Second harmonic spectroscopy of copper nanowire arrays on the (110) faceted faces of NaCl crystals

Kitsakorn Locharoenrat\textsuperscript{1,2}, Haruyuki Sano\textsuperscript{1} and Goro Mizutani\textsuperscript{1,2}

\textsuperscript{1}School of Materials Science, Japan Advanced Institute of Science and Technology (JAIST), 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan
\textsuperscript{2}JAIST 21\textsuperscript{st} COE Program, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

E-mail: mizutani@jaist.ac.jp (G. Mizutani)

Abstract. We have investigated the spectral dependence of the optical second harmonic (SH) signal from Cu nanowires deposited on the NaCl (110) faceted templates as a function of the SH photon energies from 2.4 to 4.6 eV. The SH response exhibited a peaked resonance near the SH photon energy of $2\hbar\omega = 4.4$ eV for the $p$-in/$p$-out and $s$-in/$p$-out polarization combinations. At this photon energy the SH response due to the resonant coupling between the fundamental field and the local plasmons in the wires is suggested to be dominant.

1. Introduction

Nonlinear optical techniques have been frequently used in recent years to study surface phenomena. In particular, second harmonic generation (SHG) has been established as a very powerful spectroscopy to study a wide range of physical natures at the surface and interface structures of solid-state materials [1]. Within the electric dipole approximation SHG occurs only if the medium lacks inversion symmetry. Therefore, the nonlinear susceptibility vanishes in the bulk of centrosymmetric media but has a finite value at the surface where the symmetry is broken.

Some of the SHG studies are concerned with noble metals [2-4]. Namely, Lüpke et al. have shown that the SH resonance from the bulk Cu was attributed to a coupling between the SH photon and the electronic transition [4]. However, the metallic nanostructures generally have different structural symmetries from the bulk [5]. The high-density gradient and strong delocalization of the electrons at the surface may contribute to the SHG enhancement. The plasmon contribution is probably operative for enhancing the second harmonic nonlinearity. Consequently, it is strongly expected that the study of the electronic spectra of these nanostructures may clarify the mechanism of the nonlinear optical response of metallic nanomaterials.

In this paper the spectral dependence of the SH signal from Cu nanowires is measured as a function of the SH photon energies from 2.4 to 4.6 eV. The experimental results are compared with a local field model for understanding of the electronic excitation on the surface of these metallic nanostructures.

2. Experimental

The arrays of Cu nanodots and those of Cu nanowires were prepared by a shadow deposition of Cu atoms on a faceted NaCl (110) template. The sample preparation was described in our previous paper [5].
For SHG measurements, the light source of the fundamental photon energy from 1.2 to 2.3 eV was an optical parametric generator and amplifier system driven by a mode-locked Nd:YAG laser. The excitation beam was then focused on the sample surface at the incident angle of 45°. The SH signal from the sample was detected by a photomultiplier. Finally, the absolute magnitudes were obtained by normalizing the SH response to that of the α-SiO$_2$ (0001).

3. Results
Figures 1 and 2 show the SH intensity spectra from various wire widths of Cu nanowires and 10 nm Cu nanodots as a function of the SH photon energy, respectively. The SH photon energies are chosen from 2.4 to 4.6 eV. The incident wave vector of the excitation is parallel to the $[1\bar{1}0]$ direction of the NaCl (110) faceted substrates. The polarization combinations are (a) p-in/p-out and (b) s-in/p-out, respectively. For the p-in/s-out and s-in/s-out polarization configurations, the signal was very weak and the SH intensity spectra are not shown. The experiment errors are in the range of 10%.

**Figure 1.** Measured SH intensity spectra from Cu nanowires of different wire widths as a function of the SH photon energy for (a) p-in/p-out and (b) s-in/p-out polarization configurations. The incident wave vector of excitation is parallel to the $[1\bar{1}0]$ direction of the NaCl (110) faceted substrates. The solid lines are guide to the eyes.

**Figure 2.** Measured SH intensity spectra from 10 nm Cu nanodots as a function of the SH photon energy for (a) p-in/p-out and (b) s-in/p-out polarization configurations. The incident wave vector of excitation is parallel to the $[1\bar{1}0]$ direction of the NaCl (110) faceted templates. The solid lines are guide to the eyes.
For p-in/p-out polarization configuration in figure 1 (a), the SH intensity spectra for Cu nanowires of different wire widths show steady increase above $2\hbar\omega = 3.0$ eV. The SH response exhibits a peaked resonance near 4.4 eV. The peaks are similarly observed for s-in/p-out polarization configuration in figure 1 (b). The spectra show no significant difference for the different wire widths of Cu nanowires.

On the other hand, the SH intensity spectra taken from Cu nanodots in figure 2 show a nearly flat dependence of SH intensity on the photon energy below $2\hbar\omega = 4.0$ eV. The intensity abruptly increases above $2\hbar\omega \sim 4.2$ eV, and reaches a maximum at 4.5 eV.

4. Discussion

The main peak near $2\hbar\omega = 4.4$ eV for Cu nanowires in figure 1 appears to have a similar origin as the main peak at 4.5 eV for Cu nanodots in figure 2. This may be a resonance enhancement of the SH signal with the dipolar mode of the surface plasmon in Cu nanowires. These experimental findings are consistent with the suggestion by Schider et al. that the plasmon excitation in the metallic nanostructures gave rise to the local electric field enhancement [3].

Next, we perform a theoretical analysis of the SH intensity in order to determine the values of the local field factor and then to find whether the surface plasmon resonance served as the origin of the enhancement of the SH response from Cu nanowires. We calculate the local field enhancement factor for Cu nanowires and Cu nanodots by a quasi-static theory [2]. Since the depolarization factor is zero for the electric field polarized parallel to the major axes, the field enhancement is unity for any frequencies. Therefore, the enhancement is considerably not reduced by the depolarization field.

For the electric field polarized perpendicular to the major axes, the enhancement $L_\perp$ is modified as [2]:

$$L_\perp = \left( \frac{\varepsilon_0}{q_\perp \varepsilon_m + (1-q_\perp)\varepsilon_0} \right)^2$$

The $\varepsilon_m$ and $\varepsilon_0$ is, respectively, the dielectric functions of the metal (Cu) and the surrounding host medium (SiO). The frequency-dependent dielectric constants of Cu are obtained from literature [6].

The depolarization factor $q_\perp$ for the electric field incident along the minor axes $b$ or perpendicular to the major axes $a$ is given by:

$$q_\perp = \left[ 2 + \left( \frac{b}{a} \right) \right]^{-1}$$

We substitute $b/a = 0.05$ for Cu nanowires and 1.00 for Cu nanodots in equation (2), and plot the calculated local field factor, $L_\perp^2 (\omega) L_\perp (2\omega)$, with respect to the SH photon energy. It is found that the calculated spectra is consistent with the observed SH intensity spectra for Cu nanowires, but it did not reproduce the one for Cu nanodots (not shown). In order to improve the agreement of the calculation with the experimental data, the depolarization factor in equation (2) is modified as:

$$q_\perp = \left[ 2 + \left( \frac{b}{a} \right) \right]^{-1} - \frac{1}{3} k^2 b^2 - i \frac{2}{9} k^4 b^4$$

with $k$ is equal to $2\pi / \lambda$. The first term on the right hand side of equation (3) is the usual factor due to polarization in the quasi-static limit. The second term comes from the depolarization field that depends on the minor axes $b$. The third term describes damping effect due to the spontaneous emission of radiation of the induced dipole, and also depends on the minor axes $b$. 
The calculated spectra for Cu nanowires in figure 3 still reproduce the experimental findings in figure 1. The overall agreement of the spectra of interest between the theory in figure 3 and the experiment in figure 2 for Cu nanodots improved when we took into account the damping term. It has made the spectra wider and moved the dipolar mode to the higher photon energy. Hence, these theoretical results confirm that the resonant enhancement near the SH photon energy of 4.4 eV originates from the coupling of plasmon resonance in Cu nanowires.

Figure 3. Calculated SHG local field enhancement factor as a function of the SH photon energy for Cu nanowires and nanodots based on equations (1) and (3).

As seen in figure 3 the theoretical line-shape of spectra of Cu nanodots is different from that of Cu nanowires because the particle sizes of nanodots are smaller than those of nanowires. When the sizes of particles are small through the reduction of the minor axes $b$ in equation (3), the electrons can be accelerated in the presence of the incident light. They, therefore, radiate energy in all directions. Because of this secondary radiation, the electrons lose energy experiencing a damping effect. These results are in agreement with the suggestion of Zeman et al. that the increased electromagnetic damping as the particle sizes decrease leads to smaller enhancement [7].

5. Conclusion
We have measured the photon energy dependence of the SH intensity from Cu nanowires. The main peaks of the spectra of Cu nanowires are found at $2\hbar\omega = 4.4$ eV for the p-in/p-out and s-in/p-out polarization combinations. Theoretical calculation by a local field model indicates that at this photon energy the observed SH response is induced by a resonant coupling between the fundamental field and the surface plasmon in the wires.

Acknowledgments
The authors would like to thank Dr. Sugawara of Hitachi Limited for his guidance. This research was supported in part by a Grant-in-Aid for Scientific Research from Ministry of Education, Culture, Sports, Science and Technology, JAPAN (No. 16510083).

References
[1] Boyd R W 1992 Nonlinear Optic (Boston: Academic Press)
[2] Sandrock M L, Pibele C D, Geiger F M and Foss Jr C A 1999 J. Phys. Chem. B 103 2668
[3] Schider G, Krenn J R, Gotschy W, Lamprecht B, Ditlbacher H, Leitner A and Aussenegg F R 2001 J. Appl. Phys. 90 3825
[4] Lüpke G, Bottomley D J and van Driel H M 1994 Phys. Rev. B 49 17303
[5] Locharoenerat K, Sugawara A, Takase S, Sano H and Mizutani G 2007 Surf. Sci. (in press)
[6] Palik E D 1998 Handbook of Optical Constants of Solids (San Diego: Academic Press) p 284
[7] Zeman E J and Schatz G C 1987 J. Phys. Chem. 91 634