Phenomenological studies of optical properties of Cu nanowires

Kitsakorn Locharoenrat\textsuperscript{a,b}, Haruyuki Sano\textsuperscript{a}, Goro Mizutani\textsuperscript{a,b,*}

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

Received 30 October 2006; received in revised form 1 February 2007; accepted 2 February 2007
Available online 23 March 2007

Abstract

We report on the experimental observation of surface plasmon resonance in Cu nanowires fabricated by shadow deposition method. When the incident light is polarized perpendicular to the wire axes, plasmon maxima appeared at about 2.3 eV in the absorption spectra. Plasmon resonance appeared at lower photon energy when the incident light is polarized parallel to the wire axes. Resonance peaks move to lower energy when the nanowire widths are increased. We have found that finite-difference time-domain (FDTD) simulation gives better results than Maxwell–Garnett model in explaining the relation between the light polarization and the energies of the observed absorption maxima.

Keywords: Metals; Nanowires; Optical spectroscopy; Maxwell–Garnett model; Surface plasmon resonance; Finite-difference time-domain method

1. Introduction

Interaction of light with metal nanowires has attracted attention through its applications to nonlinear optics \cite{1}, surface enhanced Raman scattering \cite{2}, and plasmonics \cite{3}. These nanowire systems strongly absorb incident light at frequencies of surface plasmon resonances. Although the optical properties of metal spheres are described by Mie’s theory in 1908 \cite{4}, the relationship between the wire geometries and their linear optical properties has not been fully investigated. Hence, the production of metal nanowires with specific size, geometry, and distribution is important to their theoretical research and technological applications utilizing surface plasmon resonance. Compared with physical methods such as electron beam lithography \cite{5}, shadow deposition is considered as a much more efficient method allowing the deposition of large areas of anisotropic nanostructures and presenting high fabrication throughput.

Cu nanowires are particularly interesting to study because the confinement of the charge carriers is prominent to such an extent that the electronic states change remarkably \cite{6}. Our previous report has shown that on faceted NaCl(110) surfaces well-organized arrays of Cu nanowires grow and their absorption spectra as a function of photon energy show strong plasmon resonance spectra \cite{7}. However, we found that the detailed experimental dependence of the peak energy positions of the absorption maxima on the polarization is different from the theoretical prediction by Maxwell–Garnett model. In this effort, we aim to discuss the observed nanowire’s plasmon resonance through a calculation by finite-difference time-domain (FDTD) method. In such an analysis, we may be able to consider a more realistic scenario in the dependence of their absorption spectra on the wire sizes.

2. Experimental

Cu nanowires were fabricated through shadow deposition technique in UHV of approximately $2 \times 10^{-9}$ Torr \cite{8}. Faceted NaCl(110) substrates were prepared as a nanoscale template by water etching and annealing at 200–400 °C for 2–4 h. The regular arrays of Cu nanowires were then deposited from a crucible aligned by 65° from the template normal on the faceted surfaces at room temperature, and they were sandwiched by 10 nm thick SiO layers. By
removing the NaCl template, we checked the morphology of the nanowire arrays by transmission electron microscopy (Hitachi: HF-2000) at an accelerating voltage of 200 kV. Fabrication parameters and sample descriptions are shown in Table 1. To probe the plasmon resonances, absorption spectra at the normal incidence as a function of the sample rotation angle are recorded for the wavelength 250–1100 nm by a spectrometer equipped with a polarizer accessory, a Xe lamp source, and a photomultiplier tube.

3. Results and discussion

Fig. 1 shows the measured absorption spectra of Cu nanowire arrays with various widths and nominal thicknesses. The nominal thicknesses were measured with the sensor plane of the thickness monitor set perpendicular to the Cu beam direction. Plasmon resonance structures are centered around 2.3 eV when the incident field is perpendicular to the wire axes as in Fig. 1a and they shift to lower energy when the field is parallel to the wire axes as in Fig. 1b. In both polarization configurations, they shift to lower photon energy when the widths of the nanowires are increased.

In the case of metal spheres embedded in dielectric materials, Mie scattering theory has succeeded in describing extinction spectra in the visible region, including the surface plasmon resonance of dipole modes [4]. For the nanowires in a nonabsorbing medium, the plasmon resonant modes are described by Maxwell–Garnett model by introducing a shape-dependent screening factor $\kappa$ for different dimensions [9]. Screening factor $\kappa$ is related to the depolarization factor $q$ via the relation $\kappa = q^{-1} - 1$. If metal nanowires are regarded as the ellipsoidal elongated particles, $q$, $(q_L)$ for an electric field incident along the long axis a (the short axis b) is estimated via the relation $q \approx [1+(2a/b)]^{-1}$ $(q_L \approx [2+(b/a)]^{-1})$. Surface plasmon resonance results in enhancement of absorption coefficients (Abs) at the resonance frequency, and it can be understood in terms of the particle polarizability $\alpha$ as

$$\text{Abs} = k \text{Im}(\alpha)$$

$$\alpha = \frac{(V/3q)(\epsilon_m - \epsilon_0)}{(-\epsilon_m + \kappa \epsilon_0)},$$

(1)

where $k$ is the wave vector ($= 2\pi/\lambda$) and $V$ is the particle volume. $\epsilon_m$ and $\epsilon_0$ are the complex dielectric functions of

Table 1
Deposition parameters and geometrical of the fabricated nanowires

| Sample code | Nominal thickness (nm) | Wire width (nm) | Periodicity (nm) | Homoeptaxial growth temperature (°C) |
|-------------|------------------------|-----------------|-----------------|--------------------------------------|
| C7          | 20                     | 17              | 27              | 200                                  |
| C8          | 10                     | 14              | 27              | 200                                  |
| C9          | 20                     | 19              | 40              | 400                                  |
| C10         | 10                     | 15              | 40              | 400                                  |

Fig. 1. Measured absorption spectra of Cu nanowires. C7–C10 indicates the sample name listed in Table 1. $\perp/\parallel$ means the electric field perpendicular (parallel) to the wire axes.
the metal and the surrounding medium, respectively. Fig. 2 shows absorption spectra calculated with Maxwell–Garnett model for metallic ellipsoidal particles with different aspect ratios. Plasmon maxima appear near 2.0 eV for the electric field perpendicular to the nanowire axes in Fig. 2a, and they shift to higher photon energy with increasing aspect ratio. On the other hand, plasmon maxima are observed below 2.0 eV for the electric field parallel to the wire axes in Fig. 2b, and they shift to lower energies with increasing aspect ratio. The resonant condition between the dielectric constant of Cu and the surrounding medium is explained as Re\{\varepsilon_m\} = -Re\{\kappa\epsilon_0\} [10]. With the increase of the aspect ratio, the screening factor \( \kappa \) of plasmon resonance for the electric field parallel to the wire axis approaches infinity and the resonance peak shifts toward lower photon energy accordingly.

However, Maxwell–Garnett model with Eq. (1) attempts only to address the aspect ratio dependence of the electric dipole response and not the dependence on the absolute sizes of the nanostructures. The actual sizes of our nanowires are over the limitation of the dipole approximation applicable to sizes much smaller than the wavelength of light. Thus, we attempt a prediction by more rigorous FDTD method to analyze the absorption spectra. This model will allow us to consider the size dependence of the electric dipole resonance.

In FDTD simulation as shown in Fig. 3, nanowires are surrounded by absorbing boundaries with small meshes of 0.1 nm periodicity, yielding geometry parameters for the long wire axes of \( a = 140–190 \) nm and the short axes of \( b = 14–19 \) nm. Simulation time is 200–500 fs to capture all over the photon energy of 1.5–3 eV. Simulation is performed until there are essentially no electromagnetic fields are left in the simulation region. If we drop one of the spatial dimensions, for example, \( z \) direction, and consider the \( x-y \) plane, the 2D Maxwell’s equations split into two independent sets of equations consisting of three vector quantities each. These are termed the TE (transverse electric) and TM (transverse magnetic) equations [11]. By considering \( x \)-polarized light traveling in the forward \( y \)-direction and \( x \)-polarized light traveling in the forward \( y \)-direction, the three electromagnetic field components \( E_x(x,y,t) \), \( E_y(x,y,t) \), and \( H_z(x,y,t) \) for each polarization direction are calculated. Optical properties of metals can be well described by using Drude model supposing that zero restoring force is applied to free electrons. Then, the dielectric function of metals is written as:

\[
\varepsilon \approx \varepsilon_0 \left( 1 - \frac{\omega_p^2}{\omega^2} \right).
\] (2)

We have used the dielectric function defined in the material database of a commercial software Lumerical FDTD Solutions 4.0 [12]. The built-in material database contains dielectric properties of copper obtained by fitting the Drude dielectric function to measured optical

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Fig. 2. Calculated absorption spectra of Cu nanowires at different aspect ratios \( a/b \) by Maxwell–Garnett model. \( a(b) \) is the long (short) wire axes of the nanowires. \( \perp(\parallel) \) represents the electric field perpendicular (parallel) to the wire axes.
constants of copper in the frequency region of interest [13]. By this FDTD method, we have calculated absorption spectra as shown in Fig. 4 as a function of the photon energy for the ellipsoidal nanowires, and with the wire widths as the minor axis lengths of $b = 14–19 \text{ nm}$ at a constant aspect ratio of $a/b = 10$. This simulation by FDTD calculation is more favorable than that of Maxwell–Garnett model from a point of view of the reproduction of the experimental data. Calculation results show the plasmon maxima near 2.4 eV when the electric field is perpendicular to the wire axes as shown in Fig. 4a, while the red-shift occurs when the electric field is parallel to the wire axes as shown in Fig. 4b. The peak positions in the latter polarization configuration are above 2.0 eV, as is consistent with the experimental results in Fig. 1b. Increasing the wire widths by increasing the size of minor axis of the ellipse ($b$) also induces a red-shift of the peak positions.

Fig. 3. Schematic image of a sample system and coordinate used in the two-dimensional FDTD calculation. $a(b)$ is the long (short) wire axes of the ellipsoid.

Fig. 4. Calculated absorption spectra of Cu ellipsoids at a fixed aspect ratio of $a/b = 10$ by FDTD method. $a(b)$ is the long (short) axes of the ellipsoids. $\perp$ shows the electric field perpendicular (parallel) to the longer axes.
The disagreement between the experiment and the calculation by Maxwell–Garnett model in terms of the polarization dependence of the absorption spectra in Fig. 2 suggests that the calculation by this model becomes inapplicable when the wire size is not negligible compared with the wavelength of incident light. When the electric field is perpendicular to the wire axes as shown in Fig. 2a, the calculated positions of plasmon maxima are observed near 2.0 eV in contrast to the experiment in Fig. 1b showing plasmon maxima around 2.3 eV. When the electric field is parallel to the wire axes as shown in Fig. 2b, plasmon maximum energies are observed below 2.0 eV, and they conflict with the experiment in Fig. 1b showing plasmon maxima above 2.0 eV. Sandrock et al. [10] have reported that the small particle limit treatment of such Maxwell–Garnett model is qualitatively correct in local field enhancement calculation only for systems of small short particle axes ($b \rightarrow 0$). However, when the retardation effect of the incident light fields was taken into account, calculation gave different results from those predicted by the quasi-static theory for the systems of $b = 15$ nm. Therefore, we can say that the nonretardation limit may not be applicable to our study with short wire axes of $b = 14–19$ nm. The present calculation taking into account the absolute wire size by FDTD simulation is judged to have improved the agreement between the experiment and the theory because it takes full account of the retardation effect.

There still remains a discrepancy between the theory and the experimental data. The measured spectra in Fig. 1(a) of samples C9, C10, and C8 show increase toward the lower photon energy, whereas the one in Fig. 4(a) calculated by FDTD method displays monotonical reduction on the lower photon energy side. Using the Drude model alone for the calculation gave different results from those predicted by the quasi-static theory for the systems of $b = 15$ nm. Therefore, we can say that the nonretardation limit may not be applicable to our study with short wire axes of $b = 14–19$ nm. The present calculation taking into account the absolute wire size by FDTD simulation is judged to have improved the agreement between the experiment and the theory because it takes full account of the retardation effect.

4. Conclusion

For arrays of Cu nanowires, we have shown that plasmon maxima for the incident electric field polarized parallel to the long wire axes appear at lower photon energy than the maxima for perpendicular polarization. By increasing the nanowire widths, plasmon maxima around 2.3 eV are shifted to lower photon energy. This experimental dependence of the energy positions of spectral absorption maxima on the light polarization and the wire width cannot be explained completely by Maxwell–Garnett model but can be explained well by FDTD calculations.

Acknowledgments

Authors would like to thank Dr. A. Sugawara of Okinawa Institute of Science and Technology, Hitachi Limited, and Mr. K. Higashimine of JAIST for their helpful advice and guidance. They are also grateful to Lumerical Solutions Incorporation for our trial use of the software. 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).

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