effects, which will lead us to a better understanding of the optical properties of nanostructures.

In our previous report,[10] we measured SH intensity from a Au nanowire array/NaCl(110) system with C_{2v} symmetry as a function of the azimuthal angle at a fixed photon energy of $2\hbar\omega=2.33$ eV. We found a large anisotropy in the SH intensity from the Au nanowires. The nonlinear response is stronger when the incident electric field and the nanowire axes are parallel than when they are perpendicular to each other. We suggested that the observed anisotropy was either

caused by the anisotropic depolarization field in the Au nanowire bulk or by the anisotropic polarization scrambling effect in the nanowire structures.[10] However, we could not arrive at a firm conclusion as to which of these two effects was the main origin of the observed anisotropy, because it is generally difficult to determine the origin of SH response only for a datum with a single excitation photon energy source.

In this article, we have measured the SH intensity of Au nanowires with C_s-symmetric structure as a function of the SH photon energy from $2\hbar\omega=2.2$ to 3.3 eV, in order to clarify the origin of the anisotropic SH response of the Au nanowires. The reason for measuring the SH spectra is to get information on the physical origin of SH intensity from the spectral shapes; we used samples with C_s symmetric structure because there is less ambiguity in the analysis of the SH intensity patterns from surfaces with lower symmetry.[11,12] By using optical SH spectroscopy, we have discovered that an anisotropic depolarization field is the main origin of the anisotropy of the SH response from Au nanowires.

II. EXPERIMENTAL PROCEDURE

The Au polycrystalline nanowires were prepared by shadow deposition in UHV (3×10^{-8} Pa).[13] The NaCl(110) substrate was etched by water for a few seconds before being loaded into the UHV chamber. In order to obtain a clean faceted surface, it was annealed at 200 °C for 8 h and then etched thermally at 450 °C for 30 min. Au was deposited at room temperature from an effusion cell aligned by 65° from the template normal as shown in Fig. 1(a). The deposition rate of Au was ~0.2 nm/min and the nominal Au thickness was 45 nm. The Au nanowires were sandwiched by 10-nm-thick SiO passivation layers. The microstructural features of the film were characterized by transmission electron microscopy. In Fig. 1(b), the continuous Au wires can be seen in dark contrast along the macrosteps of the substrate with an average width of 60 nm and period of 90 nm.

The light source for SHG measurements was an optical parametric generator/amplifier system driven by a frequency-tripled mode-locked Nd:YAG laser. To measure the azimuthal angle dependence of the SH intensity, fundamental light with photon energy from $\hbar\omega=1.09$ to 1.65 eV was directed onto the sample, which was mounted on an automatic

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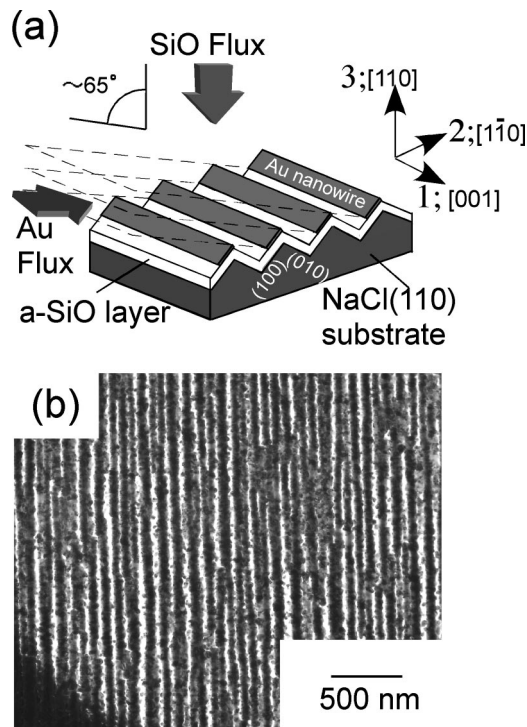a)Electronic mail: mizutani@jaist.ac.jp

FIG. 1. (a) Schematic topography of the surface of the NaCl(110) template with Au nanowires created by the shadow deposition method. (b) The Au nanowire array deposited on the stepped NaCl(110) template, as observed through bright field images. The Au nanowires seen in dark contrast run along the [001] azimuth of the NaCl(110) substrate.
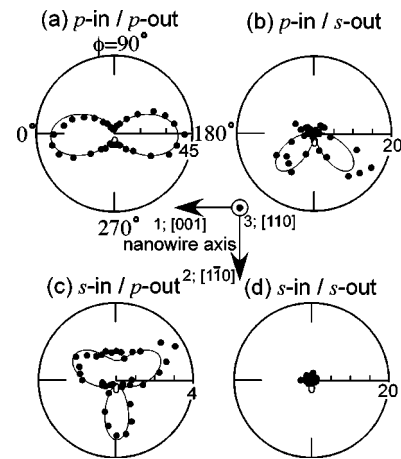

FIG. 2. SH intensity from the quasi-C_S symmetric Au nanowire arrays/NaCl(110) system for $2\hbar\omega=2.33$ eV as a function of the sample rotation angle ϕ for four different input and output polarization combination. The filled circles are experimental data. The rotation angle ϕ is defined as the angle between the plane of incidence and the [001] direction (parallel to the nanowire axis) on the NaCl(110) surface. When $\phi=270°$ the incident fundamental beam is in the same direction as the Au atomic beam during deposition. The solid lines are the best-fit theoretical patterns calculated with nonlinear susceptibility $\chi^{(2)}$ elements as adjustable parameters.

rotation stage in air at the incidence angle of 45°. The reflected SH light from the sample was collected by a series of lenses, passed through a monochromator and detected by a photomultiplier. In order to calibrate the SH intensity, α-SiO$_2$(0001) was used as a reference sample.

III. RESULTS AND DISCUSSION

Figure 2 shows the polar plots of SH intensity from the Au nanowire array (filled circles) on the NaCl(110) template as a function of the sample rotation angle ϕ around the surface normal for four different input and output polarization combinations. The SH intensity from the nanowire array depends strongly on the rotation angle ϕ. These anisotropic SH intensity patterns show lower symmetry (C_S) than in our previous work (C_{2v}).[10] This is because the nanowires are thicker (60 nm) this time, so that they are spread over the bottom edges on the NaCl(110) template and their cross section takes an anisotropic shape. This may have led to the macroscopic C_s symmetry for the whole nanowire array. In our previous paper,[10] the width of the nanowire was thinner (40 nm) and the nanowires were more like simple cylinders, since they were not influenced by the bottom edges. The linear reflection spectra of the nanowires (not shown) showed plasmon absorption for the incident field perpendicular to the nanowire axes.[10]

We have performed a phenomenological analysis of the SH intensity patterns using nonlinear optical susceptibility.[12] Assuming quasi-C_s symmetry of the Au nanowire array/NaCl(110) system, we have ten independent nonlinear sus-

ceptibility elements: $\chi_{113}^{(2)}$, $\chi_{223}^{(2)}$, $\chi_{311}^{(2)}$, $\chi_{322}^{(2)}$, $\chi_{333}^{(2)}$, $\chi_{211}^{(2)}$, $\chi_{222}^{(2)}$, $\chi_{233}^{(2)}$, $\chi_{121}^{(2)}$, and $\chi_{323}^{(2)}$. These susceptibility elements are defined to include the effect of the local field factors.[10] The numbers 1, 2, and 3 represent the [001], [1$\bar{1}$0], and [110] directions on the NaCl(110) template, respectively (Fig. 1). The nanowire axes were in direction "1" or the [001] direction. As shown in Fig. 2, we fitted theoretical SH intensity patterns (solid lines) to the experimental data (filled circles) by varying the values of the $\chi^{(2)}$ elements in the complex plane, using a least-squares fitting program.[11] Relations between the obtained susceptibility elements were $|\chi_{113}^{(2)}| > |\chi_{223}^{(2)}|$ from the p-in/p-out configuration and $|\chi_{311}^{(2)}| > |\chi_{322}^{(2)}|$ from the s-in/p-out configuration. In our previous paper for the quasi-C_{2v} symmetric Au nanowires/NaCl(110) system, a similar relation was found between $\chi_{311}^{(2)}$ and $\chi_{322}^{(2)}$ elements.

Figure 3 shows the spectra of the SH intensity from the Au nanowires/NaCl(110) system as a function of the photon energy for different polarization combinations indicated in the figure. The filled circles in both panels represent the SH intensity with the rotation angle $\phi=0°$. The filled triangles show the SH intensity at $\phi=270°$ in (a) and the averaged SH intensity at $\phi=90°$ and 270° in (b). From the analysis of the SH intensity patterns, the contribution of the nonlinear susceptibility elements $\chi_{113}^{(2)}$ and $\chi_{223}^{(2)}$ dominates the spectra represented by the filled circles and triangles, respectively, in Fig. 3(a). Similarly, the contribution of the nonlinear susceptibility elements $\chi_{322}^{(2)}$ and $\chi_{311}^{(2)}$ dominates the spectra represented by the filled circles and triangles, respectively, in Fig. 3(b). We see that the SH intensity spectra for the p-in/p-out (p-polarized input and p-polarized output) and s-in/p-out polarization combinations are quite different. In Fig. 3(a), the SH intensity spectra have peaks at $2\hbar\omega=3.3$ eV, but are flat for the photon energies from 2.2 to 3.1 eV. In Fig. 3(b) the
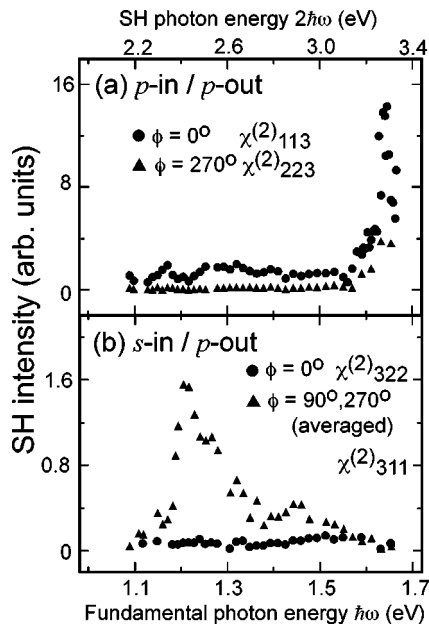
FIG. 3. SH spectra from the Au nanowire array on the NaCl(110) template: (a) *p*-in/*p*-out polarization configuration and (b) *s*-in/*p*-out polarization configuration. The filled circles are the SH intensity at the rotation angle $\phi = 0°$ (the plane of incidence parallel to the nanowire axes). The filled triangles are the SH intensity at $\phi = 270°$ for (a) and the average SH intensity at $\phi = 90°$ and 270° for (b) (the plane of incidence perpendicular to the nanowire axes).

SH spectrum at $\phi = 0°$ (filled triangles) has a broad resonant structure with a maximum at $2\hbar\omega = 2.4$ eV.

Let us focus on the origin of the large difference in SH intensity arising from the $\chi^{(2)}_{311}$ and $\chi^{(2)}_{322}$ elements, corresponding to the filled triangles and circles in Fig. 3(b). We see subsequently that the results are explained well if we assume that the origin of this anisotropy is attributed to the depolarization field in the nanowires. The depolarization factor with an ideal cylindrical nanowire with infinite length is $N_\parallel = 0$ for the external electric field parallel to the nanowire axes and $N_\perp = 0.5$ for the external electric field perpendicular to the axes.[4,6] Here, the depolarization factor N_x is defined in proportion to the induced depolarization field.[4] According to Sandrock *et al.*, the local field factor for a metallic ellipsoid is

$$L_x(\omega) = \left[\frac{\epsilon_0(\omega)}{N_x \epsilon_m(\omega) + (1 - N_x)\epsilon_0(\omega)} \right]^2, \quad (x = \parallel, \perp) \quad (1)$$

in the quasi-static treatment.[6] Here, ϵ_m and ϵ_0 represent the dielectric functions for the metal and host material, respectively. In the quasistatic treatment, the dimensions of the structure are assumed to be negligibly small relative to the wavelength of the light field. With the depolarization factor $N_\parallel = 0$, the local field factor for the electric field parallel to the nanowire axis $[L_\parallel(\omega)]$ is unity for any frequency ω. This means that there is no reduction of the internal field by the depolarization field when the incident electric field is parallel to the nanowire axis. With the depolarization factor $N_\perp = 0.5$, Eq. (1) takes on values of $L_\perp(\omega) = 1$ to 8×10^{-3} and $L_\perp(2\omega) = 0.07$ to 0.29 for the incident photon energy $\hbar\omega = 1.1$ to 1.6. This means that the internal field is considerably reduced due to the depolarization field for the incident elec-

tric field perpendicular to the nanowire axis. We also notice that the denominator of Eq. (1) does not become small for any ω in the present photon energy region due to the large imaginary part of $\epsilon_m(\omega)$, although a particle plasmon resonance is expected. This means that the plasmon resonance does not enhance the SH response for the incident electric field perpendicular to the nanowire axis. Considering that the nanowires are not ideal cylinders, and that the dynamical treatment is more sensitive to the anisotropy than the quasi-static treatment,[6] this prediction is in qualitative agreement with our experiment. Thus, we strongly suggest that the observed anisotropy of the SH response originates from the depolarization field in the nanowires.

In order to check other possibilities, we consider two candidate origins of this anisotropy in the *s*-in/*p*-out polarization configuration.[10] They are (1) the anisotropy of the electrical conductivity in the nanowires, and (2) the effect of the polarization scrambling of light fields by the curved surfaces of the nanowires.

First, the anisotropy of the electrical conductivity in the nanowires can be excluded as a main origin of the anisotropy of the SH response because the nanowire width in our study (60 nm) is much larger than the length that an electron travel during one cycle of the light frequency ($\sim 10^{-3}$ atomic radius at maximum[14]). In other words, the wires look isotropic to the electrons in them.

Second, we consider whether the polarization scrambling effect of the electric field is remarkable and gives rise to the anisotropy in the SH response. The nanowire sheet can have a polarization scrambling effect due to the edges or the curved surfaces of the nanowires. Then, by this polarization scrambling, the strong output for the *p*-in/*p*-out polarization configuration might be converted into the signal for the *s*-in/*p*-out polarization configuration. The efficiency of this polarization scrambling effect should not depend strongly on the photon energy, because it occurs for a geometrical reason. If the conversion efficiency is large enough, the spectra in the two polarization combinations should have similar shapes. However, the observed spectra for the *p*-in/*p*-out polarization combination [Fig. 3(a)] and for the *s*-in/*p*-out polarization combination [Fig. 3(b)] have quite different shapes. The SH intensity patterns in Figs. 2(a) and 2(c) are also quite different. Thus, we can say that the polarization scrambling has little influence on the observed signal for the *s*-in/*p*-out combination. From the discussion so far, we have concluded that the observed anisotropy of the SH response originates from the depolarization field in the nanowires.

Finally, we discuss the origin of the difference in the SH intensity spectra in different polarization combinations in Fig. 3. Optical SH light for the *p*-in/*p*-out polarization combination comes mainly from surface layers and that for the *s*-in/*p*-out polarization combination comes from the bulk of skin depth of the incident electric field.[15] Thus, the SH spectra in Fig. 3(a) could reflect mainly the energy levels of the top surface of the Au nanowires, while those in Fig. 3(b) should reflect the bulk electronic spectrum, or joint density of states, of the Au nanowires. The relations $N_\parallel = 0$ and $L_\parallel = 1$ also indicate that the SH intensity spectrum, shown by filled triangles in Fig. 3(b), is directly the bulk SH response.

The peak energy in Fig. 3(b) may correspond to the bulk absorption edge or the bulk bandgap at $2\hbar\omega=2.45$ eV at the L point in the Brillouin zone of Au.[16] On the other hand, we see large peaks at $2\hbar\omega=3.3$ eV in the two spectra in Fig. 3(a). In our previous paper, we found that the peak of SH resonance of Au surfaces changes its energy sensitively according to the surface structure.[10] This fact leads us to think that the electronic resonance of the SiO/Au interface might be located at this photon energy.

IV. CONCLUSION

We have obtained SH intensity spectra from an Au nanowire array of quasi-C_S symmetric structure, with an average wire width of 60 nm, prepared by shadow deposition on the self-organized NaCl(110) template, for the photon energy from $2\hbar\omega=2.2$ to 3.3 eV. We have attributed the anisotropy of the SH response for s-in/p-out polarization to the stronger depolarization field in the direction perpendicular to the nanowire axis.

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