Tuning optical properties in random arrays of plasmon resonant nanoparticles

by

Stefan Schelm

A thesis submitted in fulfilment
of the requirements for the degree of
Doctor of Philosophy

Department of Applied Physics
Faculty of Science
University of Technology, Sydney
Sydney Australia

2005

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 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 have 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 the thesis.

Signature of Candidate

Production Note:
Signature removed prior to publication.

Acknowledgements

I would like to acknowledge the help of and thank the following persons and institutions for their help and support:

My supervisors Geoff. B. Smith and Matthew R. Phillips, the Microstructural Analysis Unit staff, especially Mark Berkhan and Richard Wuhrer, the people at the Department of Physics, chiefly Nicholas Armstrong, Annette Dowd and Abbas I. Maaroof for fruitful discussions, Geoff McCredie for practical and Linda Foley for administrative help. Furthermore, I have to thank Abbas I. Maaroof particularly for his large contribution to the chapter 6.

For their cooperation and use of their samples I'd like to thank the Commonwealth Scientific and Industrial Research Organisation (CSIRO) in Lindfield, Sydney, especially Gang Wei and the CSIRO in Melbourne.

For interesting discussions, their help and use of their SNOM I would like to thank the Surface Physics Group at Newcastle University, especially Chris McNeill, Daniel Cotton and Paul Dastoor. With regard to SNOM I'd also like to thank Alexandre Bouhelier and Jan Seidel for indulging my questions and helping me to improve my knowledge about SNOM.

I would also like to thank Juan Sotelo and Jacob Jonsson for interesting discussions and help during their stay and J. Prikulis and M. Käll for letting me use some of their results of random holes in gold films.

Furthermore, I am thankful for suggestions, by the referees, for the improvement of the quality and readability of the thesis.

Last but not least, I am grateful for the financial support by the BASF AG, Germany and the help of my family.

Preface

Parts of this thesis have been published in the following papers and proceedings:

- S. Schelm and G.B. Smith "Self-assembled gold nanoparticles with organic linkers", invited chapter to be published in Nanotechnology in Biology and Medicine (CRC Press, FL, to be published in 2006)
- S. Schelm, G. B. Smith, P. D. Garrett, W. K. Fisher "Tuning the surface plasmon resonance in nanoparticles for glazing applications", Journal of Applied Physics **97** (12), 124314 (2005)
- S. Schelm and G.B. Smith "Evaluation of the limits to the resonance tunability in metallic nano-shells with a spectral averaging method", Journal of the Optical Society of America A **22** (7), 1288 (2005)
- S. Schelm and G.B. Smith "Internal Electric Field Densities of Metal Nanoshells", Journal of Physical Chemistry B **109** (5), 1689 - 1694 (2005)
- G.B. Smith, A. Maaroof, R. Allan, S. Schelm, M. Cortie, G. Anstis "Optical response of nanostructured metal/dielectric composites and multilayers" (invited paper), Proceedings of SPIE Vol.5508 (Conference 5508: Complex Mediums V: Light and Complexity, 2004)
- S. Schelm and G.B. Smith "Field profiles for spherical conductive nanoparticles and metallic-shell/dielectric-core nanocomposites", Proceeding of SPIE Vol.5509 (Conference 5509: Nanomodeling, 2004)

- S. Schelm, G.B. Smith, G. Wei, A. Vella, L. Wieczorek, K.-H. Müller, B. Raguse "Double effective medium model for the optical properties of self-assembled gold nanoparticle films cross-linked with alkane dithiols", Nano Letters **4** (2), 335-339 (2004)

- S. Schelm, G.B. Smith, G. Wei, A. Vella, L. Wieczorek, K.-H. Müller, B. Raguse "Optical properties of dense self-assembled gold nanoparticle layers with organic linker molecules", Proceedings of SPIE Vol.5221 (Conference 5221: Plasmonics, 2003)

- S. Schelm and G.B. Smith "Dilute LaB6 nanoparticles in polymer as optimized clear solar control glazing", Applied Physics Letters **82** (24), 4346-4348 (2003)

Abstract

Small conductive particles show a resonant behaviour at wavelengths where bulk or thin film samples have no features. This resonance is caused by the collective oscillation of the free electrons in the particle and is called localised surface plasmon resonance. It is influenced by the shape of the particle, the surrounding medium and particle interaction.

I studied shape, matrix and interaction effects of metallic and metal-like particles in various systems with the aim to rationally tune the resonance to specific wavelengths for different applications.

Dilute samples of small LaB_6 particles were studied with regard to their NIR blocking performance. My analysis showed that they are more efficient than the alternative materials ITO and ATO. This is mainly due to the position of the LaB_6 particle resonance, which lies precisely in the spectral region which needs to be blocked (around 1 μm). I was able to model the optical properties of the window samples, using a dilute quasi-static approach for anisotropic particles.

Different embedding matrices and particle interaction have also an influence on the localised surface plasmon resonance. An example for a combination of matrix and interaction effects is a self-assembled gold particle film with organic linkers. Structural effects were especially important in these films, as was verified by electron microscopy. The optical properties were successfully modeled, using a two level effective medium approximation.

A different way to tune the resonance is to change the shell thickness to core size ratio in metallic nanoshells. The resulting spectral shift, though, is limited by experimental realities for the metal coating and the onset of scattering for larger particles. The shell has two resonances, of which the low energy one can be tuned by the ratio mentioned above. This resonance also shows a different electric field profile to the normal dipole (and high energy shell) resonance. The field pattern also highlights a strong field gradient across the external shell interface and along the incident polarisation direction. The properties were calculated using Mie theory and the quasi-static approximation.

Finally, the far and near-field optical properties of thin silver films with randomly distributed holes were studied. They showed an enhanced absorption, due to coupling of the incident light into surface plasmon polaritons by the holes. Whereas the films did not show the enhanced transmission, which occurs in regular hole arrays, they still might provide some insight in the processes involved by helping to exclude some possible explanations.

Contents

List of Figures

List of Tables

Glossary

AFM	Atomic Force Microscope
BR	Bruggeman EMA Scheme
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DDA	Discrete Dipole Approximation
EMA	Effective Medium Approximation
LBL	Layer-by-Layer deposition
LSP	Localised Surface Plasmon
MG	Maxwell Garnett EMA Scheme
NP	Nanoparticle
NF	Near-field
PDF	Probability Density Function
SAM	Self-Assembled Monolayer
SEM	Scanning Electron Microscope
SERS	Surface Enhanced Raman Scattering
SHGC	Solar heat gain coefficient
SNOM	Scanning Near-Field Optical Microscope
SPP	Surface Plasmon Polariton
SPR	Surface Plasmon Resonance