Plasmonic excitations in ultrathin metal films on dielectric substrates

Xiaoguang Li\textsuperscript{1,2,3}, Ao Teng\textsuperscript{4}, Mustafa M Özer\textsuperscript{4,5}, Jian Shen\textsuperscript{3,4}, Hanno H Weitering\textsuperscript{4,5} and Zhenyu Zhang\textsuperscript{2}

\textsuperscript{1} Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, People’s Republic of China
\textsuperscript{2} International Center for Quantum Design of Functional Materials (ICQD)/Hefei National Laboratory for Physical Sciences at the Microscale (HFNL), University of Science and Technology of China, Hefei, Anhui 230026, People’s Republic of China
\textsuperscript{3} State Key Laboratory of Surface Physics and Department of Physics, Fudan University, Shanghai 200433, People’s Republic of China
\textsuperscript{4} Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996, USA
\textsuperscript{5} Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

E-mail: lixg@siat.ac.cn

Received 4 November 2013, revised 10 April 2014
Accepted for publication 22 May 2014
Published 24 June 2014

\textit{New Journal of Physics} 16 (2014) 065014
doi:10.1088/1367-2630/16/6/065014

Abstract

The optical properties of metals are mainly determined by their plasmonic excitations, with various intriguing phenomena associated with systems in reduced dimensions. In this paper, we present a systematic study of the plasmonic excitations in ultrathin metal films on dielectric substrates using two different theoretical approaches, and with Mg thin films on Si as prototype systems. The bulk of the results are obtained using the first approach within first-principles time-dependent local density approximation. We show that the presence of the substrate substantially modifies the plasmon hybridization of the metal films; in turn, the plasmon excitation in the films strongly enhances the absorption of the substrate. The detailed absorption spectra contain several intriguing features. Above the Mg surface plasmon mode, we observe a broad resonance due to the hybridization between the antisymmetric surface plasmon and multipole surface plasmon. Furthermore, below the Mg surface plasmon...
mode, there also exists a broad absorption feature, caused by individual electron–hole pair excitations. In the second approach, we use a semi-classical local optics model to reveal an intrinsic connection between the broad absorption feature and the multipole surface plasmon modes, which result from the single-particle and collective excitations of the same surface electrons, respectively. Our theoretical predictions on the plasmon dispersions and absorption spectra are also shown to be qualitatively consistent with the latest experimental observations using electron energy loss spectroscopy for Mg thin films grown on Si substrates.

Keywords: ultrathin metal film, surface plasmon, multipole surface plasmon, plasmon hybridization, local optics model

1. Introduction

Many novel materials can be obtained by manipulating the size, dimensionality, or environment of the systems. In particular, material surfaces are attractive playgrounds to look for many innovative physical and chemical properties. In recent years, the collective electronic excitations at metal surfaces have received tremendous attention regarding their ability to strongly interact with external electric fields. Earlier studies of collective modes focused on semi-infinite systems [1–21], where the behaviours of the various collective modes, including monopole surface plasmons [1], multipole surface plasmons [3], and bulk plasmons [22], have been well understood. The recent rapid development of plasmonics stems from the fact that the properties of plasmons sensitively depend on the size, shape, and dielectric environment of the metal nanostructures [23–29]. A particularly interesting case is metal thin films [30–39], where the plasmonic excitations show some intriguing features due to hybridization of the different plasmon modes and the influence of the dielectric environment.

In a free standing metal thin film, the surface plasmons at both surfaces will strongly interact with each other to provide two hybridized plasmon modes: the symmetric and antisymmetric surface plasmons [35, 40–42]. In a recent study, we carried out a systematic study of the dynamical behaviour of the plasmonic excitations in such freestanding metal films, focusing on the Landau damping mechanism of the plasmon decay [42]. For practical systems, we must consider the interaction of such metal films in contact with certain supporting substrates. In many earlier studies of metal overlayers, attention has been mainly focused on systems with metal substrates [30, 43, 44]. For example, Liebsch introduced a further hybridization between the antisymmetric surface plasmon and multipole surface plasmon [45], and successfully explained experimental observations on the thickness and momentum dependences of the plasmons [33]. However, the plasmon modes of the metal film on a dielectric substrate will be different from those of the metal film on a metal substrate, as demonstrated in a recent joint theoretical and experimental study of Al thin films on Si(111) [39].

In this paper, we study the plasmonic excitations in ultrathin metal films grown on dielectric substrates, using two different theoretical approaches, and with Mg thin films on Si as prototype systems. The bulk of the results are obtained using the first approach within first-principles time dependent local density approximation (TDLDA)
where the response of the metal film is described quantum mechanically, while the contribution of the substrate is incorporated through a frequency-dependent dielectric function within the Lorentz–Drude model. For such systems, we expect at least four different types of plasmon modes related to the Mg conduction electrons, including the surface plasmon and multipole surface plasmon at the metal–vacuum interface, bulk plasmon, and interface plasmon at the metal–dielectric interface. Our systematic study reveals their different hybridization behaviours from those of the free standing films. In addition, because we can theoretically distinguish between the absorption spectra of the thin films and substrates, the plasmon-induced absorption enhancement in the substrates is clearly demonstrated, a finding of important technological significance. We also see several intriguing features in the detailed absorption spectra. Above the Mg surface plasmon mode, we observe a broad resonance due to the hybridization between the antisymmetric surface plasmon and multipole surface plasmon. Furthermore, below the Mg surface plasmon mode, there also exists a broad absorption feature [46], caused by single electron–hole pair excitations. In the second approach, we use a semi-classical local optics model to reveal an intrinsic connection between the broad absorption feature and the multipole surface plasmon modes. Our theoretical predictions on the plasmon dispersions and absorption spectra are also shown to be qualitatively consistent with the latest experimental observations using electron energy loss spectroscopy (EELS) for Mg thin films grown on Si substrates [47].

The paper is organized as follows. Section 2 describes the model system of our TDLDA approach. In this section, aside from standard descriptions of the ground state and plasmonic excitations of the metal films within the jellium model, we introduce a novel description for the optical response of the substrate. In section 3, the absorption spectra of the various plasmon modes are discussed in detail. A comparison between our TDLDA results and the EELS measurements is made in section 4. We close the paper with a summary in section 5. Some details about the induced boundary charges are given in the appendix.

2. Theoretical formalism

Plasmons in metal–dielectric overlays are studied using TDLDA. We treat the metal layer within a jellium model, where the response of nearly free electrons is evaluated quantum mechanically within linear response theory. On the other hand, the responses of both the metal jellium background and the substrate are described classically by their local dielectric functions \( \epsilon(\omega) \) obtained from the bulk measurement. This separation of the quantum free electrons and classical dielectric background has been used in several related studies of similar systems [15, 16, 39, 48]. We note that for the absorption calculation, the recent study of the Al–Si system [49] did not explicitly consider the effect of the free electrons on the dielectric background. We believe this work represents the first explicit treatment of the absorption of the coupled metal film/dielectric substrate systems.

Here, we also stress the difference between our Mg–Si systems and the quantum-classical combined Ag systems studied previously [15]. In the earlier study of Ag, it was necessary to stay below the onset of interband transitions, because the response of the bound (\( d \)-) electrons is obtained by using the total response minus the free electron Drude part in the same system. Above the interband transition energy, the coupling between the bound and extended electrons...
becomes important, and the individual response of the bound (d-) electrons cannot be obtained easily. However, in the Mg–Si system, the response of Si can be directly obtained from experiments; therefore, the quantum and classical parts of the system can be well separated.

2.1. Dielectric environment

We consider a general case by dividing the classical background into three different regions with the local dielectric function

\[ \epsilon(\omega, \mathbf{r}) = \begin{cases} 
\epsilon_1(\omega) & r < r_1 \\
\epsilon_2(\omega) & r_1 < r < r_2, \\
\epsilon_3(\omega) & r_2 < r 
\end{cases} \tag{1} \]

where \( r \) is the direction perpendicular to the interface; \( r_1 \) and \( r_2 \) are the locations of the substrate/metal and metal/vacuum interfaces, respectively; \( \epsilon_1(\omega) \) and \( \epsilon_3(\omega) \) are the dielectric functions of the substrate and external environment, respectively; \( \epsilon_2(\omega) \) is the dielectric contribution from the jellium background in the metal, such as the contribution of the localized d-band electrons in noble metals [16]. For the Mg–Si system discussed in this paper, both \( \epsilon_2 \) and \( \epsilon_3 \) are equal to 1, while \( \epsilon_1(\omega) \), the dielectric function of Si, will be specified later. Hereafter for convenience, the \( \omega \) dependence of the corresponding quantities is left implicit.

The response of the rest of our system, namely, that of the nearly free electrons in the metal, is evaluated quantum mechanically within linear response theory. The effect of the classical dielectric background on this response can be introduced by an effective Coulomb interaction \( W(\mathbf{r}, \mathbf{r}') \). To derive this interaction, we solve the electric potential \( \phi(\mathbf{r}) \) of the system satisfying the Poisson equation

\[ -4\pi \left[ n(\mathbf{r}) - n_b(\mathbf{r}) \right] = \epsilon(\mathbf{r}) \nabla^2 \phi(\mathbf{r}) + \nabla \epsilon(\mathbf{r}) \cdot \nabla \phi(\mathbf{r}), \tag{2} \]

where \( n(\mathbf{r}) \) is the nearly free electron density usually contributed by the sp-electrons, and \( n_b(\mathbf{r}) \) is the charge density of the ionic jellium background, which is zero in both the Si and vacuum regions. The induced charges in the dielectric environment can be classified into two types: one is the screening charge \( n_s = (n - n_b)(1 - \epsilon)/\epsilon \) around the nearly free electrons, and the other represented by \( \nabla \epsilon(\mathbf{r}) \cdot \nabla \phi(\mathbf{r}) \) in equation (2) is the bound charge \( \sigma \) at the interface of different dielectric regions. Based on the above categorization, an effective Coulomb interaction can be written as

\[ W(\mathbf{r}, \mathbf{r}') = \frac{1}{\epsilon(\mathbf{r}')} V_C(\mathbf{r}, \mathbf{r}') + \sum_{i=1,2} \sigma_i(\mathbf{r}') V_C(\mathbf{r}, \mathbf{r}), \tag{3} \]

where \( V_C \) is the bare Coulomb interaction, \( \sigma_i \) is the induced interface charge density at \( r_i \) by a unit charge at \( r' \), and the factor \( 1/\epsilon(\mathbf{r}') \) accounts for the effect of the screening charges. Due to the translational symmetry in our system, the bare Coulomb interaction \( V_C \) can be written in a reduced form.
\[ V_C (r, r', q) = \frac{2\pi}{q} e^{-q|r-r'|}, \]  

(4)

with momentum \( q \), which is the magnitude of the momentum perpendicular to the direction of \( r \). Hereafter for convenience, the \( q \) dependence of the corresponding quantities is left implicit. The induced surface bound charges \( \sigma_i (r') \) by the charge density \( n (r') \) can be written as (see the appendix for details)

\[ \sigma_i (r') = \frac{g_1}{2\pi e (r')} \nabla V_C (r_i, r') n (r') + g_2 e^{-qD} \nabla V_C (r_i, r') n (r'), \]  

(5)

and

\[ \sigma_2 (r') = \frac{g_2}{2\pi e (r')} \nabla V_C (r_2, r') n (r') - g_1 e^{-qD} \nabla V_C (r_1, r') n (r'), \]  

(6)

where \( D = r_2 - r_1 \) is the distance between two interfaces, and

\[ g_i = \frac{e_{i+1} - e_i}{e_{i+1} + e_i} \]  

(7)

is called the surface response function, whose physical meaning has been clarified in the appendix.

At the end of this section, we note that with the corresponding dielectric functions and the Coulomb interaction as shown in equation (4), equation (3) leads to the same result as the Coulomb kernel in [39].

2.2. Ground states

In the ground state study, we have \( \omega \) and \( q \) equal to zero, and therefore \( W (r, r') \) has a simplified form \(-2\pi |r - r'|\), where an infinite constant term has been dropped. With this effective Coulomb interaction, we can go through the standard recursive procedure in solving the one-dimensional Kohn–Sham equation

\[ H_{KS} u (r) = \left(-\frac{1}{2} \frac{d^2}{dr^2} + V_{\text{eff}} [n] (r)\right) u (r) = Eu (r), \]  

(8)

where \( u(r) \) is the wavefunction apart from the phase factor \( e^{-ik_\parallel} \), and \( V_{\text{eff}} [n] (r) \) is the effective electronic potential. We consider this potential as

\[ V_{\text{eff}} [n] (r) = \int W (r, r') n (r') dr' + V_{xc} [n] (r) + V_{ps} (r), \]  

(9)

where \( V_{xc} [n] (r) \) is the exchange-correlation and \( V_{ps} (r) \) is the pseudo-potential assumed to be a step-like function. For Si, we use \( V_{ps} = -4.7 \) eV, which is the same as the work function of bulk Si. For Mg, we use a fitting value \( V_{ps} = -0.032 \) eV to ensure that the Fermi energy of Mg yields the bulk work function of 3.66 eV [55]. This background pseudopotential, which is not emphasized in previous studies, is important to yield the Schottky barrier at the Si/Mg interface. A Wigner–Seitz radius of 2.66 Bohr units is used for Mg. The length is expressed in units of Mg monolayers (1 monolayer (ML) = 2.61 Å). Assuming free electrons, the corresponding surface
and bulk plasmons of Mg are 7.68 eV and 10.86 eV, respectively. Also, we note that the nearly free electrons in our system only partially spill out into the Si; therefore, the free-electron mass is used in this study as an approximation. The wave function $u(r)$ is solved within the infinite potential (zero Dirichlet) boundary condition, and the energy cut-off of the electron-hole pair is taken as 1 Hartree for the excited state calculations described later.

In Figure 1, we compare the ground state electron density and total potential distribution of a free standing Mg film and the Mg–Si system. We can clearly see that the Schottky barrier is formed at the Mg–Si interface due to the work function mismatch, and the electron spill-out at the Mg–Si interface is much stronger compared to the free standing film due to the screening of the interface charges from the substrate. These charges also lower the potential in the substrate and induce the discontinuity in the electric field, which is indicated by the difference of the potential slope at both sides of the Mg–Si interface. Also, the bound negative charges from Si will accumulate at the interface of the Mg–Si system, and therefore increase the energy of the free electrons at lower subbands. However, for the higher energy subbands, the free electrons can largely spill out into Si. The spatial extent of these electrons will strongly reduce their energy compared to the freestanding case. Clearly, the charge transfer from the thin film to the substrate may have considerable effects on the system’s response. For example, a previous experimental observation shows that for relatively thin Al films (<10 ML) on Si, the charge transfer turns the surface plasmon dispersion from negative to positive at small $q$ values [36].

2.3. Excited states

The form of $W(r, r')$ as expressed in equation (4) is now used for the study of the excited states. After obtaining the ground state of the system, the behaviour of excited states can be
studied by evaluating its dynamic response. First, we consider the frequency dependent dielectric function of Si within the Lorentz–Drude model \[49\],

\[
\sum \epsilon = \omega = \epsilon_\infty + \frac{\omega^2}{\gamma^2 + \omega^2} = -\text{Im} \left[ \left( \epsilon + 1 \right)^{-1} \right] \quad \text{and} \quad -\text{Im} \left( \epsilon^{-1} \right), \tag{10}
\]

where \( \epsilon_\infty = 1 \). We have used four Lorentz oscillators to fit the measured dielectric function \[50, 51\], and the corresponding parameters are listed in table 1. The real \( (\epsilon_R) \) and imaginary \( (\epsilon_I) \) parts of the dielectric function are plotted in figure 2. This fitted dielectric function gives the bulk plasmon peak at 16.7 eV, which is equal to the measured value \[51\], and the surface plasmon peak around 12 eV, which is expected to have pronounced impact on the Mg–Si absorption spectra, because this energy is very close to that of the Mg bulk plasmon.

To study the response of the whole system, we start with the non-interacting density–density response function of Mg free electrons.

![Figure 2](image_url)

**Figure 2.** The real \((\epsilon_R, \text{solid line})\) and imaginary \((\epsilon_I, \text{dashed line})\) parts of the dielectric function of Si within the Drude model. The dotted lines indicate the absorption of the surface plasmon \(\omega_s\) and bulk plasmon \(\omega_p\) of Si, defined by \(-\text{Im} \left[ \left( \epsilon + 1 \right)^{-1} \right] \text{and} \quad -\text{Im} \left( \epsilon^{-1} \right)\), respectively.

**Table 1.** The parameters of the Lorentz oscillators.

| \(A_i\) | \(\omega_i\) (eV) | \(\gamma_i\) (eV) |
|---|---|---|
| i = 1 | 1.5 | 3.4 | 0.15 |
| i = 2 | 4.0 | 4.2 | 0.4 |
| i = 3 | 3.0 | 5.2 | 1.8 |
| i = 4 | 2.18 | 6.9 | 10 |

\[\epsilon(\omega) = \epsilon_\infty + i\epsilon_I = \epsilon_\infty - \sum_{i=1}^n \frac{A_i\omega_i^2}{\omega^2 - \omega_i^2 + i\gamma_i\omega},\]
\[ \chi^0 (r, r') = \sum_{a,b} \left( f_a - f_b \right) \psi_a^* (r) \psi_b (r) \psi_a (r') \psi_b^* (r') \frac{\omega + i \eta - (E_b - E_a)}{\omega + i \eta - (E_b - E_a)}, \]  

where \( a, b \) label the initial and final electronic states, respectively; \( E_a, \psi_a, \) and \( f_a \) are the energy, wavefunction, and occupation number of a given state, respectively; \( \omega \) is the energy of the external perturbation; and \( i \eta \) is a small imaginary energy, which introduces the additional relaxation mechanisms beyond the Landau damping considered here. We use \( \eta = 0.1 \) eV for all the spectra calculations. The above standard formula has been introduced by many other authors \([35, 42, 52–54]\). In the following, we derive the interacting density–density response function \( \chi \) defined in

\[ \delta n (r) = \int \delta n (r, r') V_{\text{ext}} (r') = \int \delta n (r, r') \left[ V_{\text{ext}} (r') + V_{\text{ind}} (r') \right]. \]

where \( V_{\text{ind}} \) is the electronic potential from the induced charge \( \delta n \) and \( V_{\text{ext}} \) is the external electric potential. Hereafter for convenience, the integrations over the space variables are left implicit. Different from the conventional form of \( V_{\text{ext}} \) used for free standing systems \([35, 42]\), by considering the effect of the substrate, we add an effective charge \( q_{\text{ext}} = e^{r} q_{\text{ext}} \) with \( r \) far from the whole system at the vacuum side, and use \( V_{\text{ext}} = W_{\text{ext}} \) as the external potential. On the other hand, the induced electronic potential is

\[ V_{\text{ind}} = K \delta n = K \chi V_{\text{ext}}, \]

where the kernel function \( K \) is the sum of the effective Coulomb interaction \( W \) and the additional exchange-correlation energy, which is given by

\[ K (r, r') = W (r, r') + \frac{\partial V_{\text{ext}} [n] (r')}{\partial n} \delta (r - r'). \]

Combining equations (12) and (13), we obtain

\[ \chi = \left[ 1 - \chi^0 K \right]^{-1} \chi^0. \]

The total potential can be calculated from

\[ V_{\text{tot}} = V_{\text{ext}} + K \chi V_{\text{ext}}, \]

which gives the induced charge by multiplying the non-interacting response function \( \chi^0 \). The absorption of the free electrons and the bound interface charge can then be obtained from the product of the total electronic potential and the out-of-phase component of the induced charges as

\[ P_n = \text{Im} \left[ V_{\text{tot}}^* \delta n \right] = \text{Im} \left[ V_{\text{tot}}^* \chi_0 V_{\text{tot}} \right] \]

and

\[ P_e = \text{Im} \left[ V_{\text{tot}}^* \delta \sigma \right] = \text{Im} \left[ V_{\text{tot}}^* \chi_\sigma V_{\text{tot}} \right], \]

respectively. Here, the response function \( \chi_\sigma \) of the interface charge \( \sigma \) is defined in the appendix. Because the screening charge density \( n_s \) can be evaluated from \( n_s = n (1 - \epsilon)/\epsilon \), we can obtain the absorption of the screening charges
Both the bound interface charges and screening charges are from the substrate, therefore we obtain the absorption of the substrate as \( P_\sigma + P \). Finally, the total absorption is the sum of \( P_\sigma \), \( P_\sigma \), and \( P \) as

\[
P_{\text{tot}} = \text{Im} \left[ V_{\text{tot}}^\ast \left( \frac{1}{\epsilon} \epsilon_0 \chi_{\text{tot}} \right) V_{\text{tot}} \right].
\]

3. Results and discussion

In this section, we present our TDLDA results of the absorption spectra for both the free standing Mg films and the Mg–Si systems. Using the semi-classical local optics model, we further elucidate the underlying physics of the TDLDA spectra for the Mg–Si systems. In addition, we establish the consistency between our theoretical results and the recent experimental measurement for the Mg–Si systems [47].

3.1. Absorption spectra of free standing thin films

In a free standing film, we should observe two plasmon modes corresponding to the symmetric and antisymmetric hybridizations of the two surface plasmons. Figure 3(a) clearly displays these two modes in the absorption \( P \) of the free standing film. In the same figure, we also show the absolute value of the total induced free charge \( |\delta N| = \int \rho \, dr \) and the ratio \( P/|\delta N| \), whose physical meaning will be discussed below.

Both the absorption and the induced electron density reflect the response of the system to an external field. Usually, one can find a collective mode based on the absorption spectra first, and then learn the physical character of this mode from the distribution of the induced charge \( \delta n (r) \). For example, Eckardt [53] showed that as the energy approaches a resonance, the imaginary part of the induced charge \( \text{Im} \delta n (r) \) quickly increases and the corresponding real part \( \text{Re} \delta n (r) \) changes sign at the resonance frequency. The conclusion is that the typical ‘surface oscillations’ will have this phase change in the surface region. This is an effective way to distinguish between the different plasmon modes of semi-infinite systems. However, for the thin films and other confined systems with strong coupling between different plasmon modes, it will be difficult to identify the individual modes based on this analysis. For example, the electron density oscillations of both the symmetric (figure 3(b)) and antisymmetric (figure 3(c)) modes have visible charge density oscillations across the whole thin-film region. Although in free standing films we can easily distinguish these two modes by their symmetry, it is not straightforward to categorize different plasmon modes in general, such as in the metal–dielectric overlayers, where the induced density does not have a definitive symmetry anymore. Moreover, the hybridization between the surface and other plasmon modes will further obscure the detailed information that one can otherwise gather from the charge density oscillations in simpler system.

To solve the above problem, we introduce the global quantities, the total induced charge \( \delta N \) and the ratio \( P/|\delta N| \), in order to focus on the direction of the collective charge oscillations,
and instead of dealing with the more complicated local density $\delta n(r)$. As long as we realize that $|\delta N|$ will peak for the oscillations parallel to the interfaces, while it will tend to zero for the oscillations normal to the interfaces, from the dashed line curve in figure 3(a), we clearly see the parallel and normal oscillatory behaviours of the symmetric and antisymmetric modes, respectively. The quantity $P/|\delta N|$ as shown by the solid line in figure 3(a) is further defined to extract the oscillations normal to the interfaces from the absorption spectra. This way, we can distinguish between the contributions from the different plasmon modes.

3.2. The effect of the substrate on absorption

To see the effect of the substrate on the absorption spectra, we now compare the theoretical results for a Mg film grown on a Si substrate and the free standing Mg film. In the Mg–Si system, we show the absorptions of the Mg film $P_{\text{Mg}}$ (dotted line) and the Si substrate $P_{\text{Si}}$ (dashed line) in figure 4(a). Comparing $P_{\text{Si}}$ with the Si surface plasmon curve in figure 2, we can see that the resonances around 3.5 and 13 eV are due to the Si intrinsic absorption, while the absorption around 1.5 eV and the broad envelope between 8 and 10 eV are related to $P_{\text{Mg}}$. Theoretically, the interplay between $P_{\text{Si}}$ and $P_{\text{Mg}}$ can be traced back to the association between the screening charges from the substrate and the Mg electrons, which spill from the metal to the substrate. This is a clear indication of a mechanism for the plasmon enhanced substrate absorption at the microscopic level.
Also, we can see different hybridization between PMg and the free standing absorption due to the presence of the substrate. In the free standing film, two pronounced absorption peaks corresponding to the symmetric and antisymmetric modes are due to hybridization of the two Mg surface plasmons, whose energy in the absence of interaction is around 7.7 eV. In the Mg–Si system, the coupled two modes are the Mg surface plasmon and the interface plasmon at the Mg–Si interface with energy around 3 eV, which is evaluated by \( \omega_{\epsilon} + \epsilon_{Si}(0) \). The large energy difference between the surface and interface plasmons implies weak coupling between these modes, therefore the resultant antisymmetric mode remains close to the Mg surface plasmon. On the other hand, the symmetric mode with energy lower than the interface plasmon appears around 1.5 eV.

Another aspect of the Mg–Si system is that the antisymmetric mode carries a dominant absorption weight over the symmetric mode. This is because the symmetric and antisymmetric modes are mainly contributed by the interface and surface plasmons, respectively, and the interface plasmon has a lower absorption weight than the surface plasmon due to the decay of the external field through the thin film. On the other hand, in the free standing film, due to the strong hybridization between the two surface plasmons, the absorption difference between the two surfaces cannot be exhibited. To further resolve the dominant antisymmetric mode, we apply the method introduced in the previous section to calculate the induced total free electrons \( \delta N_{Mg} \) and the ratio \( P_{Mg}/\delta N_{Mg} \). The results are shown in figure 4(b). Different from the free standing film, where \( |\delta N| \) of the antisymmetric mode is almost zero, \( |\delta N_{Mg}| \) shows clear resonance for the antisymmetric mode because the oscillating charges at both interfaces are not perfectly antisymmetric. This special asymmetric mode containing a considerable parallel

![Figure 4](image-url)
oscillatory component suppresses the contribution from the surface plasmon in the $\delta P_{\text{Mg}}$ curve. Also, we attribute the broad plasmon mode to the hybrid resonance between the antisymmetric surface plasmon and multipole surface plasmon. This is because it shows a similar oscillatory nature to the multipole surface plasmon mode, namely, the charge oscillates normal to the interfaces, and its energy is similar to the energy of the multipole surface plasmon around $0.8 \omega_p$ between the surface- and bulk-plasmon energies of Mg.

It is also worth mentioning the similarity between $P_{\text{Si}}$ and $|\delta N|$ in figures 4(a) and (b), respectively, for energies larger than 4 eV. This similarity indicates a close correlation between the enhanced absorption in the substrate and the induced density in the thin film. On the other hand, for energies smaller than 4 eV, although the induced density is very large, the enhanced absorption is relatively low due to the small intrinsic absorption of Si in this region (see figure 2).

Now, we analyse the dispersion of the various plasmon modes. In figures 5(a) and (b) for Mg thin films with different thicknesses on Si substrates, we can clearly see the low energy symmetric mode dispersing from 0 to around 2 eV. Its intensity drops quickly, because the external field decays more strongly through the thin film as $q$ increases. At small $q$, a broad resonance appears between 7 and 11 eV, which is the result of hybridization between the antisymmetric surface plasmon and multipole surface plasmon. This hybrid resonance is especially strong for the thinner films. Also, a strong absorption due to the Si surface plasmon appears around 13 eV, which is larger than the value evaluated from $-\text{Im} \left[ (\epsilon_{\text{Si}} + 1)^{-1} \right]$ as shown in figure 2. The reason for this energy shift is that the surface plasmon existence

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure5.png}
\caption{TDLDA absorption spectra for (a) a 3 ML and (b) a 10 ML Mg film on the Si substrate, respectively.}
\end{figure}
condition for Si becomes \((\epsilon_{Si} + \epsilon_{Mg}) = 0\) when it is covered by Mg. Meanwhile, the local dielectric function \(\epsilon_{Mg}\) is between 0 and 1 at energies higher than the Mg bulk plasmon, so the energy of the Si surface plasmon shifts close to its bulk plasmon value, which is evaluated from 

\[-Im \left( \epsilon_{Si}^{-1} \right)\] 

to be at 16.7 eV.

By considering the interaction between the interface and surface plasmons in the Mg overlayer, we would expect the antisymmetric mode to reach the bulk value \(\omega_p\) at small \(q\). However, further hybridization between the multipole surface plasmon and antisymmetric plasmon mode \([30, 44, 45]\) should result in two branches: one dispersing from \(\omega_p\) to the multipole surface plasmon energy \(\omega_m\), and the other dispersing from \(\omega_m\) to the surface plasmon energy \(\omega_{sp}\). In our theoretical studies, this effect can be vaguely observed in the relatively thick Mg overlayer as shown in figure 5(b). On the dispersion curve of the antisymmetric mode (changing from \(\omega_p\) to \(\omega_m\) with increasing \(q\)), we see a small kink around 8 eV, which is due to the hybridization with the multipole surface plasmon. This hybridization looks very weak, since the multipole surface plasmon is known to be underestimated in the TDLDA calculations \([56]\). On the other hand, in the case of the thin film (figure 5(a)), we see a significantly different spectrum with the appearance of the hybrid resonance. It shows negative dispersion at small \(q\), and their intensity quickly diminish as \(q\) increases. This is a clear signal for the hybridization mechanism.

Figure 6 displays the absorption spectra of the Mg–Si systems at some constant momentum \(q\). These results are extracted from figure 5 to better exhibit the appearance of a
broad absorption feature with energies below the surface plasmon. We assign this absorption feature to be the threshold resonance as in earlier studies [46], because its energy peaks around the Mg work function \( \omega_0 \). In contrast to the multipole surface plasmons and bulk plasmons, the intensity of the threshold resonance increases as \( q \) increases. This behaviour implies a close correlation between the threshold resonance and surface electrons, because the larger \( q \) corresponds to a shorter penetration length of the external field into the thin film, namely, a larger surface contribution. In the next section, we will use the semi-classical local optics model to further explore the dispersion and intensity relations of the threshold resonance and the other plasmon modes.

3.3. Dispersion and intensity of collective modes within a semi-classical local optics model

In classical studies, one usually assumes a sharp change of the electronic density profile and a delta-function-like induced charge density at the interface. Here, we divide the interface region into \( n \) layers and investigate this system within the framework of the so-called local optics model [57]. In the limiting case of \( n \to \infty \), a smooth distribution of the electron density is recovered. The obtained various plasmon modes of the system are then compared with our TDLDA results.

The whole system is divided into \( n + 2 \) layers as follows: the substrate \((i = 0)\), a series of adjacent layers labelled by \( i \) with the thickness \( l_i \) \((i = 1, 2,...,n)\) inside the film, and the vacuum \((i = n + 1)\). The Drude model is used to describe the local dielectric function for each layer as

\[
\varepsilon_i(\omega) = \varepsilon_i - \frac{\omega_{p,i}^2}{\omega^2 + i\omega\gamma_i},
\]

where \( \varepsilon_i \) is the dielectric constant in high frequency limit, \( \omega_{p,i} = \sqrt{n_i e^2 / m e_0} \) is the layer-dependent plasmon frequency, and \( \gamma_i \) is the damping parameter. The electric potential in the different layers can be written as

\[
\phi(r) = \begin{cases} 
  x_0 e^{qr}, & i = 0 \\
  x_i e^{qr(r-r_i)} + y_i e^{-q(r-r_i)}, & i = 1, 2,...,n \\
  e^{qr(r-r_n)} + \text{Re}^{-q(r-r_n)}, & i = n + 1,
\end{cases}
\]

where \( r_i \) is the coordinate of the interface between layer \( i \) and \((i + 1)\). By considering the continuities of the transverse electric field and the vertical electric displacement at \( r_i \), we obtain

\[
h_i = \frac{y_i}{x_i} = \frac{\varepsilon_i - \varepsilon_0}{\varepsilon_i + \varepsilon_0},
\]

and the recursion relation

\[
h_{i+1} = \frac{y_i}{x_i} = \frac{g_i + h_i e^{-2q l_i}}{1 + g_i h_i e^{-2q l_i}}, \text{ for } i = 1, 2,...,n,
\]

where \( h_{n+1} = R \) gives the total reflection of the system, and \( g_i = (\varepsilon_{i+1} - \varepsilon_i)/(\varepsilon_{i+1} + \varepsilon_i) \) indicates the reflection of each interface. The pole of \( g_i \) gives the frequency of the interface plasmon at \( r_i \) without hybridization as
We now evaluate the reflection $R$ of the system, whose imaginary part $ImR$ gives the absorption spectra. First, we consider a very simple system containing a silicon substrate ($\varepsilon_0 = 12$ and $\omega_{p,0} = 0$) and a metal overlayer with three layers ($n = 3$). Inside the film, the bulk plasmon energies of the three layers are taken to be $\omega_{p,i} = \{1, 0.8, 0.4\} \omega_p$, and the thicknesses of the respective layers are chosen as $l_i = \{5, 0.7, 0.3\}$ ML. Employing these parameters, we reproduce the familiar resonance structures investigated before, including the symmetric (S) and antisymmetric modes (AS), the multipole surface plasmon (MP), and the threshold resonance (TR) as shown in figure 7(a). In this figure, we can see that as $q$ increases, the intensity of the MP-AS hybridization decreases, while the intensity of the TR around $\omega_{0.4}$ gradually increases. Moreover, the dispersions of all the resonant branches follow a simple rule: as $q$ increases, the energy of a particular branch always disperses from a bulk plasmon to an interface plasmon energy. Usually, the dispersion is from the bulk plasmon of the region $i$ to the interface plasmon at $r_i$. However, as two branches cross, they switch the correspondence. Following this rule, the branches in figure 7 disperse from $\omega_{\{0, 1, 0.8, 0.4\}} \omega_p$ to the interface plasmons around $\omega_{\{0.28, 0.91, 0.63, 0.28\}} \omega_p$, respectively. In addition, we see the dispersive line crossing (hybridization) around $0.8 \omega_p$. The reason for this crossing is that as $q$ increases, the substrate ($i = 0$) will be strongly screened; accordingly, the layer $i = 1$ can be effectively viewed as a semi-infinite system, and the resonance starting from $\omega = 0$ will quickly disappear.

\[
\omega_{s,i} = \sqrt{\frac{\omega_{p,i}^2 + \omega_{p,i+1}^2}{\bar{\varepsilon}_i + \bar{\varepsilon}_{i+1}}}. \tag{25}
\]
while the branch starting from $\omega = \omega_p$ will quickly evolve to an effective semi-infinite bulk value $\omega = \omega_p / \sqrt{2}$.

However, the above three-layer setup with a special electron density profile seems somewhat artificial. A more realistic approach would be to increase the number of the layers to smoothen out the electron density distribution. In figure 7(b), we show the results for a 100-layer setup with the bulk plasmon $\omega_p = \left[1 - 0.01 (i - 1)\right] \omega_p$ and the corresponding thicknesses $l_i = 5.01$ and $l_{i=2...100} = 0.01$ ML. The obtained result clearly shows the symmetric and antisymmetric modes at the small $q$, but in contrast to our quantum studies, the AS disappears too fast as $q$ increases, indicating an overestimated screening from the outer metal layers with lower electron density. Moreover, we did not observe the MP mode.

Up to now, we have seen that the Drude type local optics model can reproduce the characteristic resonances in our quantum studies with some special model choices, however, it fails as we apply a smooth electron density profile. One problem with the Drude type dielectric function is that it does not treat the electrons close to the boundary specifically, while the free electron assumption in this region is clearly inappropriate. Actually, considerable efforts have been made to study the different optical properties between the surface and bulk regions of the same materials [58, 59]. With this motivation, we introduce a simple way to describe the role of the boundary as a confinement to electrons by using the Lorentz type dielectric functions

$$\epsilon_i(\omega) = \epsilon_i - \frac{\omega^2_{p,i}}{\omega^2 - \omega_{0,i}^2 \pm i \omega \gamma_i^i},$$

where the only difference from equation (21) is the inclusion of the intrinsic oscillation frequency $\omega_{0,i}$ of the electrons in each layer.

An important observation here is that two resonances can be supported by the system: one of them is the single particle excitation at the frequency $\omega = \omega_{0,i}$ giving $\epsilon_i = -\infty$, and the other is the collective motion at the frequency $\left(\omega_{0,i}^2 + \omega_{p,i}^2\right)^{1/2}$ giving $\epsilon_i = 0$. Interestingly, if we assume $\omega_{0,i} = 0.4 \omega_p$ indicating its close correlation with the TR mode and $\omega_{p,i}^2 = 0.5 \omega_p^2$ corresponding to half of the bulk electron density, then the collective frequency is very close to the multipole surface plasmon at $0.8 \omega_p$. This assumption implies an intrinsic connection between the TR and MP modes, and can also be used to explain the slight blue-shift of the MP as the energy of the TR increases in metals with different $r_i$ [9].

Figure 8(a) displays the absorption spectra with the Lorentz type dielectric function, where we consider $n = 2$ with $\omega_{p,i} = [1, 0.7] \omega_p$, $\omega_0 = [0, 0.4] \omega_p$, and $l = [5, 1]$ ML. Similar to the Drude model, our new dielectric function also qualitatively yields the dispersion and intensity of the characteristic resonances. As mentioned before, we have two bulk modes $\omega = \omega_{0,i}$ and $\left(\omega_{0,i}^2 + \omega_{p,i}^2\right)^{1/2}$ for each layer. Meanwhile, two interface plasmon modes can be obtained by solving $\epsilon_i + \epsilon_{i+1} = 0$ at each interface. With the above model, we obtain the interface plasmon energy at $[0, 0.28]$, $[0.32, 0.90]$ and $[0, 0.64] \omega_p$ for the interfaces at $r_0$, $r_1$ and $r_2$, respectively. The dispersions of the resonances follow the same trend as in the Drude model, namely, each branch disperses from the bulk plasmon to the interface plasmon energy as $q$ increases, and the hybridization occurs when two branches cross each other.
Finally, we discuss the results calculated within the Lorentz model employing a 100-layer setup, where \( \omega_{i} = -\sum_{l=1}^{10} p_{i} \), and \( l_{i} = 5 \), and \( l_{i=2...100} = 0.01 \) ML. In addition, we assume \( \omega_{0,i} = \omega_{p} \), mimicking the distribution of the effective confinement from the bulk to the outmost layer. Figure 8(b) displays the absorption spectra similar to our TDLDA results. The AS mode shifts quickly from \( \omega_{p} \) to \( \omega_{sp} \approx 0.7 \), while its intensity gradually drops as \( q \) further increases. In addition, the TR mode is shown as a broad absorption feature at energies lower than \( \omega_{sp} \). Most importantly, we can see a clear indication of the MP mode around \( 0.8 \omega_{p} \). Its appearance can be understood as an interplay between the surface confinement and the collective motion of the electrons in the surface region of the metal. This new understanding also explains the trade-off between the intensities of the MP and TR modes as \( q \) increases.

4. Comparison between theoretical and experimental results

We now compare our theoretical results with our recent EELS measurements performed on Mg thin films grown on Si(111) [47]. First, we stress that the spectra measured by EELS are typically obtained at some fixed incident and scattering angles of the probing electrons, while the theoretical absorption is calculated for a certain parallel momentum \( q \) transferred to the plasmons. The relation between the angles and momentum \( q \) is given by

![Figure 8. The imaginary part of the reflection from a 6 ML Mg film on the Si substrate, with the Mg film divided into (a) \( n = 2 \) and (b) \( n = 100 \) layers, respectively. The results were obtained within the local optics model described by the Lorentz dielectric functions.](image-url)
\[ q = \sqrt{2m} \left( \sqrt{E_i \sin \theta_i} - \sqrt{E_i - E_{\text{abs}} \sin \theta_f} \right) \]  

(27)

where \( E_i \) is the energy of the incident electron, \( E_{\text{abs}} \) is the absorbed energy during the inelastic scattering, and \( \theta_{if} \) are the incident and scattering angles, respectively. In the EELS measurements, the incident energy \( E_i \) and angle \( \theta_i \) are usually fixed, and the data are recorded for the scattering electrons with a certain off-specular angle defined as \( \Delta \theta = \theta_f - \theta_i \).

To compare with the experiments, we reproduce our theoretical absorption spectra of figure 5(a) together with the angle dependent energy–momentum relation at given off-specular angles (figure 9). Generally, higher energy modes would require larger off-specular scattering angles to yield appreciable intensities. For example, the strong absorption due to the Si surface plasmon, which appears around 12 eV, could only be observed at very large off-specular angles in the EELS experiments. This is consistent with the alkali metal results reported earlier [12] and the Mg measurements shown below.

Figure 10 displays the EELS measurements of a 4.5 ML film at various off-specular angles. The data is fitted with four Lorentzian peaks to reproduce the antisymmetric mode, multipole surface plasmon, bulk plasmon, and threshold resonance. As expected from our theoretical outcomes, the multipole and bulk plasmons have more pronounced intensities at the larger off-specular angles. On the other hand, the threshold resonance shows a minimum intensity around 4°. As discussed in section 3.3, in contrast to the multipole and bulk plasmons, the intensity of the threshold resonance becomes larger as \( q \) increases. This is consistent with
both our TDLDA and semi-classical results. Because the intensity of the symmetric mode will quickly damp as $q$ increases, we could expect to find this mode with relatively small off-specular angles in experimental measurements, as shown in figure 9. However, it is difficult to identify the symmetric mode, since its energy window ($\sim 0.2$ eV) overlaps with a huge elastic scattering peak and an interband Mg transition energy of 0.7 eV.

5. Summary

We studied the plasmon excitations in metal thin films grown on dielectric substrates using both the TDLDA and semi-classical local optics models. Employing Mg thin films on Si as prototype systems, we have shown that the hybridization of the plasmon modes in the metal films is substantially modified by the substrates, and the plasmon excitation in the metal films strongly enhances the absorption of the substrates, a finding of important technological significance. The threshold resonance is also clearly observed as a broad absorption peak at large momentum transfer. This feature is demonstrated within the semi-classical local optics model to be rooted.
in the same surface electrons as the multipole surface plasmon modes. Our theoretical predictions on the detailed plasmon dispersions and absorption spectra are also shown to be qualitatively consistent with our latest experimental observations for the Mg–Si systems. These findings help to pave the way for designing desirable plasmonic materials in the quantum regime.

Acknowledgments

This work was supported in part by the NNSF of China (grant nos. 91121002, 11274071, 91021019 and 11034006), the National Basic Research Program of China (grant no. 2011CB921801), USDOE (grant no. DE-FG03-02ER45958), and USNSF (grant no. 0906025). HHW was supported by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, USDOE.

Appendix A. The response function of the interface bound charges

Here, we derive the response function $\chi_{\sigma}$ of the interface bound charges $\sigma_i$ at $r_i$. The response function acts on a vector formed by local electric potential as $\Phi = (\phi(r_1), \phi(r_2), ...)^T$, giving the interface bound charge vector $\sigma = (\sigma_1, \sigma_2, ...)^T$ through

$$\sigma = \chi_{\sigma} \Phi.$$  \hspace{1cm} (A.1)

First, we consider the system with only one interface at $r_i$ and the dielectric functions $\epsilon_i$ and $\epsilon_{i+1}$ at two sides. The interface charge density can be obtained from the continuity of electric displacement field across the interface

$$\nabla \left( 2\pi \sigma_i + \nabla \phi(r_i) \right) = \epsilon_{i+1} \left[ -2\pi \sigma_i + \nabla \phi(r_i) \right]$$  \hspace{1cm} (A.2)

as

$$\sigma_i = \frac{g_i}{2\pi} \nabla \phi(r_i) = \frac{\epsilon_{i+1} - \epsilon_i}{\epsilon_{i+1} + \epsilon_i} \frac{\nabla \phi(r_i)}{2\pi}.$$  \hspace{1cm} (A.3)

The above equation shows how we obtain the surface response function $g_i$, and its connection with interface charges.

Now, we consider the system with two interfaces. The derivation can be easily extended to the $n$-interface case. We first ignore the interaction between the charges at different interfaces and write the non-interacting response function as

$$\chi_{\sigma 0} = \begin{pmatrix} g_1 & 0 \\ 0 & g_2 \end{pmatrix} \frac{\nabla}{2\pi},$$  \hspace{1cm} (A.4)

which satisfies $\left( n(r_1), n(r_2) \right)^T = \chi_{\sigma 0} \left( \phi(r_1), \phi(r_2) \right)^T$. The bare Coulomb interaction $K_n$ between the interface charges can be written as
\[ K_r = \frac{2\pi}{q} \begin{pmatrix} 0 & \psi_2(r_1) \\ \psi_1(r_2) & 0 \end{pmatrix}. \]  
(A.5)

Where \( \psi(r) = e^{-|q|r}| \). The interacting response function \( \chi_\sigma \) can then be obtained from the standard Dyson type formula as

\[ \chi_\sigma = \left( 1 - \chi_{\sigma 0} K_r \right)^{-1} \chi_{\sigma 0} = \Delta \begin{pmatrix} g_1 & g_2 e^{-qD} \\ -g_1 g_2 e^{-qD} & g_2 \end{pmatrix} \frac{\nabla}{2\pi}, \]  
(A.6)

where \( \Delta = \left( 1 + g_1 g_2 e^{-2qD} \right)^{-1} \). Now, we can evaluate the charge density \( n\left(r'\right) \) induced potential at \( r \) as

\[ \phi(r) = \frac{V_c(r, r') n\left(r'\right)}{e\left(r'\right)}. \]  
(A.7)

The \( n\left(r'\right) \) induced interface charge can thus be calculated by inserting the above equation in equation (A.1).

References

[1] Ritchie R H 1957 Plasma losses by fast electrons in thin films Phys. Rev. 106 874–81
[2] Feibelman P J 1968 Simple microscopic theory of surface plasmons Phys. Rev. 176 551–5
[3] Bennett A J 1970 Influence of the electron charge distribution on surface-plasmon dispersion Phys. Rev. B 1 203–7
[4] Harris J and Griffin A 1971 Surface plasmon dispersion Phys. Lett. A 34 51–52
[5] Feibelman P J 1974 Microscopic calculation of surface-plasmon dispersion and damping Phys. Rev. B 9 5077–98
[6] Schwartz C and Schaich W L 1982 Hydrodynamic models of surface plasmons Phys. Rev. B 26 7008–11
[7] Schwartz C and Schaich W L 1984 Multipole surface plasmons and photoemission yield spectra Phys. Rev. B 30 1059–61
[8] Kempa K and Gerhardts R R 1985 Evidence for a multipole surface plasmon at a clean aluminum surface from microscopic theory of photoyield spectra Solid State Commun. 53 579–82
[9] Liebsch A 1987 Dynamical screening at simple-metal surfaces Phys. Rev. B 36 7378–88
[10] Dobson J F and Harris G H 1988 An additional surface plasmon mode of a bare jellium aluminium surface from self-consistent microscopic calculations J. Phys. C: Solid State Phys. 21 L729
[11] Tsuei K-D, Ward Plummer E and Feibelman P J 1989 Surface-plasmon dispersion in simple metals Phys. Rev. Lett. 63 2256–9
[12] Tsuei K-D, Plummer E W, Liebsch A, Kempa K and Bakshi P 1990 Multipole plasmon modes at a metal surface Phys. Rev. Lett. 64 44–47
[13] Tsuei K D, Plummer E W, Liebsch A, Pehlke E, Kempa K and Bakshi P 1991 The normal modes at the surface of simple metals Surf. Sci. 247 302–26
[14] Plummer E W 1992 Collective oscillations at a surface or in a thin film Solid State Commun. 84 143–6
[15] Liebsch A 1993 Surface plasmon dispersion of Ag Phys. Rev. Lett. 71 145–8
[16] Liebsch A 1993 Surface-plasmon dispersion and size dependence of mie resonance: Silver versus simple metals Phys. Rev. B 48 11317–28
[17] Sellarès J and Barberán N 1994 Multipole surface-plasmon modes on simple metals Phys. Rev. B 50 1879–87
[18] Barman S R, Häberle P and Horn K 1998 Collective and single-particle excitations in the photoyield spectrum of Al Phys. Rev. B 58 4285–8
[19] Chiarello G, Formoso V, Santaniello A, Colavita E and Papagno L 2000 Surface-plasmon dispersion and multipole surface plasmons in Al(111) Phys. Rev. B 62 12676–9
[20] Silkin V M, Chulkov E V and Echenique P M 2004 Band structure versus dynamical exchange-correlation effects in surface plasmon energy and damping: A first-principles calculation Phys. Rev. Lett. 93 176801
[21] Politano A, Formoso V and Chiarello G 2008 Dispersion and damping of gold surface plasmon Plasmonics 3 165–70
[22] Pines D and Bohm D 1952 A collective description of electron interactions: II. Collective vs individual particle aspects of the interactions Phys. Rev. 85 338–53
[23] Matsubara K, Kawata S and Minami S 1988 Optical chemical sensor based on surface plasmon measurement Appl. Opt. 27 1160–3
[24] Jensen T R, Malinsky M D, Haynes C L and Van Duyne R P 2000 Nanosphere lithography: tunable localized surface plasmon resonance spectra of silver nanoparticles J. Phys. Chem. B 104 10549–56
[25] Hirsch L R, Stafford R J, Bankson J A, Sershen S R, Rivera B, Price R E, Hazle J D, Halas N J and West J L 2003 Nanoshell-mediated near-infrared thermal therapy of tumors under magnetic resonance guidance Proc. Natl Acad. Sci. USA 100 13549–54
[26] Ozbay E 2006 Plasmonics: merging photonics and electronics at nanoscale dimensions Science 311 189–93
[27] Awazu K, Fujimaki M, Rockstuhl C, Tominaga J, Murakami H, Ohki Y, Yoshida N and Watanabe T 2008 A plasmonic photocatalyst consisting of silver nanoparticles embedded in titanium dioxide J. Am. Chem. Soc. 130 1676–80
[28] Atwater H A and Polman A 2010 Plasmonics for improved photovoltaic devices Nat. Mater. 9 205–13
[29] Wang Y, Plummer E W and Kempa K 2011 Foundations of plasmonics Adv. Phys. 60 799–898
[30] Gaspar J A, Eguiluz A G, Tsuei K-D and Plummer E W 1991 Elementary excitations in alkali-metal overlayers probed by electron-energy-loss spectroscopy: quantum-mechanical effects Phys. Rev. Lett. 67 2854–7
[31] Schaich W L and Dobson J F 1994 Excitation modes of neutral jellium slabs Phys. Rev. B 49 14700–7
[32] Moresco F, Rocca M, Hildebrandt T and Henzler M 1999 Plasmon confinement in ultrathin continuous Ag films Phys. Rev. Lett. 83 2238–41
[33] Liebsch A, Kim B-O and Plummer E W 2001 Collective excitations in adsorbed alkali-metal films: Critical analysis of photoyield and electron-energy-loss spectra for K on Al(111) Phys. Rev. B 63 125416
[34] Yu Y, Jiang Y, Tang Z, Guo Q, Jia J, Xue Q, Wu K and Wang E 2005 Thickness dependence of surface plasmon damping and dispersion in ultrathin Ag films Phys. Rev. B 72 205405
[35] Yuan Z and Gao S 2006 Linear-response study of plasmon excitation in metallic thin films: layer-dependent hybridization and dispersion Phys. Rev. B 73 155411
[36] Yu Y, Tang Z, Jiang Y, Wu K and Wang E 2006 Thickness dependence of the surface plasmon dispersion in ultrathin aluminum films on silicon Surf. Sci. 600 4966–71
[37] Yuan Z and Gao S 2008 Landau damping and lifetime oscillation of surface plasmons in metallic thin films studied in a jellium slab model Surf. Sci. 602 460–4
[38] Politano A, Agostino R G, Colavita E, Formoso V and Chiarello G 2008 Purely quadratic dispersion of surface plasmon in Ag(Ni(111)): the influence of electron confinement Phys. Status Solidi—Rapid Res. Lett. 2 86–88
[39] Yuan Z, Jiang Y, Gao Y, Käll M and Gao S 2011 Symmetry-dependent screening of surface plasmons in ultrathin supported films: the case of Al/Si(111) Phys. Rev. B 83 165425
[40] Prodan E, Radloff C, Halas N J and Nordlander P 2003 A hybridization model for the plasmon response of complex nanostructures Science 302 419–22
[41] Prodan E and Nordlander P 2004 Plasmon hybridization in spherical nanoparticles J. Chem. Phys. 120 5444–54
[42] Li X, Xiao D and Zhang Z 2013 Landau damping of quantum plasmons in metal nanostructures New J. Phys. 15 023011
[43] Chiarello G, Cupolillo A, Amoddeo A, Caputi L S, Papagno L and Colavita E 1997 Collective excitations of two layers of K on Ni(111) Phys. Rev. B 55 1376–9
[44] Barman S R, Stampfl C, Häberle P, Ibañez W, Cai Y Q and Horn K 2001 Collective excitations in alkali metals on Al(111) Phys. Rev. B 64 195410
[45] Liebsch A 1991 Electronic excitations in adsorbed alkali-metal layers Phys. Rev. Lett. 67 2858–61
[46] Liebsch A, Benemanskaya G V and Lapushkin M N 1994 Near-threshold enhancement in photoemission from alkali metal overlayers Surf. Sci. 302 303–13
[47] Teng A, Kempta K, Özer M M, Hus S M, Snijders P C, Lee G and Weitering H H 2014 Quantum oscillations in the surface excitations of ultrathin Mg(0001) films (preprint)
[48] López-Bastidas C, Maytorena J A and Liebsch A 2001 Hot-electron dynamics at noble metal surfaces Phys. Rev. B 65 035417
[49] Rakic A D, Djurišić A B, Elazar J M and Majewski M L 1998 Optical properties of metallic films for vertical-cavity optoelectronic devices Appl. Opt. 37 5271–83
[50] Philipp H R and Ehrenreich H 1963 Optical properties of semiconductors Phys. Rev. 129 1550–60
[51] Stiebling J and Raether H 1978 Dispersion of the volume plasmon of silicon (16.7 eV) at large wave vectors Phys. Rev. Lett. 40 1293–5
[52] Eguiluz A G 1983 Dynamical density response function of a metal film in the random-phase approximation Phys. Rev. Lett. 51 1907–10
[53] Ekardt W 1985 Size-dependent photoabsorption and photoemission of small metal particles Phys. Rev. B 31 6360–70
[54] Prodan E and Nordlander P 2002 Electronic structure and polarizability of metallic nanoshells Chem. Phys. Lett. 352 140–6
[55] Michaelson H B 1996 Handbook of Chemistry and Physics ed D R Lide (Cleveland: CRC Press) pp 12–122
[56] Nazarov V U 1999 Multipole surface-plasmon-excitation enhancement in metals Phys. Rev. B 59 9866–9
[57] Liebsch A 1997 Electronic Excitations at Metal Surfaces (New York/London: Plenum Press)
[58] Shi N and Ramprasad R 2005 Dielectric properties of ultrathin SiO2 slabs Appl. Phys. Lett. 87 262102
[59] Nguyen H V, An I and Collins R W 1993 Evolution of the optical functions of thin-film aluminum: A real-time spectroscopic ellipsometry study Phys. Rev. B 47 3947–65