Optical Properties of Metallic Systems

A Thesis presented for the degree of
Doctor of Philosophy
by

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To my parents

Certificate of Originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of the requirements for a degree, except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in this thesis.

A part of section 2.3 contains data submitted as part of the requirements of a previous degree, and is acknowledged in the text. The remainder of chapter 2 as well as chapters 3 and 4 are based on articles written by me under the guidance of my supervisors, with the notable exception of sections 3.1 and 3.2 which are based on an article largely prepared by Matthew Arnold, of which I am a co-author. Chapter 5 presents my understanding of the background theory used in later chapters. Where the derivation of a particular author has been followed closely it is noted in the text. Chapters 6 and 7 are also based on articles written by me under the guidance of my supervisors.

Production Note:
Signature removed prior to publication.

Martin Giles Blaber

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Contributing Publications

Publications that contributed to this work. (In order of publication)

(P1) M G Blaber, N Harris, M J Ford, and M B Cortie, Proceedings of the IEEE: International Conference on Nanoscience and Nanotechnology, page 561 (2006).
"*Optimisation of absorption efficiency for varying dielectric spherical nanoparticles*"

(P2) M G Blaber, M D Arnold, N Harris, M J Ford, and M B Cortie, Physica B **394**, 184 (2007).
"*Plasmon absorption in nanospheres: A comparison of sodium, potassium, aluminium, silver and gold*"

(P3) M G Blaber, M D Arnold and M J Ford, Journal of Physical Chemistry C **113**, 3041 (2009).
"*Search for the Ideal Plasmonics Nanoshell: The Effects of Surface Scattering and Alternatives to Gold and Silver*"

(P4) M G Blaber, M D Arnold and M J Ford, Journal of Physics: Condensed Matter, **21**, 144211 (2009).
"*Optical properties of intermetallic compounds from first principles: a search for the ideal plasmonic material*"

(P5) M D Arnold and M G Blaber, Optics Express, **17**, 3835 (2009).
"*Optical performance and metallic absorption in nanoplasmonic systems*"

(P6) M G Blaber, M D Arnold and M J Ford, Journal of Physics: Condensed Matter, **22**, 095501 (2010).
"*Designing materials for plasmonic systems: the alkali-noble intermetallics*"

(P7) M G Blaber, M D Arnold and M J Ford, Journal of Physics: Condensed Matter, **22**, 143201 (2010).
"*A review of the optical properties of alloys and intermetallics for plasmonics*"

Non-Contributing Publications

Publications which do not feature in this work. (In order of publication)

- J A Edgar, H M Zareie, M G Blaber, A Dowd, M B Cortie, Proceedings of the IEEE: International Conference on Nanoscience and Nanotechnology, page 32 (2008).
  "*Synthesis of hollow gold nanoparticles and rings using silver templates*"

- N Harris, M D Arnold, M G Blaber, M J Ford, Journal of Physical Chemistry C **113**, 2784 (2009).
  "*Plasmonic Resonances of Closely Coupled Gold Nanosphere Chains*"

- M G Blaber, M J Ford and M B Cortie in "Gold: Science and Applications", edited by C Corti and R Holliday, CRC Press (2010).
  "**Chapter 2**: *The Physics and Optical Properties of Gold*"

- M D Arnold, M G Blaber, M J Ford, N Harris, Optics Express **18**, 7528 (2010).
  "*Universal scaling of local plasmons in chains of metal spheres*"

Oral Presentations

(Most recent first)

- M. G. Blaber, M. D. Arnold, M. J. Ford
  Designing Materials for Nanoplasmonics
  SMONP 2009 (2009, Melbourne, Australia)

- M. G. Blaber, M. D. Arnold, M. J. Ford
  Alkali-Noble intermetallics as replacements for gold and silver
  PECS 8 (2009, Sydney, Australia)

- M. G. Blaber, M. D. Arnold, M. J. Ford
  Can Metal Alloys Advance Plasmonics?
  AIPC 2008 (2008, Adelaide, Australia)

- M. G. Blaber, M. D. Arnold, M. J. Ford
  Low Loss Optical Alloys for Plasmonics
  ICONN 2008 (2008, Melbourne, Australia)

- M. G. Blaber, M. D. Arnold, N. Harris, M. J. Ford, M. B. Cortie
  From Absorption Efficiency to Superlensing: Potassium
  AMN3 (2007, Wellington, New Zealand)

Poster Presentations

- M. G. Blaber, M. D. Arnold, M. J. Ford
  The Optical Properties of Alkali Noble Group 3 Alloys
  ICEM 2008 (2008, Sydney, Australia)

- M. G. Blaber, M. D. Arnold, M. J. Ford
  The Optical Properties of Alkali Noble Group 3 Alloys
  WATOC 2008 (2008, Sydney, Australia)

- M. G. Blaber, M. D. Arnold, M. J. Ford and M. B. Cortie
  The Optical Properties of Gold Alloys
  Molecular Modelling 2007 (2007, Melbourne, Australia)

- M. G. Blaber, M. J. Ford, M. B. Cortie
  Plasmon absorption in a gold nanoparticle dimer
  ETOPIM7 (2006, Sydney, Australia)

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Glossary of Acronyms

AE	All-Electron
BE	Band Edge/Optical Gap
CG	Conjugate Gradients
DFPT	Density Functional Perturbation Theory
DFT	Density Functional Theory
DOS	Density Of States
DZP	Double-ζ plus Polarisation
EEL	Electron Energy Loss
EELS	Electron Energy Loss Spectroscopy
FP	Full Potential
GGA	Generalised Gradient Approximation
JC	Johnson and Christy
LAPW	Linearised, Augmented Plane Wave (method)
LCAO	Linear Combination of Atomic Orbitals
LDA	Local Density Approximation
LDOS	Local Density Of States
PBE	Perdew-Burke-Ernzerhof (GGA parameterisation)
PDOS	Projected Density Of States
P	Palik
PP	Pseudopotential
PW	Plane Wave
PW92	Perdew & Wang 1992 (LDA parameterisation)
SCF	Self-Consistent Field
SZP	Single-ζ plus Polarisation
TDCDFT	Time-Dependent Current Density Functional Theory
TDDFT	Time-Dependent Density Functional Theory
WF	Weaver and Frederikse

ϵ	Complex permittivity
$\epsilon^{'}$	Real part of the permittivity
$\epsilon^{''}$	Imaginary part of the permittivity
ϵ_{ib}	Interband contribution to the permittivity
ϵ_{∞}	Core polarizability, ocassionally used to describe residual effects.
ε_i	Single particle eigenvalues
λ	Wavelength. Also, perturbation parameter
$\mathbf{k}$	Wave vector
ω	Angular Frequency (eV)
ω_g	Optical gap/band edge (eV)
ω_p	Bare or Drude plasma frequency (eV)
ω_s	Screened plasma frequency (eV)
$\omega_{\epsilon^{''}_{\mathrm{max}}}$	ω at which $\epsilon^{''}$ is greatest (refers to interband)
$\omega^{Q_{\mathrm{LSP}}}_{\mathrm{max}}$	ω at which Q_{LSP} is greatest
ψ	Single particle wavefunction
ϕ	Pseudo atomic orbital, or, generic basis funciton
ρ_{DC}	DC resistivity ($\mu\Omega$cm)
$\mathbf{q}$	Electron momentum. Also, phonon momentum
Q_{abs}	Absorption efficiency
Q_{ext}	Extinction efficiency
Q_{LSP}	Local Surface Plasmon quality
Q_{sca}	Scattering efficiency
Q_{SPP}	Surface Plasmon Polariton quality
σ	Optical conductivity
u	Pseudo-wavefunction
x	Size parameter ($2\pi r/\lambda$)

Abstract

The continuous improvement of nanoscale fabrication techniques will ultimately result in a situation where the performance of plasmonic devices is not dependent on engineering defects, but rather on the fundamentally limiting behaviour of the underlying metals. This thesis addresses the following questions: Are silver and gold the best metals for plasmonics? What other materials are available? and finally; Can we design better plasmonic materials?

To answer these questions, classical electrodynamics calculations are performed using tabulated dielectric functions from the literature. Starting from a comparison of nanoshells made of various free electron metals, it is shown that the low plasma frequency metals sodium and potassium perform well. However, these metals are not suitable for many common uses of nanoshells. As such, the material choice is extended to all non *f*-group metals in the periodic table and a variety of additional geometries are studied, including nanorods, superlenses and a number of guiding structures. It is shown that gold, silver, the alkali metals and aluminium outperform all other metals, each over a range of frequencies and permittivities. None of the reviewed elements performs better than silver and gold.

As none of the elements seem to offer any advantage over silver or gold, the search is extended to alternative materials with tabluated dielectric functions. A review of the plasmonic properties of these materials is presented, including alloys, intermetallic compounds, high pressure materials as well as silicides, metallic glasses, and liquid metals. It is discovered that liquid sodium outperforms its solid elemental counterpart. Additionally, several materials with simple crystal structures seem to perform well, but none to the extent of silver or gold.

The number of compounds for which tabulated optical constants are available is severely limited. In order to evaluate the performance of a large number of materials, first principles quantum mechanical calculations must be performed. It is shown that the plasmonic performance can be approximately gleened from the relationship between the optical gap and the plasma frequency. However, in order to compare the calculated optical response of materials with experimental data for the elements, the Drude phenomenological scattering rate must be known. Here, for the first time, calculations of the real and imaginary components of the dielectric function including the electron-phonon scattering rate are performed in order to gauge the plasmonic performance of materials with no tabulated optical data.

A list of publications associated with this work is presented on page iv.