# Plasmonic Effects in Metal–Semiconductor Nanostructures

Alexey A. Toropov and Tatiana V. Shubina



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#### Great Clarendon Street, Oxford, OX2 6DP, United Kingdom

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First Edition published in 2015

Impression: 1

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Published in the United States of America by Oxford University Press 198 Madison Avenue, New York, NY 10016, United States of America

British Library Cataloguing in Publication Data
Data available

Library of Congress Control Number: 2014951562

ISBN 978-0-19-969931-5

Printed in Great Britain by Clays Ltd, St Ives plc

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Tatiana Shubina To my mother, Maria Shubina. (1927–2014)

Alexey Toropov To my mother, Margarita Toropova.

#### Preface

Already in 1970, about 45 years ago, it was well established that metallic structures possess valuable optical properties that are derived from their ability to support collective electronic excitations known as surface plasmons. One of the first plasmonics phenomena, surface-enhanced Raman scattering, was observed in 1977 and since that thousands of original publications and many review articles and monographs have been produced on this subject. Later, the field of plasmonics exploded when it was shown that tiny metallic structures can enable optical circuitry at the nanoscale, that an array of nanoscale holes in a thin metal film can exhibit extraordinary optical transmission, and that specially designed metallic metamaterials can operate as a left-handed medium. Driven by advances in nanofabrication, a wide range of metallic plasmonic elements have been proposed and realized. Many of these applications and the underlying physical ideas are described in several very successful textbooks.

New exciting pathways to control light in ultra-compact geometries have been opened by implementation of 'active' plasmonic devices in addition to passive metallic light-concentrating structures. Among these recent achievements are plasmonic nanolasers or spasers, as well as plasmon-enhanced light-emitting diodes, detectors, solar cells, and single quantum emitters. All these applications rely on the effects of light-matter coupling in nanostructures, comprising semiconductors and metals, or other perfect conductors like degenerate semiconductors, semimetals, or graphene. Furthermore, strong coupling between surface plasmons and excitons has been observed in plasmonic cavity structures, including both organic and inorganic semiconductors. Beyond all doubt, exciting, new fundamental science and many real-life applications should be expected in this area in the nearest future.

The purpose of this book is to give a general view of electromagnetic and quantum phenomena emerging in metal–semiconductor plasmonic structures, ranging from basic physical theory to the practical engineering applications such as single-photon sources, nanolasers, ultra-compact modulators, and so on. The essential aim of the book is to attract the attention of researchers working in the areas of optoelectronics and physics of semiconductor heterostructures to the new exiting ideas of 'active' plasmonics and to collect together the knowledge, which is necessary to initiate their own research. Thus the potential readers of the book are researchers and graduate-level students in physics, optical and electrical engineering, and material science.

The choice of materials and structures described in this book is mainly defined by our research experience in the fields of nanophysics and nanophotonics. Basically, we provide the data which are most frequently used in our everyday practice; therefore, we believe that they can be useful for other researchers dealing with active plasmonics. The content is divided into three parts. The first part contains general information on plasmonic effects in metal structures, as well as electronic and optical properties of semiconductor structures, acting as building blocks of the devices of active plasmonics. The second part describes characteristics of particular materials, both conducting and semiconducting, which can be of value for the design of hybrid plasmonic structures. Thus, these two parts serve as a kind of handbook useful for many readers. They are expected to provide a concise but consistent description of the basic theoretical approaches and necessary material data, reducing the main text, where possible, to a conceptual level. The third part describes the existing theoretical approaches to the description of light-matter coupling in metal-semiconductor structures and presents proof-ofconcept experimental observations. This part is essentially devoted to the practical applications of active plasmonics, both implemented and proposed.

While the book is generally aimed at experienced researchers and graduate students, some parts of it should be readable and useful for a wider audience, including senior undergraduate students, who are interested in the area of modern nanophotonics.

Alexey Toropov and Tatiana Shubina Saint Petersburg, Russia

### Acknowledgements

This book owes much to our collaboration with researchers in different fields—technology, spectroscopy, and theory. It is our pleasure to express our gratitude to Sergey Ivanov, Eugeniius Ivchenko, Nikolay Gippius, Mikhail Glazov, Vladimir Kosobukin, Valentin Jmerik, Aimé Vasson, Joël Leymarie, Fujio Minami, Alexander Andrianov, and Bo Monemar. We sincerely appreciate Sonke Adlung (OUP) for offering an incentive to write this book and patience during its prolonged writing. Financial support of the Russian Science Foundation (#14-22-00107) was very timely during the preparation of the manuscript.

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# Introduction

- 1.1 Milestones of plasmonics
- 1.2 Scope of this book

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Plasmonics has a long history as a part of technology. The Lycurgus cup and amazing stained glass windows: all these art treasures rely on plasmonic properties of tiny metallic particles (a detail of a window in the Canterbury Cathedral is shown as the headpiece). On the other hand, the scientific background of plasmonics was established only during the last century, based on acquirements of classical and afterwards quantum electrodynamics. Moreover, plasmonics for the purposes of nanophotonics has a very recent history. Not accidentally, it coincides in time with the development of nanotechnology and nanometrology. Thus, we are dealing with a dynamically developing branch of modern physics, possessing rich history.

#### 1.1 Milestones of plasmonics

At the time of emerging radio communication, Zenneck (1907) and Sommerfeld (1909) obtained the particular solution of the Maxwell equations for exponentially decaying electromagnetic waves propagating along a boundary between two media, initially earth and air. Later, it was recognized that this solution is relevant to surface plasmons (SPs) excited at a metal-dielectric interface in plasmonic structures. Also, vice versa, the theory developed by Mie (1908) to describe the scattering and absorption of an electromagnetic field by spherical metallic particles has been applied to many natural objects-clouds, mist, and interstellar dust. Further, the mysterious Wood's anomalies (Wood 1902) in light reflection from a metal diffraction grating have been explained by Fano (1941) in terms of the interference of impinging light with the plasmons. Pines and Bohm (1952) considered the energy loss, observed when bombarding metals by an electron beam, as appearing due to the interaction with plasmons. Based on this suggestion, Ritchie (1957) proposed SPs in a thin metal foil, for which energy dispersion is dependent on the foil thickness. This model was developed by Stern (1967) to describe the behaviour of two-dimensional (2D) SPs observed in thin conducting films. All these developments resulted in development of the concept of surface plasmon polaritons (SPPs).

Probably, plasmonics would be no more than a part of classical electrodynamics but for the discovery of the surface enhanced Raman scattering (SERS) by Fleischmann et al. (1974). The researchers demonstrated that vibration modes in molecules absorbed on a silver surface can be enhanced up to 10<sup>5</sup>-10<sup>6</sup> times. Such strong amplification of optical processes had not been known before. Although many details in SERS were not clear and the contribution of chemical enhancement can be hardly excluded, the resonant character of the enhancement was doubtless (Moskovits 1985). The enhancement arises when the frequency of the illuminating light coincides with the resonance frequency of localized surface plasmons (LSPs) in small particles forming the rough metal surface. Different related phenomena, such as the surface-enhanced second-harmonic generation, four-wave mixing, absorption, and emission, have exhibited similar resonant enhancement. They are evidence of the amazing ability of SPs to concentrate electromagnetic fields at the sub-wavelength scale in the close vicinity of a metal surface. In particular, they promote resolution beyond the diffraction limit, realized in the innovative plasmonic microscope (Rothenhäusler and Knoll 1988).

In this book, we focus on the performance of plasmonics related to semiconductor-metal nanostructures. Two situations represent particular interest for our consideration, namely: (i) a source of radiation near a metal surface supporting SPs; and (ii) conversion of plasmonic excitations themselves into light, which determines the functioning of plasmonic structures as optical antennas. As shown below, both have been intensively studied previously.

When a radiating dipole is situated near a metal surface, the lifetime of spontaneous emission is decreased (Purcell 1946) and the spectrum of spontaneous