Nanoparticles and nanocomposites for display applications

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I certify that all material in this thesis which is not my own work has been identified and that no material has previously been submitted and approved for the award of a degree by this or any other University.

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Abstract

The optical response of metallic structures has attracted significant interest for various applications in recent years. Of particular relevance to display applications is the ability to optimize the intensity and wavelength of the radiation which is scattered by the structure. In this thesis, original studies are presented across three main sections which investigate the optical response of a variety of composite structures formed from metal and dielectric elements.

In the first section, the optical response of planar structures comprised of continuous metal and dielectric layers is discussed. An extensive study is conducted into the transmission pass-band characteristics exhibited by these structures, in particular the dependence on parameters such as metal layer thickness, layer spacing and the number of periods.

The second and third sections include examples of structures in which the metallic elements are non-continuous. The simulations required here are considerably more involved, and so an introduction is given to the computational techniques used in subsequent chapters, accompanied with results for a test structure. The structures in the second section include single metallic nanoparticles and particle pairs which exhibit localised surface plasmon resonances (LSPRs). It is also shown that when particles are arranged into periodic arrays, the properties of the LSPR may be significantly modified by long-range and short-range interactions. This has implications both in terms of the line shape of the optical response, and the sensitivity of the optical response to changes in the surrounding refractive index.

The third section includes an investigation into metallic layers which have been perforated with periodic arrangements of holes. These structures have attracted considerable attention in recent years due to the enhanced transmission which is observed when the periodicity of the hole array facilitates grating coupling to surface plasmon-polariton (SPP) modes associated with the metal film. It is shown that these structures also support localised resonances similar to those of metallic nanoparticles. A comparison is made between the LSPRs observed in metallic nanoparticle and nanohole arrays for which the periodicity is non-diffracting for frequencies in the vicinity of LSPRs. In the final part of the thesis the role of LSPRs in facilitating a negative index of refraction in electromagnetic metamaterials having a fishnet-type structure is investigated.

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Figure 6.2: Schematic representations of the dispersion relations are shown for (a) an air - Ag planar interface and (b) an air-Ag shallow monograting. The red lines represent the SPP dispersion curves, and dashed black lines are the diffracted and non-diffracted light lines. It is assumed that the dielectric function of the Ag may be described using a Drude model.

Figure 6.3: The simulated zeroth-order transmittance spectrum is shown for a 200 nm thick Ag film perforated with an array of cylindrical holes with diameter 150 nm and periodicity 600 nm. The sample is illuminated at normal incidence in air, and is situated on a glass ($n_r = 1.52$, $n_i = 0.00$) substrate.

Figure 6.4: The time-averaged electric field distribution is shown for the structure in Figure 6.3. A cross section is taken parallel to the upper metal surface (a) and through the centre if the structure (b). The sample is illuminated at normal incidence with an incident wavelength of 700 nm.

Figure 6.5: The simulated zeroth-order transmittance spectrum is shown for a 200 nm thick Ag film perforated with an array of cylindrical holes with diameter 150 nm and periodicity 900 nm. The sample is illuminated at normal incidence in air, and is situated on a glass ($n_r = 1.52$, $n_i = 0.00$) substrate.

Figure 6.6 *reproduced from reference 11*: The dark field scattering intensity is shown for nanoholes with diameters ranging from 60 nm to 500 nm, fabricated from a 20 nm thick Au film. The samples are fabricated on a glass ($n_r = 1.52$, $n_i = 0.00$) substrate and are illuminated at normal incidence in air.

Figure 6.7: Experimental transmittance spectra are compared against simulated transmittance and absorbance spectra obtained for 8 μm square arrays of 90 nm diameter holes in a (a) 20 nm thick Au film and (b) 90 nm diameter, 20 nm height cylindrical Au particles with periodicity 200 nm, illuminated at normal incidence in air. The dashed gray curve in both (a) and (b) shows the experimental transmittance spectrum obtained from a 20 nm Au film illuminated at normal incidence in air.

Figure 6.8: Field profiles are shown at the absorbance maximum of the hole and particle array structures. The upper profiles show the instantaneous scattered electric field vector for (a) the hole and (b) the particle arrays, taken at the same instant in phase for each structure. The arrows above (a) and (b) indicate the vector of the incident electric field. The centre plots show the time-averaged scattered electric field profiles for (c) the hole and (d) the particle. In (e) and (f), a line plot has been taken through the centre of the

structures along the dashed line shown in (c) and (d), and the time-averaged electric field magnitude is shown as a function of position across the unit cell.

Figure 6.9: Comparison between experimental and simulated transmission spectra for 90 nm diameter hole ((a) and (c)) and particle ((b) and (d)) arrays with periodicity 200, 225 and 250 nm.

Figure 6.10: The experimental (left) and simulated (right) transmittance spectra are shown for hole arrays with periodicity 250 nm and hole diameters ranging from 70 nm to 100 nm. The arrays are on a glass (n_r = 1.52, n_i = 0.00) substrate, and are illuminated at normal incidence in air. The dashed gray curves show the experimental and simulated data for a planar Au film with thickness 20 nm.

Figure 6.11: The simulated transmittance spectra are shown for hole arrays with periodicity 200 nm. The solid black line represents the simulated transmittance for arrays of 70 nm diameter cylindrical holes. The dashed and dash-dot lines represent the simulated transmittance of rectangular holes with dimensions 45 nm × 90 nm illuminated with light having the electric field polarised along the long (dashed) and short (dash-dot) axes. The arrays are on a glass substrate (n_r = 1.52, n_i = 0.00), and are illuminated at normal incidence in air.

Figure 7.1: Simulated transmittance (T) and absorbance (A) spectra at normal incidence for a planar Ag layer (20 nm thickness) perforated with an infinite square array of 60 nm diameter cylindrical holes with periodicity 150 nm (shown in the inset). The surrounding medium has refractive index (n_r = 1.52, n_i = 0.00).

Figure 7.2: Simulated transmittance (T) and absorbance (A) spectrum at normal incidence for a single Ag layer (20 nm thickness) and a multi-layer structure consisting of 5 layers of 20 nm Ag separated by 110 nm (A). The surrounding medium has refractive index n_r = 1.52, n_i = 0.00. The grey line illustrates the resonant frequency for a single layer of 20 nm Ag perforated with holes having diameter 60 nm and periodicity 150 nm. The inset figures (B-E) show the time-averaged electric field magnitude at the resonant frequencies of the FP modes for a cross section taken perpendicular to the stack.

Figure 7.3: Simulated transmittance (T) and absorbance (A) spectra for a planar structure consisting of 5 layers of Ag with thickness 20 nm separated by 110 nm, perforated with an infinite square array of cylindrical holes with 60 nm diameter and 150 nm periodicity. The surrounding medium has refractive index n_r = 1.52, n_i = 0.00. The solid line corresponds to illumination at normal incidence, the dashed and dotted lines correspond to illumination with TE polarized light at angles 23.5° (sin θ = 0.4) and 36.9° (sin θ = 0.6) respectively. The grey line at 545 THz represents the resonant frequency for a single layer of Ag perforated with an identical array of holes (Figure 7.1).

Figure 7.4: Contour plot showing the magnitude of the simulated absorbance as a function of frequency and sin θ (where θ is the incident angle) for TE polarized light illuminating the structure in Figure 7.3.

Figure 7.5: The magnitude of the simulated absorbance is plotted as a function of frequency and spacing between two non-perforated (top) and perforated (bottom) Ag layers with thickness 20 nm. The perforated structure consists of an infinite square array of cylindrical holes with diameter 60 nm and periodicity 150 nm. The results are for normal incidence, with surrounding medium n_r = 1.52, n_i = 0.00. The dashed line

represents the separation of the metal layers in the structures described in Figures 7.2 and 7.3.

Figure 7.6: The simulated transmittance is shown for a structure comprised of 6.5 periods of 20 nm Ag / 120 nm glass (n_r = 1.52, n_i = 0.00), perforated with an infinite square array of cylindrical holes having periodicity 300 nm and diameters ranging from (a) 20 nm to 100 nm and (b) 20 nm to 45 nm. The structure is illuminated at normal incidence in a glass surrounding medium.

Figure 7.7: (a) The simulated transmittance is shown for a structure comprised of 6.5 periods of 20 nm Ag / 120 nm glass, perforated with an array of cylindrical holes having periodicity 200 nm and diameters ranging from 60 nm to 100 nm. The permittivity of the metal is assumed to be $\varepsilon = -32 + 1.8i$ across all wavelengths. (b) The simulated transmittance (T) and absorbance (A) is shown for 60 nm diameter holes. The structures are illuminated at normal incidence in a glass surrounding medium.

Figure 7.8: The simulated transmittance is shown for a 12.5 period structure of 20 nm Ag / 120 nm glass, perforated with an array of square cylindrical holes having periodicity 300 nm and diameters ranging from 40 nm to 100 nm. The structure is illuminated at normal incidence in a glass surrounding medium (n_r = 1.52, n_i = 0.00).

Figure 7.9: The simulated transmittance (T) and absorbance (A) spectra are shown for (a) a single layer of Ag with thickness 20 nm, perforated with an infinite square array of cylindrical holes with periodicity 225 nm and diameter 90 nm, (b) a multilayer structure comprised of 4.5 periods of planar 20 nm Ag / 140 nm glass layers. The structures are illuminated at normal incidence in a glass surrounding medium.

Figure 7.10: Simulated transmittance (T) and absorbance (A) spectrum at normal incidence for a planar structure consisting of 5 layers of Ag with thickness 20 nm separated by 140 nm, perforated with an infinite square array of cylindrical holes with 90 nm diameter and 225 nm periodicity. The structure is illuminated at normal incidence in a glass surrounding medium.

Figure 8.1: A conventional lens having a positive index of refraction (n_1) is used to form an image of a point source. The arrows represent 'ray' directions.

Figure 8.2: The use of a planar isotropic slab having $n_1 = -1 + 0i$ and thickness d for the imaging of a point source. The arrows represent 'ray' directions.

Figure 8.3 *reproduced from 9*: The experimental sample used by Shelby et al. consisted of copper split ring resonators and copper wire strips on circuit board material. The rings and wires are positioned on opposite sides of the board.

Figure 8.4: The magnetic response of a continuous metallic ring (CMR).

Figure 8.5: Split ring resonators exhibit an LC resonance which is associated with the effective capacitance of the dielectric gap and the effective inductance of the loop which defines the ring.

Figure 8.6: An example of a circular pair of split ring resonators (SRRs), with illustrated dimensions corresponding to those in Equation 8.11.

Figure 8.7 *reproduced from reference 4*: Diagram of a 21 layer fishnet structure formed from layers of Ag with thickness 30 nm and MgF_2 with thickness 50 nm. The structure has been milled to produce a square array of rectangular holes with dimensions 565 nm × 265 nm, and periodicity 860 nm (a). Simulated and experimental index of refraction data obtained for the 'fishnet' structure shown in (b).

Figure 8.8: The structural dimensions of a single layer of the fishnet structure which was analysed by Soukoulis et al. [15] is shown (a), this layer stacked to form periodic structure where the layers are separated by t (b). Assuming the incident electric field is polarized in the direction shown, the equivalent electrical circuit model for this arrangement may be simplified to that shown in (c).

Figure 8.9: An illustration of the surface currents which are formed in the slab and neck regions of the fishnet structure in the uppermost layer of the fishnet structure at the frequency of the magnetic resonance ω_m. In a metamaterial, the directions of the surface currents in adjacent layers are aligned anti-parallel.

Figure 8.10: The real (hollow circles) and imaginary (solid circles) components of the effective refractive index obtained using Equation 8.19 are shown for three homogeneous layers with parameters (a) $\varepsilon = 3$, $\mu = 2$ (b) $\varepsilon = -3$, $\mu = 2$ and (c) $\varepsilon = -3$ $\mu = -2$.

Figure 8.11: The real (hollow circles) and imaginary (solid circles) components of the effective refractive index obtained using Equation 8.20 are shown for three homogeneous layers with parameters (a) $\varepsilon = 3$, $\mu = 2$ (b) $\varepsilon = -3$, $\mu = 2$ and (c) $\varepsilon = -3$ $\mu = -2$.

Figure 8.12: The extraction procedure described in section 8.2 was used to determine the effective refractive index from the simulated transmission and reflection coefficients obtained from finite element simulations (a). This is compared with the published data of Zhang et al. [4] (b).

Figure 8.13: The time-averaged electric field distribution is shown at the resonant frequency for a single metallic layer of the fishnet structure in Figure 8.7. The arrows above and alongside the field distributions indicate the polarisation direction of the incident electric field.

Figure 8.14: Simulated transmittance (i) and absorbance (ii) spectra are shown for an infinite array of 90 nm diameter holes in a 20 nm thick Ag film with periodicity 225 nm (A), an infinite array of 90 nm diameter, 20 nm height cylindrical Ag particles with periodicity 225 nm (B) and a 20 nm thick continuous Ag film (C). In all simulations the structures were illuminated at normal incidence in vacuum. The inset of (ii) shows the instantaneous scattered electric field vector across the unit cell of the hole and particle array structures. Both profiles are shown at the same instant in phase for radiation incident with frequency 6.25×10^{14} Hz (λ_{vac} = 480 nm). The arrows above the field distributions indicate the direction of the incident field vector.

Figure 8.15: The simulated absorbance is plotted as a function of frequency and spacing between two layers of hole (i) and particle (ii) arrays. In both structures the Ag layer thickness is 20 nm, and the cylindrical holes/particles with diameter 90 nm are arranged into regular square arrays with periodicity 225 nm. For 20 nm layer spacing (shown by the dashed line) the absorbance of each arrangement is plotted as a function of frequency as an inset figure. In (a-d), the instantaneous scattered electric field vector has been plotted for a cross section perpendicular to the stack at the resonant frequencies labelled A-D in the

greyscales (i) and (ii). The arrows above the field profiles indicate the direction of the incident electric field vector.

Figure 8.16: The instantaneous charge and field distributions are illustrated for two metallic nanoparticles which interact through the overlap of their resonant electromagnetic fields. Plasmon hybridisation can occur in particles separated by distances which are a few 10s of nm in vacuum, resulting in two coupled LSPRs associated with the anti-symmetric (a) and symmetric (b) distribution of charge across the structure.

Figure 8.17: The effective refractive indices are shown as a function of frequency for the five layer stacked hole array (i) and particle array (ii) structures. In the inset, the real and imaginary parts of the effective permittivity ε and permeability μ are shown for the stacked hole array (a,b) and particle array (c,d) structures. The dashed vertical lines in plots (i) and (ii) represent the resonant frequencies of the symmetric (dashed vertical black line) and anti-symmetric (dashed vertical gray line) coupled LSPRs for the equivalent two layer structure studied in Figure 8.15.

Figure A.1: An incident wave $\mathbf{k}_i$ strikes a planar interface between two media with different dielectric properties, giving rise to a reflected wave $\mathbf{k}_r$, and a refracted wave $\mathbf{k}_t$.

Figure A.2: Reflection and refraction of an incident plane wave which is polarised perpendicular to the plane of incidence.

Figure A.3: Reflection and refraction of an incident plane wave which is polarised parallel to the plane of incidence.

Figure A.4: The transmission and reflection of light in an arrangement formed from *N* isotropic layers.

Figure D.1: Labelled photographs of the external connections of the thermal evaporation system are shown (a) and (b). Other types of evaporation chambers may be formed using glass bell-jars (c).

Figure D.2: Labelled photographs of the internal connections of the thermal evaporation system.

Figure D.3: Photographs of two samples (20 nm Ag – 120 nm SiOx – 20 nm Ag) viewed in reflection at normal incidence are shown. In (a) the vector from the source to the substrate is parallel to the surface normal of the substrate. In (b), the sample has been aligned at an angle of 60˚ and is rotated at 120 revolutions per minute.