Dispersion relations for coupled surface plasmon-polariton modes excited in multilayer structures

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Abstract
The coupled surface plasmon-polariton (SPP) modes excited in an Al/SiO₂/Al multilayer structure were analyzed using angle-resolved electron energy-loss spectroscopy (AREELS) with a relativistic electron probe. The dispersion relations for the coupled SPP modes were then directly observed and compared with predicted relations obtained via calculations. Good agreement was noted between the experimental and calculated results. In the multilayer structures, the dispersion relation for the coupled SPP modes was found to be sensitive to the thickness of each film, which could be interpreted qualitatively by the electron energy-loss probability calculated for thin aluminum (Al) films and narrow Al gaps using Kröger’s formula. It was demonstrated that significant differences in the excitation probability for SPPs could be observed depending on the coupling modes.

Keywords
surface plasmon-polariton, electron energy-loss spectroscopy, dispersion relation, coupled mode, waveguide, multilayer

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Introduction
Surface plasmon-polariton (SPP) waves can be excited at the interface between a dielectric material and a metal [1]. Such SPP waves arise out of coupling of the collective oscillations of free electrons with the electromagnetic near field at the interface. Owing to the dual electric and photonic nature of SPPs, they have been exploited in applications such as integrated optical circuits [2], molecular sensors [3] and nanoscale lasers [4]. There are a number of geometries that support SPPs, such as planar films [5] and cylindrical wires [6].

A metallic film supports SPP waves that propagate along its interface with a dielectric material. The propagating SPP waves are accompanied by electromagnetic waves that decay exponentially in the perpendicular direction. The propagation and decay lengths are characteristic parameters of propagating SPP waves, which depend on the structures and dielectric constants of both sides of an interface. When the thickness of a metal film becomes less than the decay length of the electromagnetic near field, the SPP waves excited on both surfaces can interact with each other and split into two modes [5]. In such cases, one mode has a symmetrical charge distribution on its top and bottom surfaces, while the other mode is antisymmetrical. The symmetrical mode conforms to a dispersion relation that has shifted to the low-energy side from an SPP that was excited on a single surface, called a short-range (SR) mode, which has both short propagation and decay lengths. In contrast, the dispersion relation for the antisymmetrical mode, which has both long propagation and decay lengths [7,8], is shifted to the high energy side and is referred to as a long-range (LR) mode. The long propagation length of the LR mode is suitable for application to integrated optical devices.
In the case of molecular sensors, a multilayer structure composed of a core dielectric film covered with two metallic thin films of the same thickness is more convenient because of its rigid structure [3,9].

Previously, scanning transmission electron microscopy (STEM) combined with cathodoluminescence (CL) or electron energy-loss spectroscopy (EELS) have been widely used to investigate surface excitations on nanostructures, such as radiation losses on dielectric nanostructures [10,11], localized surface plasmon resonances on metal nanostructures [12–17] and surface exciton-polaritons [18]. The spatial distributions of luminescence, or excitation probabilities due to SPPs, have been visualized by CL or EELS imaging. When Fabry–Perot-type SPP resonance is set up in nanostructures such as nanowires, the SPP map obtained by such imaging provides the spatial distribution of the standing waves, thus enabling the dispersion relations for SPP waves to be determined using a resonance condition [19,20]. Even without forming standing waves, the dispersion relations for SPP waves can be measured by angle-resolved CL, where CL spectra are measured as a function of the radiation angle [21].

However, these methods require structures such as steps or end faces in order to generate radiation or SPP standing waves, and therefore, cannot be applied to flat multilayer structures. An alternative method that can be used to measure the dispersion relation for SPP waves is angle-resolved EELS (AREELS), in which the SPP wave vectors are measured as the scattering angle of incident electrons. It should be noted that the split between SR and LR modes in a thin metal film was verified by a dispersion measurement using AREELS many years ago [22]. The dispersion relations for Čerenkov guided modes that depend on the thickness of dielectric film were also measured by AREELS [23].

In this work, we performed AREELS measurements on multilayer structures to obtain the dispersion relations for coupled SPP modes. In this method, the dispersion curve for coupled SPP modes, which depends on the film thickness in the multilayer, is analyzed by the energy-loss probability as a function of the energy and the scattering vector (known as an \(E-q\) map), which is calculated for the thin metal film and the narrow gap using Kröger’s formula [24,25].

**Methods**

In this work, \(E-q\) maps for Al/SiO\(_2\)/Al multilayer structures were measured using the AREELS method with a high angular dispersion by changing the specimen height in image mode with spot illumination [26]. Figure 1 shows a schematic diagram of the method. An angular selection slit is placed at the entrance plane of the spectrometer, which allows us to restrict electron collection to those scattered perpendicular to the direction of energy dispersion. The scattering angle (\(\theta\)) is proportional to the component of the scattering vector (\(q_{\perp}\)) perpendicular to the direction of incident electrons. Using a two-dimensional AREELS pattern allows us to directly visualize the energy-loss probability as a function of the energy loss (\(E\)) and \(q_{\perp}\). A sample \(E-q\) map is shown in Fig. 1. When the direction of electron incidence is normal to the specimen surface, the component of the scattering vector \(q_{\perp}\) is equal to the wave vector \(k\) of the SPP wave propagating along the surface. Therefore, an \(E-q\) map provides the dispersion relations for SPP waves.

The AREELS measurement was performed at room temperature using a 200 kV transmission electron microscope (JEM-9080 TKP1) equipped with a cold field emission gun and an omega filter installed as a spectrometer. The energy resolution determined from the full-width at half-maximum of the zero-loss peak was 0.4 eV. The wave number resolution determined from the full-width at half-maximum of a direct beam on the \(E-q\) map was \(6.2 \times 10^{-3}\) nm\(^{-1}\). A 4-\(\mu\)m-diameter specimen area was illuminated by an incident electron beam with a convergent semi-angle of 6.4 mrad. The \(E-q\) maps were measured by a charge-coupled device (CCD) camera. The pixel size in the \(E-q\) maps corresponded to 27 meV and
5.2 × 10^{-4} \text{ nm}^{-1} along the loss energy and the scattering vector axes, respectively. Each \( E-q \) map was acquired in 10 s. Ten \( E-q \) maps taken under the same conditions were superimposed to improve the signal-to-noise ratio.

Two different Al/SiO\(_2\)/Al multilayer structures, hereafter samples A and B, were prepared using vapor deposition. For sample A, a commercial SiO\(_2\) film was used for the core dielectric layer, while a thick SiO\(_2\) film produced by electron beam evaporation was used for sample B. Thermal evaporation was used to deposit Al films on both sides of the core dielectric layers. After the AREELS measurement, cross-sectional samples of both multilayer structures were fabricated by focused ion beam (FIB) milling. High-angle annular dark-field (HAADF) STEM images were then taken to measure the multilayer structural thickness of each film.

The experimental \( E-q \) maps were then compared with the calculated SPP dispersion curves to identify their modes. Figure 2a shows a multilayer structure model in which the thin oxide layers outside the Al films were taken into account because the samples were aerated before AREELS measurement. Using the dielectric function (\( \varepsilon \)) and the thickness (\( t \)) of each film, the boundary conditions for electromagnetic fields at each interface give the SPP wave dispersion relations as follows:

\[
1 + K_{i,m} K_{m,0x} e^{2\alpha_{m} t_{m}} + K_{m,0x} K_{0x,0} e^{2\alpha_{ox} t_{ox}} + K_{i,m} K_{0x,0} e^{2\alpha_{ox} t_{ox}} = 0, \tag{1}
\]

where

\[
K_{i,m} = \frac{\alpha_{i}/\varepsilon_{i} \left( \tanh \alpha_{i} t_{i} \right)}{\alpha_{i}/\varepsilon_{i} \left( \coth \alpha_{i} t_{i} \right) - \alpha_{m}/\varepsilon_{m}}, \tag{2}
\]

\[
K_{m,0x} = \frac{\alpha_{m}/\varepsilon_{m} - \alpha_{ox}/\varepsilon_{ox}}{\alpha_{m}/\varepsilon_{m} + \alpha_{ox}/\varepsilon_{ox}}, \tag{3}
\]

\[
K_{0x,0} = \frac{\alpha_{ox}/\varepsilon_{ox} - \alpha_{0}/\varepsilon_{0}}{\alpha_{ox}/\varepsilon_{ox} + \alpha_{0}/\varepsilon_{0}}. \tag{4}
\]

The indices \( i, m, ox \) and 0 indicate the insulator film (SiO\(_2\)), metal film (Al), oxide layer (AlO\(_x\)) and vacuum, respectively. Parameter \( \alpha \) represents the wave vector component of the electromagnetic wave.

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**Fig. 1.** Schematic diagram of AREELS method proposed by Midgley [25]. By changing the specimen height in the image mode with spot illumination, the diffraction pattern is formed at the image plane of the objective lens, so that the entrance plane of the spectrometer corresponds to the reciprocal plane. \( k_0 \) and \( k_1 \) represent wave vectors of incident and scattered electrons, respectively. An angular selection slit is placed at the entrance plane of the spectrometer to limit electron collection to those scattered perpendicular to the direction of energy dispersion. The gap in the center part of the slit is closed to prevent the intense direct beam from saturating the CCD detector.
that is perpendicular to the interface and is described by

$$
\alpha_n = \sqrt{k^2 - \varepsilon_n \left( \frac{E}{\hbar c} \right)^2} \quad (n = i, m, ox, 0). \tag{5}
$$

When $\alpha$ is real, electromagnetic waves become near fields perpendicular to the interface. However, when $\alpha$ is imaginary, they become far fields. The hyperbolic functions in $K_{i,m}$ are related to the symmetry of the SPP charge distribution. The hyperbolic tangent in Eq. (1) gives the dispersion relation of the AC mode, while the hyperbolic cotangent gives the dispersion relation of the SC mode.

In this calculation, the dielectric functions for SiO$_2$ and AlO$_x$ were used along with the optical data measured by Philipp [27], Hass [28] and Cowan et al. [29]. The dielectric function of Al was assumed to follow the Drude model without damping,

$$
\varepsilon_m = 1 - \frac{E_p^2}{E^2}. \tag{6}
$$

Here, $E_p$ is the excitation energy for bulk plasmons, which is 15 eV for Al [22]. The dispersion relation between the excitation energy $E$ and the wave vector $k$ for SPPs is calculated by solving Eq. (1) numerically. Figure 2b shows the calculated dispersion relations for sample A. Since we consider four interfaces in the multilayer structure, four coupled SPP modes are excited with a charge distribution, as shown in Fig. 2c. When 3-nm-thick aluminum oxide layers are assumed in a multilayer structure, the dispersion curves (red) are systematically shifted to the low-energy side compared with the blue curves, which are calculated for a structure without the aluminum oxide layers. This clarifies the significant effects of the thin oxide layers on dispersion relations.

**Results**

Figure 3a and b shows cross-sectional HAADF images of samples A and B, respectively. The brightest regions are the Fe layers that were deposited to protect the multilayer structure from being damaged by FIB processing. In sample A, a 23-nm-thick SiO$_2$ film is sandwiched by two 16-nm-thick Al films, while in sample B, a 61-nm-thick SiO$_2$ film is sandwiched by two 10-nm-thick Al films. It was impossible to measure the thickness of the oxide layers on aluminum surfaces from these images. Although the interfaces are not so flat, the roughness of interfaces is considerably small compared with the wavelengths of SPP, and hence, we ignored the effect of the roughness in the SPP simulations.

Figure 4a and b shows the $E$–$q$ maps obtained for samples A and B, respectively, with the calculated
dispersion curves superimposed. In Fig. 4a, three experimental dispersion curves, which are in good agreement with the calculated dispersions (solid curves), can be clearly observed when the thickness of the aluminum oxide layer is assumed to be 3 nm. Accordingly, the multilayer structure of samples A and B can be expressed as AlO\(_x\)(3 nm)/Al(13 nm)/SiO\(_2\)(23 nm)/Al(13 nm)/AlO\(_x\)(3 nm) and AlO\(_x\)(3 nm)/Al(7 nm)/SiO\(_2\)(61 nm)/Al(7 nm)/AlO\(_x\)(3 nm), respectively. From the comparison between the \(E-q\) map and the calculated dispersion curves, we can assign the three distinct curves observed in the \(E-q\) map to the AC-SR, SC-SR and AC-LR modes. However, the SC-LR mode could not be detected experimentally. In Fig. 4b, the AC-SR, SC-SR and AC-LR modes also appear. The dispersion curves for the AC-SR and SC-SR modes approach each other at high wave vectors, so they are observed as a broad curve in the \(E-q\) map. The narrow separation between the dispersion curves for the AC and SC modes is due to the thick SiO\(_2\) film between the Al films compared with sample A, as will be discussed later. The fact that no
intensity associated with the SC-LR mode could be detected for sample B might be related to the low excitation probability of that mode, which is independent of the thickness of each film in the multilayer structure.

In order to compare the intensity of coupled SPP modes excited in samples A and B, the angle-resolved spectra for several scattering vectors were extracted from the $E-q$ maps, as shown in Fig. 5. Figure 5a shows the spectra for sample A, with the structure $\text{AlO}_x(3\text{ nm})/\text{Al}(13\text{ nm})/\text{SiO}_2(23\text{ nm})/\text{Al}(13\text{ nm})/\text{AlO}_x(3\text{ nm})$, in which the main excitations in the low scattering vector region are the SR modes, and the AC-LR modes can be observed at $q=0.04$ and $0.05\text{ nm}^{-1}$. The intensity of the LR mode is weaker than that of the SR modes. The spectra for sample B, with the structure $\text{AlO}_x(3\text{ nm})/\text{Al}(7\text{ nm})/\text{SiO}_2(61\text{ nm})/\text{Al}(7\text{ nm})/\text{AlO}_x(3\text{ nm})$, are shown in Fig. 5b. Here, the SC-SR mode is observed as a shoulder peak at $q=0.02$ and $0.03\text{ nm}^{-1}$, but it merges into the AC-SR mode in the high scattering vector region. The peak of AC-LR mode can be observed at $q=0.03$ and $0.04\text{ nm}^{-1}$, but its intensity is significantly weaker than that of the SR modes, and it disappears at $q=0.05\text{ nm}^{-1}$ even though it can be observed at $q=0.05\text{ nm}^{-1}$ in sample A. This result suggests that the excitation probability for the coupled SPP modes depends on the thicknesses of the metal and the dielectric films. When the scattering is compared at a fixed scattering vector, the intensity of the SR modes tends to be higher than that of the LR modes in both samples.

Discussion

In this section, we discuss the excitation probabilities for the coupled SPP modes using Kröger's formula, which provides the $E-q$ maps of the symmetric structures composed of two equivalent interfaces such as thin-film or narrow-gap structures [24,25]. Although Kröger's formula cannot be applied to multilayer structures, the characteristics of the SR and LR modes, or the SC and AC modes, excited in thin films or narrow gaps can be examined separately by using this formula to calculate the $E-q$ maps for two symmetric structures.

Figure 6 shows the $E-q$ maps calculated for thin Al films (Fig. 6a and b) and a narrow gap between two semi-infinite Al metal regions (Fig. 6c and d), which are assumed to be in a vacuum. The thicknesses of the Al film in Fig. 6a and the gap width in Fig. 6c

![Fig. 5. Angle-resolved EELS obtained from the $E-q$ maps of (a) sample A and (b) sample B. The red, green, blue and black profiles were obtained at $q=0.02, 0.03, 0.04$ and $0.05\text{ nm}^{-1}$, respectively.](image-url)
correspond to those in sample A, while those in Fig. 6b and d correspond to those in sample B. In the Al film $E-q$ maps shown in Fig. 6a and b, the excitation probabilities for the SR modes are higher than those for the LR modes, with the difference becoming more significant for the thinner Al films. These features are notably apparent in the experimental results seen in (Fig. 5a and b). Figure 6c and d indicates that the excitation probabilities for the AC modes are higher than those for the SC modes and that the difference becomes more significant in the narrow gap. However, the excitation probabilities for the LR mode in Al film and the SC mode in the narrow gap are low compared with other modes, so it is expected that the excitation probability for the coupled SPP (SC-LR) between these modes is also quite low. Actually, this can be seen clearly in the experimental results as the difference in the intensities between the SC-LR modes and the others. Therefore, the reason why the SC-LR mode could not be
detected in the experiment can be its low excitation probability. Since we performed our AREELS measurements under normal incidence conditions, the low excitation probability of the SC-LR mode might be related to this scattering geometry.

There is a common trend related to the SPP excitations in the Al film and Al gap. Specifically, the energy separation and the difference in excitation probabilities between the two coupled modes become larger when two equivalent interfaces come into close proximity to each other, as shown in Fig. 6. In other words, the coupling of SPPs becomes stronger as the film thickness or the gap width decreases. The coupling strength depends not only on the distance between the two interfaces, but also on the decay length of the SPPs, because modes with a large decay length can easily couple with each other for a fixed film thickness or gap width. The decay length is inversely proportional to the wave vector $\alpha$ defined by Eq. (5), so the higher energy mode has a larger decay length at the fixed propagating wave vector $k$ of SPPs. Therefore, the coupling strength of the SR mode with lower excitation energy should be sensitive to the film thickness or the gap width. When the SR or LR mode couples in the multilayer structure, the coupling of the SR mode is weaker than that of the LR mode because of its short decay length. This fact suggests that the difference in excitation probability between the AC-SR and SC-SR modes should be minor compared with that between the AC-LR and SC-LR for a fixed gap width. In fact, the peaks of the AC-SR and SC-SR modes observed at 0.05 nm$^{-1}$ show almost the same intensities in sample A, as shown in Fig. 5a, which indicates that their coupling is not very strong. This can be attributed to the fact that the calculated decay lengths of those peaks are comparable with the thickness of the SiO$_2$ film (23 nm).

Contrastingly, as the gap width increases, the energy separation between the AC and SC modes narrows due to the weak coupling, as shown in Fig. 6d. Actually, in sample B, it was observed that the dispersion curve of the SC-SR mode merges into that of the AC-SR mode as shown in Fig. 4b. This indicates that the behavior of the dispersion curve can be interpreted by the coupling strength of SPPs, depending on the decay length as well as the thickness of each film in the multilayer structure. Sample B has a thick SiO$_2$ film and a thin Al film in comparison with sample A, which leads to a weaker coupling and smaller decay length. Most notably, the decay lengths of the SR modes in sample B [calculated by Eq. (5)] are smaller than the thickness of the SiO$_2$ film (61 nm), which means that the coupling of the SR modes should be very weak. This is why the dispersion curves for the AC-SR and SC-SR modes rapidly merge into each other.

**Concluding remarks**

In the AREELS measurements performed for two types of Al/SiO$_2$/Al multilayer structures, three dispersion curves for coupled AC-SR, SC-SR and AC-LR modes were observed, but the SC-LR mode could not be detected because of its low excitation probability. The obtained dispersion curves agreed well with the calculated curves when an aluminum oxide layer was present on the surfaces, which indicates that the dispersion relations are very sensitive to multilayer surface conditions. The experimental $E$–$q$ maps showed different intensities among the coupled SPP modes, which was attributed to the fact that, in multilayer structures, the excitation probabilities depend on the film thicknesses. We concluded that AREELS measurements using fast electrons at normal incidence are suitable for performing analyses of the AC-SR and SC-SR modes, and are applicable to the AC-LR mode. However, they cannot detect the SC-LR mode easily.

**References**


