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1999 J. Phys.: Condens. Matter 11 2211

(http://iopscience.iop.org/0953-8984/11/10/008)

J. Phys.: Condens. Matter **11** (1999) 2211–2222. Printed in the UK PII: S0953-8984(99)95911-8

Ellipsometric study of optical properties of liquid Ga nanoparticles

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Received 13 July 1998

Abstract. The investigation of the optical properties of liquid Ga nanoparticles embedded in a dielectric matrix by means of spectroscopic ellipsometry is reported. The particles, which have the shape of truncated spheres and a radius which is varied in a controlled way between 5 and 16 nm, are grown by the evaporation–condensation technique. The results are discussed in terms of the current effective medium models and give new information on the distribution of the particles in the matrix as well as on their optical properties. A resonance peak due to the plasmon–polariton electron excitations in the particles is observed in the imaginary part of the effective dielectric function of the layer. Its position shifts to higher photon energies and the half width of the resonance increases with the decrease of the particle size. The dielectric function of the particles is parametrized using the Drude dispersion equation. The obtained electron damping parameter increases with the decrease of the particle size in accordance with the predictions of the size theories of the optical properties of small particles.

1. Introduction

Properties of small metal and semiconductor particles and clusters have been a subject of high interest during recent years both for theoretical and experimental research as well as for technological applications. In particular, optical properties of nanometre size metal particles in island films or embedded in a dielectric matrix have been extensively studied [1]. The most pronounced feature in the optical spectra of these systems is the resonance absorption, caused by the excitation of collective oscillations of the conduction electrons gas in the particles. The position and width of the resonance peak depend on the shape and size of the particles, their optical constants and the interaction between them as well as on the host dielectric matrix. On the other hand, the optical constants of the small particles are modified with respect to those of the bulk material due to classical size and quantum size effects. Thus, for the determination of optical constants of particles from transmission, reflection or ellipsometric measurements, we need an appropriate theoretical model, that accounts for these factors.

Most of the experimental results on optical properties of metal nanoparticles can be interpreted in the framework of the classical electromagnetic theories using a size dependent optical dielectric function of particles. The Mie theory gives the optical extinction coefficient and the surface plasmon–polariton modes of small absorbing spheres [2], while the effective

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0953-8984/99/102211+12$19.50

medium theories give an effective dielectric function of the granular media, consisting of particles embedded in a homogeneous matrix ([1, 3–9] and references therein). The Maxwell–Garnett effective medium theory, developed for a three-dimensional distribution of spherical particles, leads to an isotropic effective dielectric constant, while the theory of Yamaguchi [6], developed for particles distributed on a surface, leads to an anisotropic dielectric function. Both models have been extensively used in the analysis of the experimental data from optical transmission or/and reflection ([1, 3–5, 9–13] and references therein) and spectroscopic ellipsometry measurements [14–16] on discontinuous metallic thin films. Although the Maxwell–Garnett theory in some cases [4] could explain the experimental data, it was found that the Yamaguchi theory gives a more adequate description of the optical properties of two-dimensional granular metallic systems [13–15]. A number of classical [1, 17, 18] and quantum mechanical [1, 19–21] theories have been developed to predict the size effect on the optical dielectric function of small metal particles and to explain the observed broadening and shift of the absorption resonance peak when decreasing the particle size.

In the present paper, the spectroscopic ellipsometry measurements are used to study the size dependence of the optical constants of nanometre size liquid Ga particles, embedded in an SiO_x dielectric matrix. The effective medium formalism and the Drude dispersion equation are employed in the analysis of experimental data. The results obtained using the three-dimensional isotropic Maxwell–Garnett and the two-dimensional anisotropic Yamaguchi models are presented and compared.

2. Experiment

The particles were grown by evaporation–condensation of high purity gallium on a dielectric substrate in ultrahigh vacuum. The details of the growth technique are given in [22]. This technique allows us to obtain nanoparticles with a relatively low size dispersion ($\leqslant$20%) and regular shape, which is that of a truncated sphere. The volume of the truncated spheres is more than 80% of that of ideally perfect spheres with the same radius. The samples were prepared as follows. First, a 5 nm thin film of SiO_x was evaporated on the Al_2O_3 substrate and then Ga was deposited. Metal particles were formed in the liquid state on the sample surface by a self-organization process due to the partial wetting character of Ga with respect to SiO_x. Then the substrate temperature was lowered until they are solidified and the samples were covered by an additional layer of SiO_x with an equivalent mass thickness of 10 nm, that preserves the particle shape and protects them from chemical reactions due to the air contact.

The melting point of Ga in nanoparticles is considerably lowered with respect to the bulk material and they are liquid at the room temperature [23].

The ellipsometric measurements were performed on four samples with equivalent mass thickness of the deposited Ga layer of 2, 3, 4.5 and 7 nm, labelled as Ga20, Ga30, Ga45 and Ga70 hereafter. The equivalent mass thickness d_m is defined as the thickness of the layer that would be formed if the evaporated material were uniformly distributed on the surface. The corresponding values of the mean radius of the particles, measured by TEM [24], and the volume fraction Q_v of the Ga in the SiO_x layer are given in table 1.

Ellipsometry is an optical method that measures the change in the polarization state of a polarized light after reflection from the sample surface, defined as the complex ratio ρ of the reflection coefficients of the parallel (r_p) and perpendicular (r_s) polarization of light. The quantities, obtained from an ellipsometric experiment are the values of the polarization angles ψ and Δ, determined from the equation:

$$\rho = \frac{r_p}{r_s} = \tan\psi\, e^{i\Delta}.$$

Table 1. The nominal mass thickness d_m, radius R and volume fraction Q_v of Ga particles for different samples.

Sample	d_m [nm]	R [nm]	Q_v
Ga20	2	5	0.118
Ga30	3	7	0.167
Ga45	4.5	11	0.231
Ga70	7	16	0.318

The measurements were performed with a spectroscopic ellipsometer Sopra model MOSS ES4G with an rotating polarizer. Ellipsometric functions $\tan\Psi$ and $\cos\Delta$ were obtained in the interval of photon energies between 1.5 and 5 eV with a step of 0.02 eV for two angles of incidence: 60 and 65°. The spectral resolution was better then 4 meV over the whole spectral region.

3. Data analysis

3.1. Effective medium formalism

According to the effective medium theories, if the particle size is small compared with the probe wavelength, the particulate medium is optically equivalent to a homogeneous material characterized by a frequency dependent effective dielectric function, that is determined by the optical dielectric functions of the metal and the dielectric matrix as well as by the shape and the geometrical distribution of the metal particles and the interaction between them.

The complex effective dielectric function of the corresponding equivalent plane-parallel film is generally anisotropic and in the Maxwell–Garnett type effective medium theories is given by the expressions [6]:

$$\varepsilon_{\parallel} - \varepsilon_m = \alpha_{\parallel} Q \tag{1}$$

$$\frac{1}{\varepsilon_m} - \frac{1}{\varepsilon_{\perp}} = \frac{\alpha_{\perp} Q}{\varepsilon_m^2} \tag{2}$$

where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the complex components of the effective dielectric tensor in the planes parallel and perpendicular to the film plane, $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the corresponding polarizabilities of the individual particles and ε_m is the complex dielectric constant of the matrix. The filling factor Q of the metal in the film is usually expressed by the ratio d_m/d_{opt}, where d_{opt} is the thickness of the optically equivalent film. For two-dimensional particle distributions, the parameter Q depends on the definition of the effective film thickness, and, as it is pointed out in [7], its value should be interpreted as a parameter related to the surface distribution and to the surface coverage of the particles rather then the volume fraction of the particles in the film.

The polarizability $\alpha_{\parallel,\perp}$ is given by [9]:

$$\alpha_{\parallel,\perp} = \frac{\varepsilon_m}{F_{\parallel,\perp} + \varepsilon_m/(\varepsilon_p - \varepsilon_m)}. \tag{3}$$

Here $F_{\parallel,\perp}$ are effective depolarization factors of the particles, given as

$$F_{\parallel,\perp} = L_{\parallel,\perp} + \beta_{\parallel,\perp} \tag{4}$$

where $L_{\parallel,\perp}$ is the geometric depolarizing factor of the particle, depending on its shape, ε_p is the particle complex dielectric function and $\beta_{\parallel,\perp}$ is a term which depends on the interaction between particles.

In the case of the three-dimensional distribution of spherical inclusions ($L_{\|} = L_{\perp} = 1/3$) and Lorentz–Lorenz interaction, the effective depolarization factors $F_{\|,\perp}$ are given as:

$$F_{\|} = 1/3 - Q/3 \tag{5}$$

$$F_{\perp} = 1/3 + 2Q/3. \tag{6}$$

Then the equations (1) and (2) are equivalent and lead to the original Maxwell–Garnett theory where $\varepsilon_{\|} = \varepsilon_{\perp}$ and the effective medium is isotropic.

In the effective medium theory of Yamaguchi [6], developed for the case of two-dimensional distributions of ellipsoidal particles on a surface between two semi-infinite media, assuming a static-field dipole–dipole interaction between them, the polarizability is given by:

$$\alpha_{\|,\perp} = \frac{2\varepsilon_m\varepsilon_s}{\varepsilon_m + \varepsilon_s}\frac{1}{F_{\|,\perp} + \varepsilon_m/(\varepsilon_p - \varepsilon_m)} \tag{7}$$

where ε_s is the substrate dielectric constant and the effective depolarization factors $F_{\|,\perp}$ are

$$F_{\|} = L_{\|} + \frac{\gamma^2}{24\eta^3}\frac{\varepsilon_m - \varepsilon_s}{\varepsilon_m + \varepsilon_s} - \frac{\pi^2}{24}\frac{2\varepsilon_m}{\varepsilon_m + \varepsilon_s}\frac{d_m}{a} \tag{8}$$

$$F_{\perp} = L_{\perp} + \frac{\gamma^2}{12\eta^3}\frac{\varepsilon_m - \varepsilon_s}{\varepsilon_m + \varepsilon_s} + \frac{\pi^2}{12}\frac{2\varepsilon_s}{\varepsilon_m + \varepsilon_s}\frac{d_m}{a}. \tag{9}$$

Here γ is the axial ratio of a particle with the shape of a rotational ellipsoid, η is the distance between the point-dipole moment of a particle and its mirror image in the substrate, divided by the particle height, and a is the mean distance between particles.

In this and in other two-dimensional theories [6–9, 25, 26], the effective medium is anisotropic even if the particles have spherical shape due to the different interaction terms for the components of the electric field parallel and perpendicular to the film plane.

3.2. Resonance plasma optical absorption

The Maxwell–Garnett type theories predict resonance peaks in the absorption spectrum of a metal–dielectric composite layer, resulting from the collective excitations of the conduction electrons in the metal particles.

From equations (1)–(3), (7) it follows that $\mathrm{Im}(\varepsilon_{\|})$ and $\mathrm{Im}(l/\varepsilon_{\perp})$ have peaks at frequencies where the denominators of the corresponding polarizabilities $\alpha_{\|}$ and $\alpha_{\perp}$ have their minimum. When the dielectric constant of the metal is given by the free-electron Drude dispersion equation:

$$\varepsilon_p = 1 - \frac{\omega_p^2}{\omega(\omega - \mathrm{i}\Gamma)} \tag{10}$$

(where ω_p is the bulk plasma frequency and Γ is the damping parameter) and $\omega^2 \gg \Gamma^2$, the shape of the resonance peaks is Lorentzian [9, 11, 12]. Then the resonance frequencies $\omega_{R\,\|}$ and $\omega_{R\,\perp}$ are given by

$$\omega_{R\,\|,\perp} = \omega_p\left(\frac{F_{\|,\perp}}{\varepsilon_m - (\varepsilon_m - 1)F_{\|,\perp}}\right)^{1/2} \tag{11}$$

and the half width of the resonance curve is equal to the damping parameter Γ of the metal.

Thus, in the absorption spectrum of p-polarized light at high angles of incidence, two peaks could be observed [10]. One of them, corresponding to the collective electron excitations parallel to the film surface, is at lower photon energies and is present also in the absorption spectrum of s-polarized light. The second absorption peak—due to the excitations perpendicular to the film surface—is located at higher photon energies and for our samples is above the upper limit of the measured ellipsometric spectra.

3.3. Optical model

To obtain information about the optical properties of the metal particles from ellipsometric measurements, we need an optical model that gives us the possibility to calculate the reflection coefficients r_p and r_s as a function of the wavelength and the angle of incidence of the light. Then, the quantities $\tan\Psi$ and $\cos\Delta$ can be derived and the values of the parameters that describe the optical model are obtained from the experimental ellipsometric data by a best-fit numerical procedure.

In the framework of the effective medium formalism, the effective dielectric constant of a film of particles, embedded in a dielectric matrix, depends on the following parameters: the dielectric constant of the matrix, the dielectric constant of the particles, the filling factor Q of the metal in the film, and—in the theory of Yamaguchi—also on the dielectric constant of the substrate and on the geometrical parameters a, γ and η in equations (8) and (9). As Ga particles are nearly spherical, the axial ratio γ is fixed equal to 1. The values of the parameter η are obtained from the film geometry.

The optical constants of the SiO_x matrix are determined by the stoichiometric parameter x, as well as by the density of the material, resulting from the evaporating conditions. As these parameters are not exactly known, the tetrahedron model [27] is used to calculate the dielectric function of SiO_x. This model represents the SiO_x material as a mixture of Si-based tetrahedra, whose dielectric function is obtained through scaling of the dielectric function of the amorphous Si [27]. The resulting dielectric function is calculated by the Bruggeman effective medium theory, assuming also the presence of voids. Thus, the dielectric function of the SiO_x is characterized by two parameters—the stoichiometric parameter x and the volume fraction Q_{void} of the voids in the material.

The optical constants of the metal are obtained from the Drude equation (10) and are determined by two parameters—the bulk plasma frequency ω_p and the damping parameter Γ.

Therefore, the model describing the optical properties of the granular layer depends on the following parameters: the bulk plasma frequency ω_p and the damping parameter Γ of the Ga, the stoichiometric parameter x of the SiO_x matrix and the volume fraction Q_{void} of voids in the material, the mass thickness d_m of the particle metal layer and the thickness of the effective layer d_{opt}. In the theory of Yamaguchi there is one additional parameter—mean interparticle distance a. The dielectric constants of the substrate are taken from [28].

When the Maxwell–Garnett effective medium theory is used, the value of the effective dielectric constant $\varepsilon_\parallel$ as a function of the photon energy is calculated using equations (1)–(6). When the Yamaguchi theory is used, the values of the two components $\varepsilon_\parallel$ and $\varepsilon_\perp$ of the effective dielectric tensor are obtained from the equations (1), (2) and (7), (9) and the ellipsometric functions $\tan\Psi$ and $\cos\Delta$ are calculated using the expressions for the reflection coefficients from an isotropic substrate with a surface anisotropic film whose optical axis is perpendicular to the film plane [6].

4. Results and discussion

The calculations showed that the two models—isotropic Maxwell–Garnett and the anisotropic Yamaguchi model—could represent adequately the experimental data. The quality of the fit is comparable for the two models for all samples. An example of a fit is shown in figure 1(a), (b) where the experimental and best-fit $\tan\Psi$ and $\cos\Delta$ ellipsometric spectra calculated using the Maxwell–Garnett model are drawn for the sample Ga30 at the angle of incidence 65°. The results from the best-fit procedure are given in table 2 for the Maxwell–Garnett model and in table 3 for the Yamaguchi model.

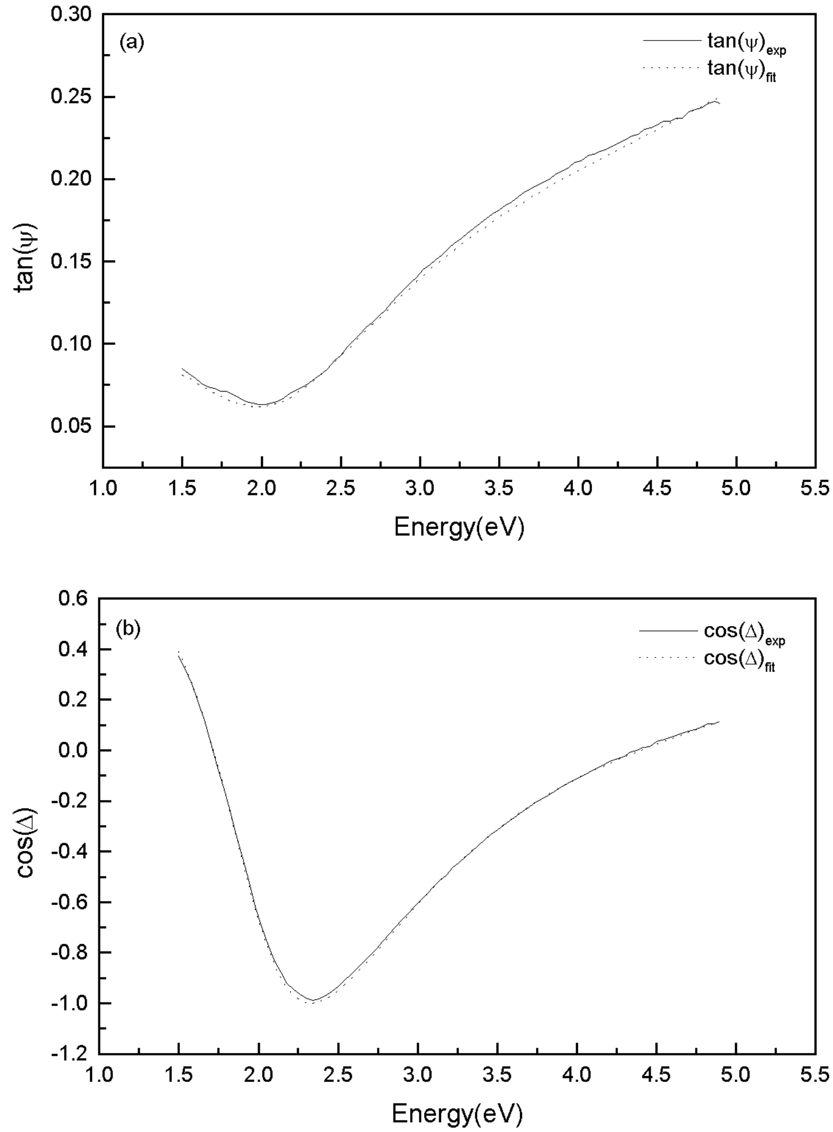

Figure 1. Experimental (solid line) and best-fit (dashed line) ellipsometric spectra for sample Ga30 at angle of incidence 65°: (a) tan Ψ (b) cos Δ.

Table 2. Best-fit values of the parameters of the Maxwell–Garnett model (see the text for parameter description).

Sample	ω_p (eV)	Γ (eV)	x	Q_{void}	d_m (nm)	d_{opt} (nm)	Q	Q_s
Ga20	10.28	3.28	0.99	0.25	2.3	11	0.21	0.26
Ga30	10.65	2.83	0.61	0.48	2.8	7.5	0.37	0.34
Ga45	10.84	2.31	0.79	0.38	3.5	7.7	0.45	0.43
Ga70	10.53	2.15	0.80	0.45	4.9	9.6	0.51	0.55

Table 3. Best-fit values of the parameters of the Yamaguchi model (see the text for parameter description).

Sample	ω_p (eV)	Γ (eV)	x	Q_{void}	d_m (nm)	d_{opt} (nm)	a (nm)	Q
Ga20	10.43	2.94	1 (fixed)	0.46	1.7	6.9	3.6	0.25
Ga30	10.12	2.65	1 (fixed)	0.45	2.6	7.3	5.5	0.36
Ga45	9.76	2.22	1 (fixed)	0.39	3.8	7.1	9.1	0.53
Ga70	9.28	2.08	1 (fixed)	0.44	5.3	8.1	11.9	0.65

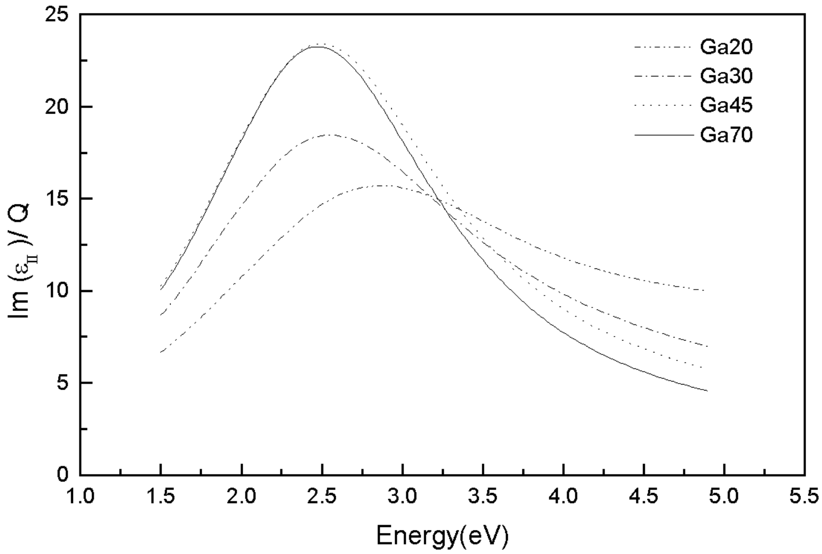

Figure 2. Calculated $\mathrm{Im}(\varepsilon_{\|})/Q$ functions using the Maxwell–Garnett model.

Ellipsometry is a method that is sensitive to the anisotropy in the film. When the anisotropy is high, the inversion of ellipsometric data, assuming the film to be isotropic, does not converge [30]. On the other hand, if the film is very thin and only weakly anisotropic, the assumption of isotropy could give also an explanation of the experimental data [14, 15]. It has been pointed out that in the measurements of anisotropic layers and crystals, the ellipsometric response is determined mainly by the value of the component of the dielectric tensor that is parallel to the sample surface and to the plane of incidence [31, 32]. Thus, it could be expected that the optical response of the samples is determined mainly by the $\varepsilon_{\|}$ and by the resonance absorption due to the excitations parallel to the film surface.

The calculated value of the imaginary part of $\varepsilon_{\|}$ divided by $Q(Q = d_m/d_{opt})$ is given in figure 2 for the Maxwell–Garnett and in figure 3 for the Yamaguchi model. It is seen that both models predict a similar behaviour of the resonance curves with a characteristic shift [1] of the resonance frequency to higher energies when decreasing the mass thickness of the particle layer (and the diameter of the particles) and broadening of the resonance peak. In both theories the width of the peak in $\mathrm{Im}(\varepsilon_{\|})$ is determined mainly from the damping parameter Γ and is nearly independent of the other fitting parameters, that determine the position and the height of the resonance curve.

Factors that could contribute to the broadening of the resonance peak in $\mathrm{Im}(\varepsilon_{\|})$ are: the increase of the collision frequency of the conduction electrons in the Ga particles, statistical

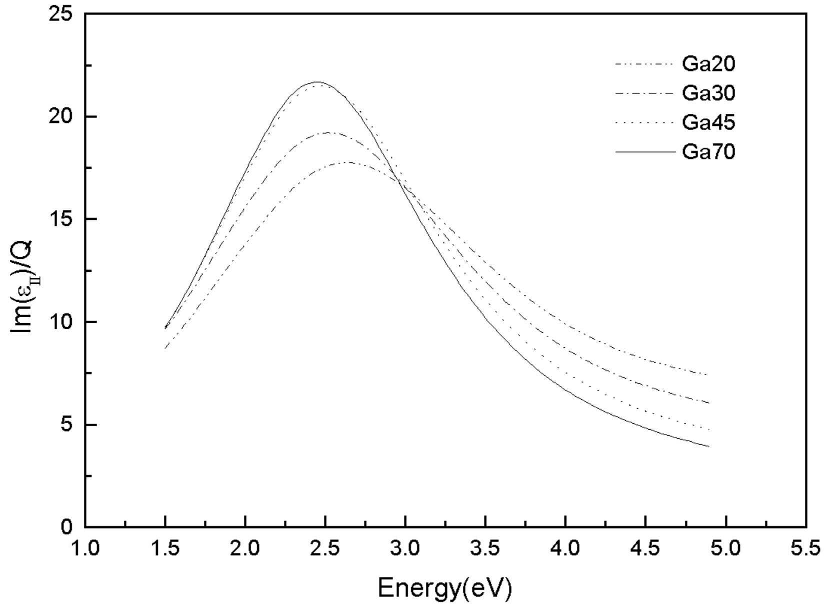

Figure 3. Calculated $\mathrm{Im}(\varepsilon_\parallel)/Q$ functions using the Yamaguchi model.

distribution of the depolarizing factor due to a variation in the shape of the particles and retarded dipole–dipole interaction between particles [33]. In our samples Ga particles are nearly spherical [22] and consequently the shape variation does not affect considerably the width of the resonance. The retarded dipole–dipole interaction could have a significant contribution if the interparticle distance is comparable with the wavelength of light and should increase with the increase the particle size. Therefore, for small spherical particles, the main factor that determines the width of the absorption peak is the collision frequency of the conduction electrons in the Ga particles.

According to the classical theory of the size effect on the dielectric constant of the small metal particles, a decrease of the diameter of the particles does not change the plasma frequency ω_p of the conducting electrons, but leads to the increase of the damping parameter Γ due to an additional scattering of the electrons from the surface of the particles. Such effect takes place if the mean free path of the electrons is comparable with the radius of the particle. The theoretically predicted dependence of the damping parameter Γ on the particle radius R is [34]:

$$\Gamma = \Gamma_{bulk} + A\frac{v_F}{R} \tag{12}$$

where v_F is the Fermi velocity, Γ_{bulk} is the damping parameter in the bulk material and A is a constant that includes details of the scattering processes. For isotropic electron scattering $A = 1$ [34]. The same functional dependence of Γ on R was also obtained in quantum mechanical theories.

The experimentally obtained values of Γ fit well the function (12) as shown in figures 4 and 5. Obtained values of the Fermi velocity of the electrons are $v_F = 2.05 \times 10^6$ m s^{-1} and $v_F = 1.57 \times 10^6$ m s^{-1} for the Maxwell–Garnett and the Yamaguchi models correspondingly, when $A = 1$ is assumed. The obtained value of v_F from the Yamaguchi model is close to the value of 1.64×10^6 m s^{-1} given in [35]. The Maxwell–Garnett model gives higher values for the damping parameter Γ. The difference decreases with the increase of the particle diameter.

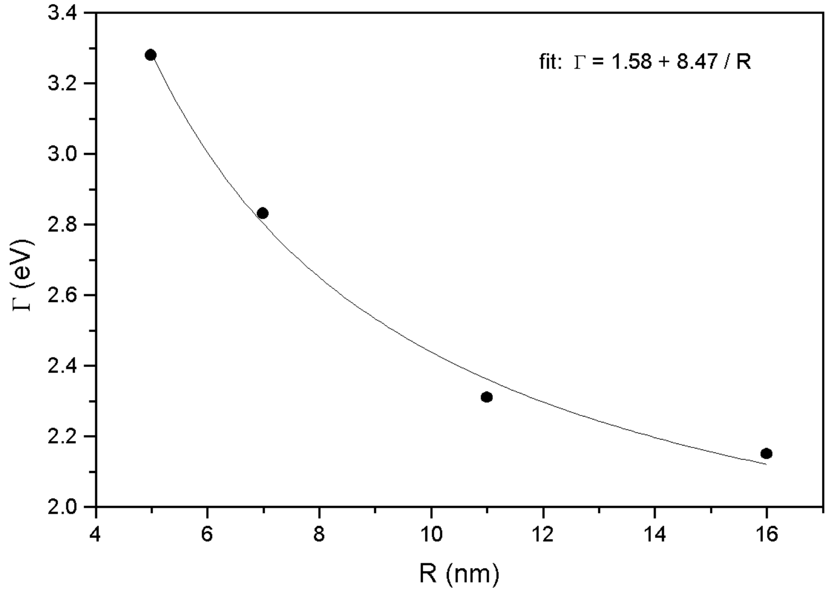

Figure 4. Obtained values (symbols) of the electron damping parameter Γ as a function of the particle radius using the Maxwell–Garnett model and best fit to equation (12) (solid line).

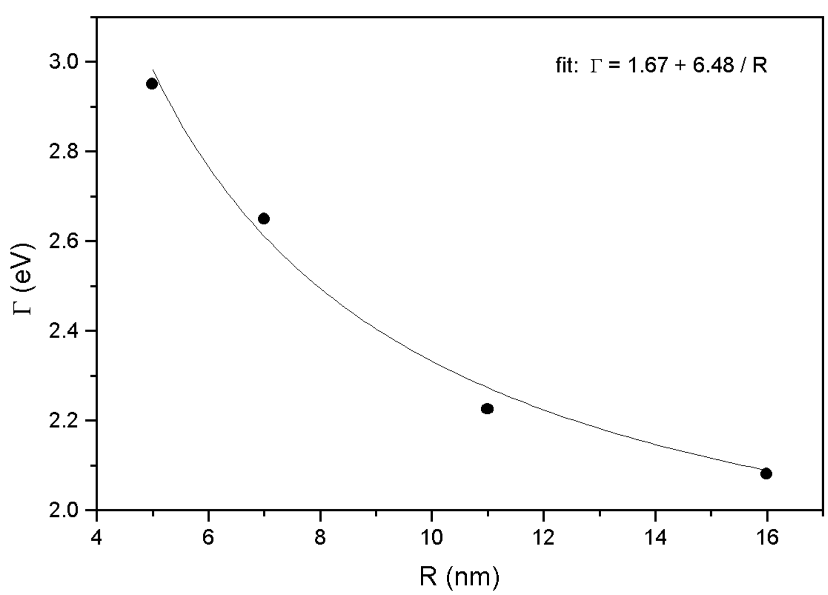

Figure 5. Obtained values (symbols) of the electron damping parameter Γ as a function of the particle radius using the Yamaguchi model and best fit to equation (12) (solid line).

Both models give nearly the same value for the bulk damping parameter. The discrepancy could be attributed to the fact that Maxwell–Garnett theory does not account for the anisotropy in the film caused by the two-dimensional distribution of the particles, that is greater for the smaller particles [29].

As an equally good fit was obtained using the isotropic Maxwell–Garnett and the anisotropic Yamaguchi effective medium theories, it could be concluded that the ellipsometric response is determined mainly by the parallel component $\varepsilon_\parallel$ of the effective dielectric tensor. The equations that give the value of $\varepsilon_\parallel$ have the same form in both theories, the only difference being the expression for the effective depolarization factor $F_\parallel$. The Maxwell–Garnett theory does not account for the effect of the substrate and for the dipole–dipole interaction between particles, that is included in the theory of Yamaguchi by using the concept of mirror dipoles. In our case, the effect of the Al_2O_3 substrate is not high because the particles are grown on a thin layer of SiO_x and the refractive index of the embedding matrix is not very different from that of the substrate.

The obtained value for the Ga plasma frequency ω_p is around 10 eV for all samples, although an error of the order of 1 eV should be taken into account due to uncertainties in the knowledge of the dielectric constant of the SiO_x matrix. This value is lower than the value of ≈14 eV found in the literature for the bulk liquid Ga [37, 38]. The discrepancy might be related to some peculiar aspects of the liquid state of the nanoparticles, which will be the object of further investigations.

The parameter Q could be interpreted as related to the surface coverage of the particles as follows. The surface coverage Q_s is given by the expression:

$$Q_s = \frac{\pi R^2 N}{S} \tag{13}$$

and, for our samples, the volume fraction Q_v of the particles in the SiO_x layer (given in table 1) could be expressed as:

$$Q_v = \frac{\frac{4}{3}\pi R^3 N}{dS} \tag{14}$$

where R is the radius of the particles, N their number, S the sample surface and d is the physical thickness of the layer, that is equal to the sum of the particle diameter and the thickness of the layer of SiO_x, deposited on the substrate before the formation of the particles. From (13) and (14) the relation between Q_v and Q_s is obtained:

$$Q_s = \frac{3}{4}\frac{d}{R}Q_v. \tag{15}$$

The obtained values of Q using the effective medium theories (given in tables 2 and 3) are in agreement with calculated values of the surface coverage Q_s (given in table 2). A TEM investigation [23] of the Sn particles grown by the same technique has shown that the surface coverage increases initially with the increase of the metal mass thickness from about 25% and exhibits a saturation around 55%.

The obtained values of Q and their dependence on the particle mass thickness are similar to those obtained in other optical studies of metal island films [4, 14, 15, 29, 36].

5. Conclusions

The optical properties of liquid Ga nanoparticles in the SiO_x dielectric matrix are studied by spectroscopic ellipsometry as a function of the particle size. The Maxwell–Garnett and the Yamaguchi effective medium theories are used to calculate the effective dielectric constant of the layer with particles and to construct the optical model for the samples used for the fitting the experimental data. It was found that although the Maxwell–Garnett theory does not account for the anisotropy in the film, resulting from the particle interaction, both models give similar results and the difference decreases with increasing particle size. This result could be explained by the fact that the ellipsometric response is determined mainly by the component of the effective dielectric tensor parallel to the sample surface.

A resonance peak due to the collective excitations of the conduction electrons in the particles is observed in the imaginary part of the obtained parallel component of the effective dielectric function of the layer. The position of the peak shifts to higher photon energies and the half width of the resonance increases with decreasing particle size.

The dielectric function of the liquid Ga particles can be characterized by the Drude free-electron dispersion equation with a size dependent damping parameter that increases with decreasing particle size. These size effects are explained by the prediction of the classical size theory for the optical properties of small particles. The obtained value of the Fermi velocity of the Ga within this model is in accordance with reference data.

Acknowledgments

One of the authors (DT) undertook this work with the support of the ICTP Programme for Training and Research in Italian Laboratories, Trieste, Italy. This work is supported by the Saint-Gobain Company through a fellowship of one of the authors (MP) with Scuola Normale Superiore, Pisa.

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