Excitation and detection of surface-plasmon polariton waves on Cu(111) with gratings of rare gas monolayers

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We excited surface-plasmon polariton waves (SPPWs) on Cu(111) by coupling optical beams with adsorbed xenon gratings. The SPPWs's excitation causes a resonancelike dip in the angle-resolved reflectivity difference measurement. From the resonance we determined optical constants $\varepsilon_{\mathrm{Cu}}(633\ \mathrm{nm}) = -9.53 + i0.142$ and $\varepsilon_{\mathrm{Cu}}(780\ \mathrm{nm}) = -13.44 + i0.18$. The grating-coupled SPPWs can be used to study mass transport on thin films.

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Surface-plasmon polariton waves (SPPWs) are propagating electromagnetic waves confined to the interface between a metal and a dielectric material [1–4]. SPPWs have been studied extensively in the past few decades. Earlier works focused on polariton waves in planar geometry [1–11]. In recent years interest in SPPWs has been renewed significantly in response to the emergence of photonic materials, metamaterials, and nanophotonics in which plasmonics play important roles [12]. The renewed interest is also fueled by applications in biosensing [13–15].

In planar geometry the wave vector of an SPPW is a function of compositions and optical constants of the metal and dielectric materials. As a result, by measuring the SPPW wave vector, one can determine some of the material parameters such as optical constants [3,16]. When a thin film is added at the interface between a semi-infinite metal and a semi-infinite dielectric with known optical constants, the modified wave vector of the SPPW can be used to determine the film thickness [7–10,13–16]. In addition, as we will show in this Letter, when an SPPW is excited by coupling with an ultrathin grating at the interface between a metal and a dielectric, the excitation of the SPPW causes a resonancelike dip in the reflectivity that varies quadratically with the depth of the grating [11]. By following the dip one can study the mass transport on the thin film.

In this Letter we report a novel experimental study of SPPWs on single crystalline Cu(111) by coupling a monochromatic optical beam with an ultrathin dielectric grating on Cu(111) and detecting the SPPW with an angle-resolved optical reflectivity difference technique. The dielectric grating consists of thickness-modulated rare gas monolayers on Cu(111). Ultrathin rare gas gratings can be readily formed and removed in a modest temperature range from 30 to 300 K so that the grating-coupled excitation of SPPWs can be conveniently performed.

The experimental setup is shown in Fig. 1. The substrate is a 12 mm diameter × 2 mm thick single crystalline Cu(111) inside an ultrahigh vacuum chamber. The Cu substrate is cleaned with a combination of ion sputtering and thermal annealing before being cooled to 38 K. To form a thin layer of Xe on Cu(111), we expose the Cu(111) surface to 99.999% pure xenon gas with the exposure time determined by an *in situ*, angle-resolved, oblique-incidence reflectivity difference (OI-RD) ellipsometer [17,18]. The ellipsometer is also used to excite and detect the SPPW on Cu(111). At 38 K adsorbed Xe atoms wet Cu(111) and form a uniform lattice-matched crystalline layer [18].

To form a grating from a uniform Xe layer, we use a single 7 ns laser pulse at 532 nm. We split the pulse into two and recombine them at the Cu surface to form an interference pattern. The thermal desorption produced by the interference pattern yields a Xe thickness grating. At 38 K, the Xe grating remains unchanged during the subsequent experiment. The interference pattern and the resultant grating have a spatial periodicity of $2a = 5.445\ \mu\mathrm{m}$ [19].

To excite and detect the SPPW on Cu(111) through the Xe thickness grating, we employ the angle-resolved OI-RD ellipsometer as illustrated in Fig. 1.

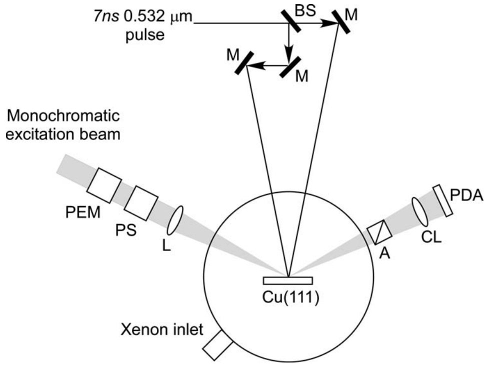

Fig. 1. Optical setup for xenon grating-coupled excitation of SPPW on single crystalline Cu(111). M, dielectric mirrors; BS, beam splitter; PEM, photoelastic modulator; PS, phase shifter; L, spherical lens that focuses a monochromatic light beam on Cu(111) with a span of 8°; A, polarizing analyzer; CL, cylindrical lens that images the reflected light into a line across a 152-element photodiode array (PDA).

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We use a 10 mW He–Ne laser and a 20 mW 780 nm diode laser as monochromatic light sources. The laser beam is initially collimated and p polarized before passing through a photoelastic modulator (PEM) that changes the laser beam from p polarized to elliptically polarized at 50 kHz and then through a phase shifter made of a rotatable quartz wave plate. We focus the beam on the Cu surface with a spherical lens so that the incidence angle spans a range of 4° near 68.0° for 633 nm and 64.0° for 780 nm. With a precision rotation stage, the incident angle is determined to within ±0.1°. We pass the reflected beam through an analyzer and then focus it into a line in the plane of incidence across a 152-element photodiode array detector. Each photodiode element detects the reflected light over an angular width of $\delta\theta = 0.026°$. By scanning through 152 photodiode elements we obtain the angle-resolved OI-RD, defined as $\Delta_p - \Delta_s \equiv (r_p - r_{p0})/r_{p0} - (r_s - r_{s0})/r_{s0}$ [17]. r_{p0} and r_{s0} are the complex reflectivity for p- and s-polarized light from a bare Cu(111), while r_p and r_s are the reflectivity from the Xe-covered Cu(111).

To see how the OI-RD signal responds to the excitation of a grating-coupled SPPW, we express the Xe thickness grating into a Fourier series,

$$d(x) = \langle d \rangle + d_1 \cos\left(\frac{\pi x}{a}\right) + d_2 \cos\left(\frac{2\pi x}{a}\right) + \cdots . \quad (1)$$

The OI-RD signal can be shown to have the following form [17]:

$$\Delta_p - \Delta_s \cong -i \frac{4\pi\varepsilon_{\mathrm{Cu}} \tan^2 \phi_{\mathrm{inc}} \cos \phi_{\mathrm{inc}}}{(\varepsilon_{\mathrm{Cu}} - 1)(\varepsilon_{\mathrm{Cu}} - \tan^2 \theta_{\mathrm{inc}})} \frac{(\varepsilon_{\mathrm{Xc}} - \varepsilon_{\mathrm{Cu}})(\varepsilon_{\mathrm{Xc}} - 1)}{\varepsilon_{\mathrm{Xc}}} \times \left[\frac{\langle d \rangle}{\lambda} + \frac{g}{(\phi_{\mathrm{inc}} - \phi_{\mathrm{SPR}}) + i\Gamma_{\mathrm{SPR}}} \left(\frac{d_1}{\lambda}\right)^2 \right], \quad (2)$$

where $\varepsilon_{\mathrm{Cu}} = \varepsilon'_{\mathrm{Cu}} + i\varepsilon''_{\mathrm{Cu}}$ is the optical constant of Cu, $\varepsilon_{\mathrm{Xe}}$ is the optical constant of a bulk-phase Xe, ϕ_{SPR} is the angle at which the SPPW on Cu(111) is maximally excited and given by the phase-matching condition [4]

$$\sin \phi_{\mathrm{SPR}} + \lambda/2a = \sqrt{\varepsilon'_{\mathrm{Cu}}/(\varepsilon'_{\mathrm{Cu}} + 1)}, \quad (3)$$

and g is a real number for Cu and varies weakly with ϕ_{inc} near ϕ_{SPR}. The real part of $\Delta_p - \Delta_s$ is thus expected to exhibit a resonancelike dip at ϕ_{SPR} with a half-width at half-maximum (HWHM)

$$\Gamma_{\mathrm{SPR}} = -\varepsilon''_{\mathrm{Cu}}(\varepsilon'_{\mathrm{Cu}}/(\varepsilon'_{\mathrm{Cu}} + 1) - \varepsilon'_{\mathrm{Cu}})/2 \times \cos \phi_{\mathrm{SPR}} \varepsilon'^3_{\mathrm{Cu}} \sqrt{\varepsilon'_{\mathrm{Cu}}/(\varepsilon'_{\mathrm{Cu}} + 1)} \approx \varepsilon''_{\mathrm{Cu}}/(2 \cos \phi_{\mathrm{SPR}} \varepsilon'^2_{\mathrm{Cu}}). \quad (4)$$

We give a brief physical argument why the second term in Eq. (2) is proportional to $(d_1/\lambda)^2$ and why we expect to observe the SPPW excited with an ultrathin grating. The electric field E_{SPPW} of a grating-coupled SPPW is proportional to the product of the incident electric field E_{inc} with $k_x = (2\pi/\lambda)\sin \phi_{\mathrm{inc}}$ and the first Fourier component of the grating with $q^{(+)} = +2\pi/2a$, i.e.,

$$E_{\mathrm{SPPW}} \sim E_{\mathrm{inc}}(d_1/\lambda)\left(\frac{1}{\phi_{\mathrm{inc}} - \phi_{\mathrm{SPR}} + i\Gamma_{\mathrm{SPR}}}\right) \times \exp[i(2\pi/\lambda)(\sin \phi_{\mathrm{inc}} + \lambda/2a)x].$$

When the polariton wave is backcoupled to the grating, it yields an extra electric field δE_R in the specular reflection direction that is proportional to the product of E_{SPPW} and the first Fourier component with $q^{(-)} = -2\pi/2a$, i.e.,

$$\delta E_R \sim E_{\mathrm{inc}}\left(\frac{1}{\phi_{\mathrm{inc}} - \phi_{\mathrm{SPR}} + i\Gamma_{\mathrm{SPR}}}\right)(d_1/\lambda)^2 \times \exp[i(2\pi/\lambda)(\sin \phi_{\mathrm{inc}})x].$$

δE_R yields the second term in Eq. (2). Without the resonance enhancement factor $\sim 1/\Gamma_{\mathrm{SPR}}$, the second term is less than the first by a factor of $2\pi d_1/\lambda$ and thus is negligible. With the resonance factor, the second term becomes comparable to the first and thus is observable. Away from ϕ_{SPR}, the first term dominates and is mostly imaginary. We use the off-resonant $\mathrm{Im}\{\Delta_p - \Delta_s\}$ to control the Xe exposure time and determine the mean thickness $\langle d \rangle$ of the Xe layer.

In Fig. 2 we display the angle-resolved $\mathrm{Re}\{\Delta_p - \Delta_s\}$ at 633 nm from a Xe-grating covered Cu(111). The initial thickness of the Xe layer is six monolayers (or 2.13 nm). After the grating is formed $\langle d \rangle$ is reduced to 2.5 monolayers (0.89 nm). $\mathrm{Re}\{\Delta_p - \Delta_s\}$ exhibits a resonancelike dip at $\phi_{\mathrm{SPR}} = 70.4° \pm 0.1°$ with $\Gamma_{\mathrm{SPR}} = 0.145° \pm 0.005°$, as expected from Eq. (2). $\mathrm{Im}\{\Delta_p - \Delta_s\}$ shows the dispersive behavior near the resonance (not shown here).

The measured resonance angle ϕ_{SPR} has a small contribution from the finite Xe thickness. By repeating the experiment using a Xe grating with $\langle d \rangle \sim 0.18$ nm (close to one half of a monolayer), ϕ_{SPR} shifted down to $70.2° \pm 0.1°$ with the same width.

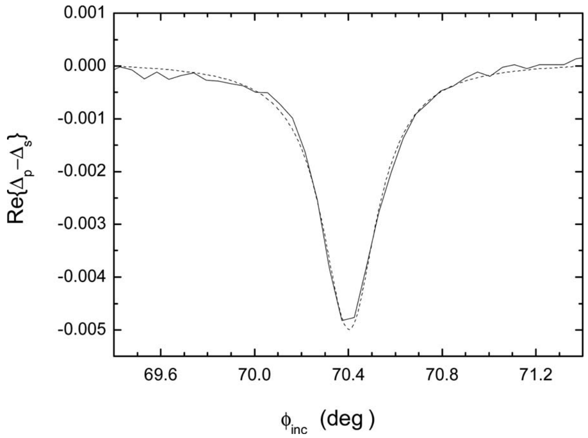

Fig. 2. $\mathrm{Re}\{\Delta_p - \Delta_s\}$ as functions of incidence angle ϕ_{inc} for a He–Ne laser beam at $\lambda = 633$ nm reflecting off a Xe-grating covered Cu(111). The dip corresponds to the excitation of the SPPW. The dashed curve is a fit to Eq. (2).

From $\phi_{\mathrm{SPR}}(\langle d\rangle \sim 0) = 70.2° \pm 0.1°$ and $\Gamma_{\mathrm{SPR}}(\langle d\rangle \sim 0) = 0.145° \pm 0.005°$, we determined the optical constant of single crystal Cu at 633 nm to be $\varepsilon_{\mathrm{Cu}}(633\ \mathrm{nm}) = (-9.53 \pm 0.09) + i(0.142 \pm 0.007)$ using Eqs. (3) and (4). The uncertainty in $\varepsilon'_{\mathrm{Cu}}(633\ \mathrm{nm})$ was determined from the accuracy of incidence angle measurement. The uncertainty in $\varepsilon''_{\mathrm{Cu}}(633\ \mathrm{nm})$ was determined by those of $\varepsilon'_{\mathrm{Cu}}(633\ \mathrm{nm})$ and the width of the resonance.

In Fig. 3 we display the angle-resolved $\mathrm{Re}\{\Delta_p - \Delta\}$ for a diode laser at 780 nm from a Xe-grating covered Cu(111). The mean thickness of the grating $\langle d\rangle$ was two monolayers (0.71 nm). Again $\mathrm{Re}\{\Delta_p - \Delta_s\}$ exhibits a resonance dip at $\phi_{\mathrm{SPR}} = 63.76° \pm 0.1°$ with the HWHM $\Gamma_{\mathrm{SPR}} = 0.070° \pm 0.005°$. $\mathrm{Im}\{\Delta_p - \Delta_s\}$ exhibits the dispersive behavior near the resonance angle (not shown). ϕ_{SPR} shifts down to $63.66° \pm 0.1°$ when $\langle d\rangle$ is reduced to nearly zero. From $\phi_{\mathrm{SPR}}(\langle d\rangle \sim 0) = 63.66° \pm 0.1°$ and $\Gamma_{\mathrm{SPR}} = 0.070° \pm 0.005°$, we determined the optical constant of single crystal Cu at 780 nm to be $\varepsilon_{\mathrm{Cu}}(780\ \mathrm{nm}) = (-13.44 \pm 0.24) + i(0.18 \pm 0.02)$.

We now discuss the results of our present work. On optical constants of Cu the discrepancy between our measurement and the values reported in the literature at 633 and 780 nm is significant, particularly for the imaginary part $\varepsilon''_{\mathrm{Cu}}$ [20–23]. At 633 nm the literature values of $\varepsilon'_{\mathrm{Cu}}(633\ \mathrm{nm})$ vary from −9.37 to −15.06, while the values of $\varepsilon''_{\mathrm{Cu}}(633\ \mathrm{nm})$ vary from 0.7 to 1.64. The latter are larger than what we measured by a factor 5 to 10. At 780 nm the literature values of $\varepsilon'_{\mathrm{Cu}}(780\ \mathrm{nm})$ vary from −21 to −26, while the values of $\varepsilon''_{\mathrm{Cu}}(780\ \mathrm{nm})$ vary from 1 to 2.6. Again the literature values of $\varepsilon''_{\mathrm{Cu}}(780\ \mathrm{nm})$ are larger than our measurement by 1 order of magnitude. The large discrepancy may be attributed in part to the fact that most literature values were determined from evaporated films or polycrystalline Cu. In many optical studies on single crystalline metals one often needs optical constants to determine *a priori* the absorption of an incident light from the transmittance into the metal given by $\sim 2\varepsilon''/|\varepsilon'|^{3/2}$. The knowledge of an accurate ε'' is thus crucial when the optical absorption must be known accurately. There have been no systematic accurate measurements of optical constants of single crystalline copper in the red and near-infrared ranges. Our present scheme offers a reliable way for measuring optical constants of single crystalline metals in the frequency range where the SPPW exists.

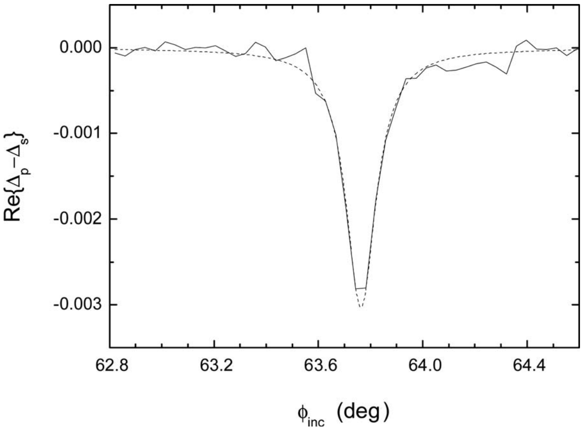

Fig. 3. $\mathrm{Re}\{\Delta_p - \Delta_s\}$ versus incidence angle ϕ_{inc} for a diode laser at $\lambda = 780$ nm reflecting off a Xe-grating covered Cu(111) at 780 nm. The dashed curve is a fit to Eq. (2).

Another application of grating-coupled SPPW excitation is in the study of the mass transport of rare gas atoms. From Eq. (2) we expect the resonance dip in the reflectivity difference signal to vary quadratically with d_1 as defined in Eq. (1). Let D be the diffusion constant by which the mass transport of rare gas causes the thickness modulation to diminish so that $d_1 \sim \exp(-\pi^2 Dt/a^2)$, the evolution of the dip in Figs. 2 and 3 at elevated temperatures can then be used to extract D. A further application of rare gas templates is to fabricate complex structures for novel surface plasmonics studies [12].

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