Plasmonic reflectance anisotropy spectroscopy of metal nanoclusters in a dielectric multilayer. Theory

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Abstract. A theory of plasmonic reflectance anisotropy spectroscopy (RAS) is developed for nanocluster layer at an interface. The model of identical ellipsoidal metal particles occupying the sites of rectangular lattice is used to calculate the effective plasmonic polarizability of nanoparticles. The anisotropic local field due to optically induced dipole plasmons and their interface-conditioned images is taken into account. Within the theory, resonant reflectance anisotropy spectra recently observed for In nanoclusters on InAs surface are explained, the anisotropy being associated with the difference between frequencies of plasmons with orthogonal in-layer polarizations. The frequency difference is treated in terms of anisotropy of the particles shape or/and the layer structure, its sign being opposite for the two types of anisotropy. The plasmonic RAS is concluded to serve as a method for investigating the anisotropy of nanocluster arrays.

1. Introduction

Currently, considerable attention is paid to the optical properties of metal nanocluster arrays. Particularly, reflectance anisotropy spectroscopy (RAS) technique was recently found to reveal the plasmonic anisotropy of metal nanoparticle layers formed on semiconductor surfaces [1–4]. Since the interface does not contribute to RA spectra, it was attributed to inherent macroscopic anisotropy of the nanocluster arrays that is not displayed with conventional methods of diagnostics. Plasmonic nature of the spectral feature observed for In clusters on InAs(001) surface was confirmed by its red shift with increasing nanoparticle size and permittivity of surrounding media [3].

The observed RA spectra were interpreted within the model of regular nanoparticle array with interacting dipole plasmons for In/InAs system [2, 5] and the model of effective medium for In/GaAs [1]. Despite the conceptual difference between these approaches, similar estimations of ellipsoidal indium clusters anisotropy were obtained from the experimental plasmonic reflectance anisotropy spectra. The essential advantage of regular lattice model [5, 6] is the presence of collective plasmon modes, whose properties can be related to the shape of the clusters and the structure of the layer. The effect of anisotropic layer structure is inherently absent in the effective medium model.

This paper presents a theory of plasmonic RAS developed for metal nanoparticle arrays in layered dielectric media. The model of quasi-point dipoles arranged in rectangular lattice at the interface is investigated, the anisotropic local field of dipole plasmons induced in nanoparticles being taken into account. We consider the effects of both nanoparticle shape and the layer structure on the anisotropic optical resonance. Within the model we explain the spectra observed in [2, 3] and fit them to estimate the anisotropy of the In/InAs structures under study.
2. General theory

The paper is aimed at studying the photon-energy dependent RA spectra

\[ \frac{\Delta R}{R} = 2 \frac{R_x - R_y}{R_x + R_y}. \quad (1) \]

Here, \( R_\alpha \) is the reflectivity of the monochromatic linearly polarized wave \( E^{inc}(z, \rho) = e_\alpha \hat{E}^{inc} \exp \left(i \sqrt{\varepsilon_0 k_0^2} z \right) \) incident normally onto a structure along the \( z \)-axis, the polarization subscript \( \alpha \) being \( x \) or \( y \). Hereafter, we consider the interface \( z = 0 \) between two homogeneous isotropic media, the total permittivity tensor being \( \varepsilon_{\alpha\beta}^{(0)}(z, \omega) = \delta_{\alpha\beta} \varepsilon_2(\omega) \) with \( \varepsilon^{(0)}(z, \omega) = \varepsilon_1 \) for transparent medium at \( z < 0 \) and \( \varepsilon^{(0)}(z, \omega) = \varepsilon_2(\omega) \) at \( z > 0 \). Nanoparticles are centered at the sites \( \rho_n = n_x A_x \cdot e_x + n_y A_y \cdot e_y \) of rectangular lattice with the periods \( A_x \) and \( A_y \) in the plane \( z = z_0 = -h < 0 \) near the interface (figure 1).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\linewidth]{figure1.png}
\caption{Model of ellipsoidal nanoparticles occupying a rectangular lattice at the interface.}
\end{figure}

In general [6], the reflectivities \( R_\alpha \) are determined by the total electric field \( E(z, \rho; \omega) \) obtained from the sequence of equations

\[ \sum_{\nu} \left[ \sum_{\mu} \text{rot}_{\nu\mu} \text{rot}_{\mu\nu} - \varepsilon^{(0)}(z, \omega) k_0^2 \delta_{\alpha\nu} \right] \begin{bmatrix} E^{(0)}(z, \rho) \\ D^{(0)}_{\nu}(z, \rho - \rho') \end{bmatrix} = 4\pi k_0^2 \begin{bmatrix} 0 \\ P_{\alpha}(z, \rho) \end{bmatrix}, \quad (2) \]

where \( \rho = (x, y) \), \( k_0 = \omega/c \), and \( c \) is the speed of light. Equations (1) and (2) give the unperturbed (in absence of nanoparticles) electric field \( E^{(0)} \) and tensor Green’s function \( \hat{D}^{(0)} \), respectively. These solutions of equations (1) and (2) and their Fourier transforms

\[ \{ E^{(0)}(z; \kappa), \hat{G}^{(0)}(z, z'; \kappa) \} = \int d^2 \rho \exp(-i \kappa \cdot \rho) \{ E^{(0)}(z, \rho), \hat{D}^{(0)}(z, z', \rho) \} \quad (5) \]

satisfy the Maxwell’s boundary conditions at \( z = 0 \). In equation (4), the perturbation is provided by the polarization \( P(z, \rho; \omega) \) of nanoparticles. Given the components \( \chi^{(0)}_{\alpha\alpha}(\omega) \) of diagonal plasmon polarizability tensor for a single nanoparticle, its dipole moment induced by the field \( E \) is \( P_{\alpha}(z, \rho) = \chi^{(0)}_{\alpha\alpha}(\omega) E_{\alpha}(r_n) \). The related polarization of an array of the identical particles is expressed as

\[ P_{\alpha}(z, \rho) = \delta(z - z_0) \sum_n \delta(\rho - \rho_n) \chi^{(0)}_{\alpha\alpha}(\omega) E_{\alpha}(z_0, \rho_n), \quad (6) \]

where the delta function \( \delta(z - z_0) \delta(\rho - \rho_n) \) implies that the local plasmons are treated as quasi-point dipoles. Equation (4) with the polarization (6) is rewritten as the equivalent integral equation
\[ E_\alpha(z, \rho) = E_\alpha^{(0)}(z, \rho) + \sum_{n, \beta} D_{\alpha \beta}^{(0)}(z, z_0, \rho - \rho_n) \hat{\chi}_{\beta \rho}^{(0)}(z_0, \rho_n). \]  

(7)

For a regular lattice, the self-consistent solution of equation (7) is obtained using the representations of dipole moment \( p_{n, \alpha} = \chi_{\alpha \beta} E_\beta^{(0)}(\mathbf{r}_n) = \chi_{\alpha \alpha} E_\alpha(\mathbf{r}_n) \), where the effective polarizability \( \hat{\chi} \) taking account of dipole interactions is introduced for nanoparticles [5, 6]. From equation (7) rewritten for the near field \( E_\beta(z_0, \rho_n) \) one obtains the tensor

\[ \hat{\chi} = \chi^{(0)} \left[ \hat{\mathcal{J}} - \sum_{n} \hat{\mathcal{J}}^{(0)}(z_0, z_0, \rho_n) \hat{\chi}^{(0)} \right]^{-1}, \]

(8)

where prime means exclusion of term with \( n = 0 \) corresponding to self-interaction of dipoles. On using equation (8) and the representation

\[ \sum_{n} \exp(-i \mathbf{k} \cdot \rho_n) = (2\pi)^2 (A_x A_y)^{-1} \sum_{m} \delta(\mathbf{k} - \mathbf{b}_m), \]

equation (7) is transformed to the relation

\[ E_\alpha(z, \rho) = E_\alpha^{(0)}(z, \rho) + \sum_{m, \beta, \gamma} e^{i \mathbf{b}_m \cdot \rho} \mathcal{G}_{\alpha \beta}^{(0)}(z, z_0, \mathbf{b}_m) \frac{\hat{\chi}_{\beta \gamma}}{A_x A_y} E_\gamma^{(0)}(z_0, \rho). \]

(9)

containing summation over the reciprocal lattice vectors \( \mathbf{b}_m = 2\pi (m_x \mathbf{e}_x + m_y \mathbf{e}_y + m_z \mathbf{e}_z)^{-1} \), \( \mathbf{m} = (m_x, m_y) \), where \( m_x \) and \( m_y \) are integers. For short-period lattices \( |\mathbf{b}_{m=0}| > A_x^{-1} \gg k_0 \), and normally radiated field is given by the only contribution with \( \mathbf{b}_{m=0} = 0 \) in equation (9), the other field components vanishing at sub-wavelength distances \( |z - z_0| \sim A_x \ll k_0^{-1} \) from the interface. Then only diagonal tensor components \( \chi_{\alpha \alpha} \) and \( \mathcal{G}_{\alpha \alpha}^{(0)}(z, z_0, 0) \) in equation (9) turn to be non-zero, and the polarizations of incident \( \mathbf{E}^{\text{inc}} \) and radiated \( \mathbf{E} \) waves coincide. As a result, equation (9) gives for reflectivity of light polarized along the \( \alpha \) th axis the following expression

\[ R_\alpha = \left| r_\alpha^{(0)} + \Delta r_\alpha \right|^2, \]

\[ \Delta r_\alpha = \frac{2\pi k_0}{\sqrt{\varepsilon_1}} \frac{\chi_{\alpha \alpha}}{A_x A_y} \left( e^{-i \sqrt{\varepsilon_1} k_0 h} + r_\alpha^{(0)} e^{i \sqrt{\varepsilon_1} k_0 h} \right)^2, \]

(10)

where \( r_\alpha^{(0)} = (\sqrt{\varepsilon' - \varepsilon''}) / (\sqrt{\varepsilon' + \varepsilon''}) \) is reflectivity of the interface.

3. Plasmonic polarizability of nanoparticles in a layer

Next we investigate the reflectance anisotropy spectrum (1) within the model of identical ellipsoidal nanoparticles (figure 1) whose polarizability components are

\[ \chi_{\alpha \alpha}^{(0)} = \frac{a_x a_y a_z}{3} \frac{\varepsilon - \varepsilon_1}{(\varepsilon - \varepsilon_1) N^{(0)} + \varepsilon_1}, \]

(11)

the principal axes of the tensor \( \chi^{(0)} \) are assumed to coincide with the unit vectors \( \mathbf{e}_\alpha \) of the lattice. The particles are supposed to be formed of metal with the permittivity \( \varepsilon(\omega) = \varepsilon_{\infty} - \omega_p^2 / (\omega^2 + i \gamma), \)

where \( \omega_p \) is the plasma frequency and \( \gamma^{-1} \) is the electron relaxation time. The pole of (11) with \( \varepsilon(\omega) \) determines the frequency \( \omega_{\alpha}^{(0)} = \omega_p \sqrt{N^{(0)}/\varepsilon_0^{(0)}} \) of dipole plasmon polarized along \( \alpha \) th semi-axis of
ellipsoid, $\varepsilon^{(z)} = (\varepsilon_x - \varepsilon_1)N^{(z)} + \varepsilon_1$. The plasmonic anisotropy is related to the particle shape through the depolarization coefficients $N^{(z)}$ depending on the ratios of semi-axes lengths.

In quasi-static approximation, the tensor $\hat{\chi}$ of effective plasmonic polarizability is obtained from equation (8) on substituting the resonant plasmonic components $S^{(z)}$ to give

$$
\chi_{aa} = \left[ \frac{1}{x^{(0)}} - \frac{1}{e_1 A_{aa}^3} \left( S_{a}^{(d)} + \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} S_{a}^{(i)} \right) \right]^{-1}
$$

(12)

The lattice sums

$$
S^{(d)}_a = A_{a}^3 \sum_{n=0} \frac{3\rho_{n,a}^2 - \rho_n^2}{\rho_n^5}, \quad S^{(i)}_a = \left( \frac{\omega}{2\hbar} \right)^3 + A_{a}^3 \sum_{n=0} \frac{3\rho_{n,a}^2 - (\rho_n^2 + 4\hbar^2)}{(\rho_n^2 + 4\hbar^2)^{3/2}}
$$

(13)

corresponding to the fields of in-layer dipoles and their images are derived from the term $\sum_n \rho^{(0)}_{aa}(z_0, z_0, \rho_n)$ in which the retardation is neglected.

**Figure 2.** Theoretical spectra $\Delta R/R$ and $R_x, R_y$ calculated, respectively, from equations (1) and (10) with (14) for (a) weak $(\hbar \omega_x = 3.62 \text{ eV}, \hbar \omega_y = 3.58 \text{ eV})$ and (b) strong $(\hbar \omega_x = 3.75 \text{ eV}, \hbar \omega_y = 3.45 \text{ eV})$ frequency anisotropy specified by the difference $\hbar |\omega_x - \omega_y|$ at $\hbar \Gamma_{x,y} = 0.04 \text{ eV}$ used as a scale.

The effective polarizability of $\alpha$-polarized plasmon of a particle (12) can be reduced to the form

$$
\frac{k_0}{A_x A_y} \chi_{aa}(\omega) \approx \frac{\Omega^2_\alpha}{\omega^2 - \omega^2 - i\omega \Gamma_\alpha}
$$

(14)

To interpret, equation (14) is the resonant polarization response of nanoparticles determining the long-wavelength plasmon mode of the layer. The parameters of components $\chi_{xx} \neq \chi_{yy}$ providing theoretical reflectance anisotropy spectra (1), (10) are derived from equation (12) as follows

$$
\omega_\alpha = \omega_\alpha^{(0)} \left[ 1 - \frac{a_\alpha a_{\alpha,\alpha}}{3A_{\alpha}^3} \varepsilon^{(\alpha)} N^{(\alpha)} \left( S_{\alpha}^{(d)} + \text{Re} \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} S_{\alpha}^{(i)}(h) \right) \right]^{1/2}
$$

(15)
\[ \Gamma_\alpha = \gamma + \frac{a_x a_y a_z}{3A_\alpha^2} \frac{\omega_\alpha^{(0)}}{\epsilon_\alpha^{(a)}} N(\alpha) S(\alpha) \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2}, \]

(16)

\[ \Omega_\alpha^2 = \frac{\omega_\alpha}{c A_\alpha A_\gamma} \frac{a_x a_y a_z}{3} \left( \frac{\omega_\alpha^{(0)}}{\epsilon_\alpha^{(a)}} \right)^2 \frac{\epsilon_1}{\epsilon_\alpha^{(a)} N(\alpha)}. \]

(17)

In the above model, the anisotropy \( \omega_\alpha \neq \omega_\gamma \) of frequencies (15) can be attributed to either the particle shape anisotropy \( a_x \neq a_y \) or/and the lattice anisotropy \( A_x \neq A_y \).

Typical theoretical spectra \( \Delta R/R \) for weak and strong anisotropy whose measure is \( |\omega_\alpha - \omega_\gamma|/\Gamma \) are compared in figure 2, the two spectra are seen to be qualitatively different. To verify equations (15) - (17) from experiment, we fit measured spectra \( \Delta R/R \) of In clusters on InAs(001) surface [3] using formula (14) and considering its parameters as fitting ones. The result of such fitting is shown in figure 3, where only the frequencies \( \omega_\alpha \neq \omega_\gamma \) are taken different, and \( \Gamma_\alpha \) and \( \Omega_\alpha \) are the same for polarizations \( x \) and \( y \). The shape of measured (fitted) spectra \( \Delta R/R \) (figure 3) is seen to be similar to the weak-anisotropy theoretical spectrum \( \Delta R/R \) (figure 2a), despite the difference of \( \Gamma \). To conclude, this estimation gives evidence of weak anisotropy responsible for spectra \( \Delta R/R \) measured in [2, 3], whose representative is the spectrum \( \Delta R/R \) in figure 3.

**Figure 3.** Spectrum \( \Delta R/R \) of In nanocluster array on InAs surface (measured in [3], dots), and spectrum (1), (10) fitting the experimental one using function (14), solid line. The plasmon energies \( \hbar \omega_y = 3.40 \text{ eV} \) and \( \hbar \omega_x = 3.52 \text{ eV} \) are shown with arrows. The other parameters of function (14) are \( \hbar \Gamma = 1.17 \text{ eV} \) and \( \hbar \Omega = 0.77 \text{ eV} \) for both polarizations.

4. **Estimation of layer anisotropy**

Given the conclusion that \( |\omega_\alpha - \omega_\gamma| \ll \Gamma \), we introduce the parameters \( \omega_\parallel = (\omega_x + \omega_y)/2 \), \( \Gamma \) and \( \Omega \) of hypothetical optically isotropic layer whose small anisotropic deformation provides the fitting \( \Delta R/R \) spectrum (figure 3). The calculated parameters (15) - (17) depending on the semi-axes ratio \( a_x/a \) for spheroidal particles \( (a_x = a_y = a) \) and square lattice \( (A_x = A_y = A) \) are presented in figure 4.

Bearing in mind a small splitting \( \Delta \omega_\parallel = \omega_x - \omega_y \), we consider spectra \( \Delta R/R \) (figure 3) as anisotropy-conditioned deviation from \( \Delta R/R = 0 \) corresponding to isotropic layer model with plasmon frequency \( \omega_\parallel \). For anisotropic layer of ellipsoidal particles with \( a_x, a_y = A \pm \Delta A/2 \) in a square lattice (I), or the rectangular lattice \( A_{x,y} = A \pm \Delta A/2 \) occupied by spheroids (II), the frequencies \( \omega_\alpha(a_x, A_\alpha) \) from equation (15) are expanded near \( a \) and \( A \) up to linear terms in \( \Delta a \) and \( \Delta A \) as

\[ \frac{\omega_x - \omega_y}{\omega_\parallel} = C_1 \frac{\Delta a}{a} + C_\parallel \frac{\Delta A}{A}. \]

(18)
Measured the relative difference \( 2(\omega_x - \omega_y)/(\omega_x + \omega_y) \), the coefficients \( C_1 \) and \( C_\parallel \) allow to estimate the necessary deformations \( \Delta a/a \) of nanoparticles or \( \Delta A/A \) of lattice, respectively [5].

![Figure 4](image)

**Figure 4.** (a) Plasmon frequencies calculated from (15) for a single spheroid (1), for a single spheroid with its image at \( h/a_z = 3 \) (2), \( h/a_z = 2 \) (2') and \( h/a_z = 1.1 \) (2''), and for a layer of spheroids affected by dipoles and their images at \( h/a_z = 3 \) (3). (b) Decay rate (16) and (c) oscillator strength (17) of plasmons in the layer of spheroids. The parameters are shown depending on semi-axes ratio \( a_z/a \), the condition \( R_a < 1 \) is met for thick pieces of curves in (a–c). The theoretical values marked by circles at \( a_z/a \approx 0.2 \) (\( a_z = 4 \) nm) are very close to fitted ones at \( a = 20 \) nm and \( A = 50 \) nm.

With the above parameters of isotropic model, the anisotropy coefficients \( C_1 \approx 1.12 \) and \( C_\parallel \approx -0.28 \) are estimated. According to equation (18), the observed frequency splitting \( \Delta \omega_\parallel/\omega_\parallel = 0.12/3.45 \) could correspond to the deformation of spheroids \( a_y/a_z \approx 3.1\% \) at \( \Delta A = 0 \), or deformation of lattice \( A_y/A_z \approx -12.6\% \) at \( \Delta a = 0 \). Then, the splitting \( \Delta \omega_\parallel > 0 \) could indicate that the particles are flattened and/or the lattice is strained along the \( x \)-axis.

5. **Conclusion**

We have developed a theory of reflectance anisotropy spectra caused by long-wavelength plasmon modes excited in metal nanoparticle layer under the normal incidence of light. The anisotropic plasmons are shown to be responsible for appearance of the resonant reflectance anisotropy spectra which are absent for isotropic layers of nanoparticles. Particularly, within the proposed model the characteristic reflectance anisotropy spectra of indium nanoclusters on InAs surface are interpreted and fitted to estimate the anisotropy of nanoparticle array under study.

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