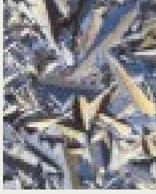

7.6. Laser Spectroscopy

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7.6.1. Introduction

Understanding the relationship between structure and function represents a central issue of basic materials research. Fundamental physical, chemical and/or biological properties and functions of materials are determined by the dynamics of elementary excitations in the ultrafast time domain, i.e. between 1 fs (1 femtosecond = 10^{-15} s) and approximately 1 ps (1 picosecond = 10^{-12} s). Such nonequilibrium and relaxation dynamics which are determined by microscopic interaction processes, can be observed in real-time by optical techniques using femtosecond laser pulses for inducing and probing the linear or nonlinear material response. Experiments with fs time resolution have provided a wealth of new information on transient electronic and vibrational properties of materials and on fast processes which are essential for realizing new functional properties [1].

The comparably high peak intensities of ultrashort optical pulses at moderate average power are essential for a quantitative characterization of the nonlinear optical properties of materials which are applied for optical frequency conversion, multiplexing and switching, processes underlying modern optoelectronic and all-optical information technology. With increasing data transmission and processing rates, optical information technology moves towards the ultrahort time domain, requiring the implementation of ultrafast technology into communication systems. This is illustrated in Fig. 7.14 showing different optical technologies and their characteristic time/frequency range.

The rapidly increasing relevance of nanostructured materials for research and technology calls for new techniques to optically address and analyze individual nanostructures and to transmit information between them. This has led to the development of new nanooptical techniques, in particular microscopies with sub-wavelength spatial resolution, which allow optical studies of single nanostructures [2]. The spatio-temporal dynamics of elementary excitations on a nanometre scale is accessible by combining nanooptical and ultrafast techniques.

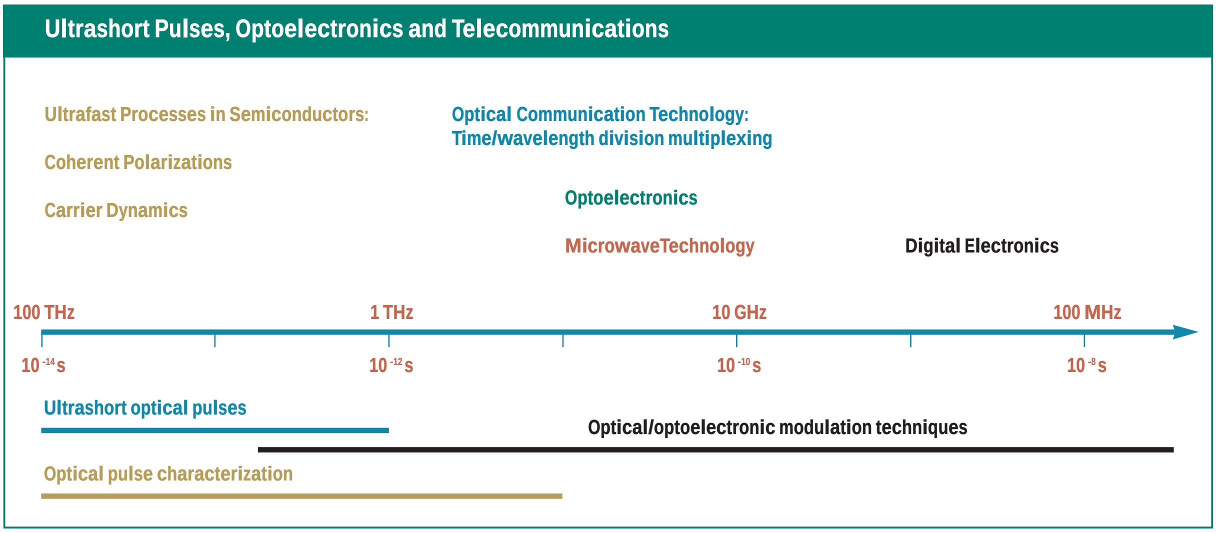
7.6.2. State of the Art

In this section, the state of the art of ultrafast material science and nanooptics is reviewed briefly and some future trends are outlined.

(a) Pulse generation, shaping, and characterization

Generation, shaping and characterization of fs pulses provide the basis for studying ultrafast processes and developing ultrafast technologies. Present technology is

Fig. 7.14. Characteristic time and frequency scales of optical and electronic technologies (upper part). In the lower part, the time ranges covered by ultrashort pulses, modulation technqiues and optical pulse characterization are given.



mainly based on mode-locked solid state lasers and amplifiers which are combined with nonlinear optical techniques for frequency conversion and with pulse compression methods. The wavelength range from 100 nm in the deep ultraviolet up to 300 µm in the far-infrared is now covered continuously with pulse durations of less than 200 fs. In addition, soft X-ray pulses at wavelengths between 5 and 100 nm and incoherent hard X-ray transients with wavelengths below 1 nm are available. The average output powers range from several µW up to about 10 W, the corresponding peak intensities are between several 10^3 W/cm^2 and 10^{15} W/cm^2.

Coherent pulse shaping techniques allow the generation of individual pulses or pulse sequences with tailored optical phase characteristics and the compression of pulses down to about 2 fs duration. For a phase-resolved characterization of pulses, methods like frequency-resolved optical gating, spectral phase interferometry, and electrooptic sampling are available. Highly sensitive techniques of nonlinear time-resolved spectroscopy are applied to monitor the ultrafast time evolution of optical polarizations and nonequilibrium populations.

(b) Ultrafast structural characterization

Ultrafast techniques which are able to grasp transient structures and nuclear motions in solids, liquids, and macromolecular systems play an increasingly important role for understanding microscopic transformation processes and chemical properties of materials. Temporally and spectrally resolved infrared methods are applied to monitor the creation, disappearance and the mutual coupling of functional groups in molecules through their vibrational absorption bands and to follow nuclear motions in real-time. Spectroscopic techniques of nuclear magnetic resonance (NMR) which works on substantially slower time scales, are being adapted for infrared spectroscopy in the pico- and femtosecond domain. First experiments have demonstrated the potential of two-dimensional infrared spectroscopy for structural characterization of biologically relevant molecules [3]. Time resolved X-ray diffraction represents another new, yet not fully implemented approach to study transient species, e.g. during phase transitions in solids or solid-liquid phase transitions [4].

(c) Imaging, microscopy and nanooptics

Ultrafast imaging methods, optical microscopy using femtosecond pulses, and nanooptical techniques provide direct information on the stationary and transient structure of materials. In optical coherence tomography (OCT), partly transparent biological materials, e.g. tissue, are irradiated with fs pulses and information on the spatial structure of the layer investigated is extracted from the time structure of the back-scattered light. This technique enables *in situ* imaging of the microstructure of materials and has found medical application. In multi-photon microscopy, fs lasers serve as a light source for multiphoton excitation of organic chromophores embedded in the samples. Two-photon microscopy has developed into a standard technique of biomedical imaging.

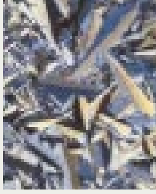
Imaging in the mid- and far-infrared (THz) range has become a tool for studying the structure of porous material and detecting specific material constituents, e.g. water traces. Here, fs optical pulses serve for the generation and phase-resolved detection of electric field transients in the THz range.

Microscopy with subwavelength spatial resolution, i.e. confocal and near-field scanning optical microscopy (NSOM), is applied for optical characterization of structures on a length scale of typically 50 to 100 nm. Though this spatial resolution is usually not sufficient to optically image nanostructures, single nanostructures can be addressed optically and local excitations can be created at a well-defined nanometre distance from a nanostructure. The electronic structure of individual semiconductor and metal nanostructures and single macromolecules as well as local disorder potentials in extended quantum structures like semiconductor quantum wells have been studied, partly at cryogenic temperatures. While those experiments provide information on stationary properties, confocal microscopy and NSOM with femtosecond pulses can map the spatio-temporal dynamics of material excitations. Such time-resolved techniques have been implemented recently and first experiments on carrier transport in low-dimensional semiconductor nanostructures have been performed. Near-field techniques have also been used to write nanometre structures onto materials.

(d) Areas of application

The techniques outlined above have been applied in the following areas of materials research:

- Bulk and nanostructured semiconductors: Coherent polarizations and their influence on the optical spectra, ultrafast redistribution and thermalization of nonequilibrium carriers, and carrier cooling and trapping have been studied in great detail. A closed picture of the hierarchy of relaxation processes has been established by combining experimental and theoretical research. Detailed knowledge exists on microscopic quantum coherence, Coulomb and phonon scattering, and on manybody and nonlinear optical effects. Coherent all-optical control has been demonstrated with excitonic polarizations and photoinduced currents. This research



has led to semiconductor devices with completely new and/or strongly improved functional properties.

- Metals, metallic nanoparticles, and correlated materials including high-T_C superconductors: Single-particle and collective excitations of the carrier system, lifetimes of image states at surfaces and the related nonlinear optical properties including Faraday rotation and other magnetic phenomena, are being studied in experiments with sub-10 fs time resolution. Correlated materials represent a new field of research in which the investigation of low-energy excitations, e.g. close to or below the superconducting energy gaps, is particularly important, as the electronic structure and optical spectra at higher photon energies are not fully understood. In general, our knowledge in this field is still much more limited than for semiconductors.

- Phase transitions of solids and material processing with femtosecond pulses: Order-disorder phase transitions, e.g. melting, and optically induced changes of crystal structure are being monitored via changes of the nonlinear optical properties, e.g. through second harmonic generation at surfaces, and by detecting transient structures by time-resolved X-ray diffraction. Material processing and structuring with femtosecond pulses frequently occurs under nonthermal conditions and with reduced thermal load on the material, leading to an improved quality of the processed samples.

- Molecular systems in the liquid and solid phase, adsorbates on solid surfaces: The dynamics of electronic, vibronic and vibrational excitations as well as photochemical reactions are the main research topics in this field which is frequently called “femtochemistry”. As chemical reactions involve nuclear motions on a 10 to several 100 fs time scale, ultrafast techniques are an ideal tool to follow the pathway of a reaction, identify transition states and monitor the formation of products. There are first experiments in which the outcome of a reaction has been manipulated by tailored pulses or pulse sequences, demonstrating the potential for optical control of chemical reactivity.

Ultrashort pulses

Pulse durations:	2 fs (2·10^{-15} s) - 5 ps
Wavelength range:	100 nm - 300 µm + soft/hard X-ray
Peak power:	up to 1020 W/cm^2

- Control and quantitative analysis of optical phase (electric field).
- Different measurement techniques for real-time probing of optical polarizations and nonlinear material excitations in the wavelength range indicated above. Time resolution up to about 5 fs.
- Control of material excitations by interaction with tailored pulses and/or pulse sequences.
- Nonthermal material processing with ultrashort pulses.

Nanooptics – optics on a sub-wavelength length scale

Near-field scanning optical microscopy (NSOM):

Spatial resolution	> 20 nm (λ/20)
Temperature range	5 - 300 K
Detection sensitivity	single photons

Confocal microscopy:

Spatial resolution	>250 nm (λ/2)
Temperature range	5 - 300 K (resolution >500 nm)
For both:	
Spectral resolution	determined by laser source and detection system
Time resolution	determined by laser source (> 50 fs)

Table 7.8. Summary of Experimental Techniques in Laser Spectroscopy.

During the last decade, the number of research groups performing basic research on ultrafast phenomena has increased substantially. In Europe, there are now approximately 50 groups active in ultrafast material science, the main competitors being laboratories in the U.S. and – to somewhat lesser extent – in Japan. European scientists have introduced key innovations in ultrafast laser technology and are among the top researchers in several areas of basic research, e.g. solid state physics or ultrafast processes in soft matter. In Japan, a 10-years-programme on “Femtosecond Technology” aims at a combination of fundamental research with technological applications, mainly in telecommunications and ultrafast optoelectronics. Japanese groups play a leading role in optical telecommunications with ultrahigh data transmission rates. In contrast to Japan and the U.S., the interest and involvement of European industry in ultrafast material science is still very limited.

7.6.3. Expectations and Needs

In the following, some future trends of research in ultrafast optics and nanooptics are outlined together with a crude estimate of the period after which major goals may be achieved:

- New femtosecond sources: Compact low-cost fs sources pumped by semiconductor diode lasers and mode-locked lasers working at high (GHz) repetition rates for technological applications (including telecommunications). Sources for ultrashort hard (keV) X-ray pulses at kHz repetition rate for time-resolved X-ray diffraction and absorption. Development of new laser materials and components, e.g. high-power diode lasers for new pumping wavelengths. Phase shaping and nonlinear conversion of pulses in an extended wavelength range (2 to 5 years).

- New and much more sensitive techniques for investigating transient structures and phase transitions by ultrafast infrared and X-ray techniques represents a very important direction of research which could lead to revolutionary new insight into the properties of condensed matter. Both laser-based methods and the use of free electron lasers providing short hard X-ray pulses will be important (5 to 10 years).

- Optical coherence tomography with extremely short pulses (improved depth resolution) and in extended wavelength ranges (mapping of different constituents, 2 to 5 years).

- Mid- and far-infrared near-field imaging with sub-100 nm spatial resolution, single pulse imaging (instead of scanning methods). New local probe designs for sub-wavelength optical microscopy with improved spatial resolution including single molecule probes, higher sensitivity and stability of local probe microscopies, multi-probe microscopies (5 to 10 years).

An interdisciplinary research environment is essential for competitive and successful research on and development of new optical techniques. This requires a long-term combination of material science, engineering, physics, chemistry and biology in joint European projects and networks.

A rapid transfer of new techniques into materials research requires a close cooperation of groups developing techniques with those applying them as the feedback of users is necessary for optimizing new techniques.

Support of dedicated competence centers which provide experimental facilities for cooperative research and accept guest scientists also for longer periods, is recommended, as ultrafast experiments require expensive equipment and highly specialized knowledge and skills.

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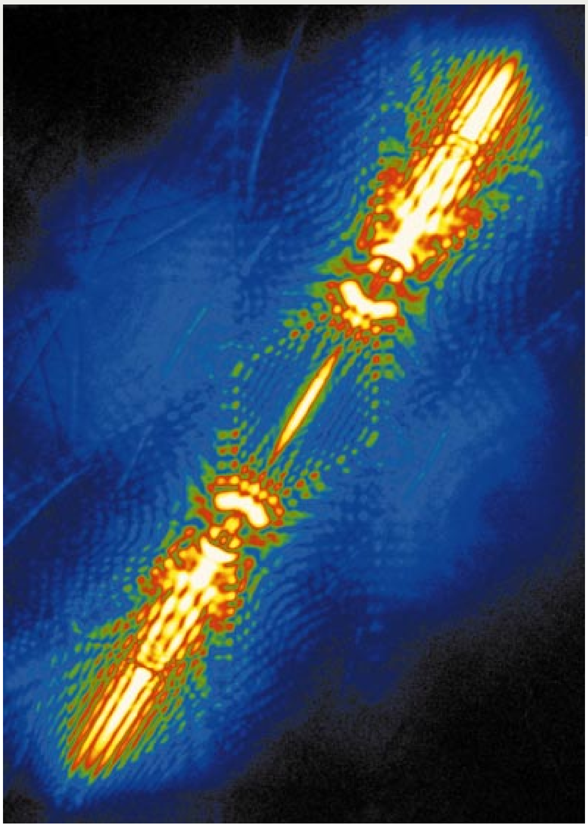

Convergent beam electron diffraction (CBED) pattern of Si. Details of (220) diffraction disc near the [III] zone axis. Information can be gained on the local bonding of atoms (ions) in the unit cell from the intensity distribution.