CHAPTER 1
General introduction
Imagine, a beautiful day is about to start. The sky is clear while the sun is just below the horizon, but dawn has started. Far away, against the rising sun, the silhouette of a small house at the summit of a mountain can be seen. The contours of the mountain and the roof of the house are in sharp contrast with the sky. When the sun rises and starts to illuminate the beautiful landscape, many colors appear. Green trees on the left of the mountain while the right side is covered with colorful flowers. Even the roof of the house has turned bright red.

This is an example how light provides valuable information about objects and matter. It allows us to see, to experience colors, but also to extract fundamental data, such as the molecular composition of a sample. Light can interact with matter in different ways. It can be, among others, reflected, absorbed, scattered or emitted by an object (see Fig. 1.1). Analyzing the optical properties of objects can provide us valuable information about very small things, such as molecular structures or chemical reactions, or very large objects, such as the composition of a star or solar system. For example, the color of the sky can be explained by analyzing the light scattering by the molecules in the atmosphere. The general scattering efficiency scales with $\lambda^{-4}$. The blue colors in the electromagnetic spectrum are thus scattered more efficiently in all directions and are directed into our eyes more effectively.

**Figure 1.1:** Possible interactions of light and matter.
The research enclosed in this thesis focuses on obtaining chemical information at the smallest possible scale using visible light as a probe. The combination of different techniques enables access to a wide variety of sample properties at a large range of sizes. The possibilities and limitations of new tools providing easy-to-use methods using optical imaging beyond the diffraction limit are explored.

### 1.1 Microscopy

The word microscopy is derived from the Greek words *mikrós*, “small”, and *skopeîn*, “to look” or “to see”. A microscope is an instrument that is meant to make very small objects visible for the human eye. Starting in the 17th century, it became an important instrument when people started to study human tissue. The Dutch scientist Antonie van Leeuwenhoek became famous when he discovered the red blood cell, spermatozoa and single cell organisms using an optical microscope of his own manufacture [1]. These discoveries opened a whole new area of research. The optical microscope became a very important tool in learning about how the human body works and about the tiny features of life in general, and it is still a very important tool in many fields of research in the present days.

Interestingly, very little has changed in the original setup over the centuries. A conventional optical microscope still consists of a set of lenses, which was sufficient when people were interested in single cells and micro organisms, ranging in size from 10 to 20 µm [2]. However, the objects of interest have changed; nowadays, one wants to look at smaller objects and wants to extract more information from a sample. At present, interests have moved from studying the organelles of cells towards the single molecule level to study proteins and their interaction, or the growth of thin layers in material sciences - a scale that is no longer accessible with standard optical microscopy. Using non-optical methods, such as scanning probe microscopy (SPM) or scanning electron microscopy (SEM), imaging at higher spatial resolution is already possible. However, adding optical information, to gain access to chemical properties, is still challenging. In this thesis, an effort is made to combine both high-resolution imaging with spectroscopic surface analysis. In addition, the focus is on suitability for a wide variety of applications, including higher temperatures and different atmospheres as most high-resolution techniques are limited in this respect.

#### 1.1.1 Improving resolution

Visible light (400 - 700 nm wavelength), is one of the most important and versatile, non-destructive methods to obtain information about sample properties or to “view”
characteristics of a sample. Light can be characterized in two ways, as a wave with a wavelength and frequency, or quantum mechanically as photons with a distinct energy. To understand the behavior of light at the nanoscale, we consider light as a wave. Ernst Abbe found in 1873 [3] that the spot size $d$ of a beam with wavelength $\lambda$ focused through a lens with numerical aperture $NA$ is defined by:

$$d = \frac{\lambda}{2NA}$$  \hspace{1cm} (1.1)

The best objective lenses have an $NA$ of around 1 in air resulting in a maximum resolution of about $\lambda/2$. Observing objects smaller than 200 nm is thus very difficult using conventional techniques and visible light.

Reaching the fundamental resolution limit is not straightforward, even when the best optics is available. In normal wide-field microscopy a large part of the sample is illuminated, which is partly scattered and disturbs the image. In 1955 the scanning confocal fluorescence microscope was invented [4]. In this system the sample is illuminated with a laser that is scanned across the sample. A pin hole in front of the detector blocks all the out-of-focus light (see Fig. 1.2). In addition, since this is a fluorescent technique, only fluorescence parts of the sample are recorded while the rest remains dark. At the expense of signal intensity, significant gain in resolution is observed. However, the fundamental diffraction limit, of course, still exists.

### 1.1.2 Imaging beyond the diffraction limit

As one can infer from Eq. 1.1, imaging beyond the diffraction limit is challenging using optical methods. Recently, Nobel prize winning super-resolution techniques using fluorescence microscopy have been demonstrated. Well-known examples are stochastic optical reconstruction microscopy (STORM) and photoactivated localization microscopy (PALM). These methods rely on photo switchable fluorophores and point spread function fitting to increase the resolution down to several nanometers [5, 6]. Stimulated emission depletion microscopy (STED) is another method that uses stimulated emission to increase imaging resolution [5, 6].

In many fields, these kind of tricks cannot be used because fluorescent labeling is not possible or too complicated. In these cases, instruments and hyphenated techniques that enable imaging beyond the diffraction limit are required, most of which, however, rely on non-optical methods. For example, electron microscopy is an excellent technique to obtain nanometer resolution images of conducting samples. An electron beam has a much shorter wavelength than an optical beam and can therefore be focused more tightly [7].
1.1.3 Scanning probe microscopy

In particular, scanning probe microscopy (SPM) is an important technique for high-resolution surface characterization. By scanning a physical needle over a sample surface, properties such as topography, stiffness or electrical conductance can be measured with high spatial resolution, even down to the atomic level [8, 9]. The versatility of this method makes it an interesting technique to further investigate the opportunities it yields. Replacing the scanning tip with an optical fiber, for example, allows one to simultaneously gather optical information about a sample surface, as in scanning near-field optical microscopy (SNOM). As the tip is scanned at close proximity to the surface, it is possible to obtain a resolution that is better than what is possible with a conventional microscope. As the research presented in this thesis is based on a combination of SPM and SNOM, a more extensive review of these techniques is provided in chapter 2.

Figure 1.2: Schematic view of a confocal microscope.
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1.1.4 Spectroscopy at the nanometer scale

As shown in Fig. 1.1, light can interact with matter in different ways. Extracting molecular information using light - matter interaction is called spectroscopy. When a (semi-) transparent set of molecules (i.e. a liquid or gas) is illuminated with an optical beam, most of the light is transmitted, some can be absorbed, and a small part is scattered. When energy transfer between the optical beam and the molecules takes place, fundamental information, such as molecular composition of the substance can be obtained.

To explain light and matter interactions at a molecular level, the quantum mechanical interpretation of light can be used, which states that an optical wave can also be interpreted as photons with a distinct energy. A photon fitting an energy level of a molecule (electronic transition or molecular vibration) can be absorbed and induce excitation. Analysis of the energy exchange between a substance and light results in a spectrum specific for that substance.

Unfortunately, spectroscopic information at the nanoscale is hampered by the diffraction limit. Enabling spectroscopy at the nanoscale requires the combination of different methods. SNOM is one of the techniques that can be used to focus light on a sample more tightly to allow spectroscopic analysis at high spatial resolution.

1.2 Scope of this thesis

Combining optical surface analysis and physical sample characterization provides access to chemical information as well as the physical properties at high spatial resolution. Several application areas, including catalysis, material sciences or biology, require sub-wavelength optical imaging tools that support extreme environments. Imaging in liquids or at elevated temperatures is often difficult using conventional methods. In this work a set of tools is presented that combine high-resolution optical and morphological surface analysis and can be used in harsh conditions.

To develop new tools, some criteria can be set:

- The chemical composition can best be characterized using (optical) spectroscopy;
- For the physical properties, such as the morphology and hardness, scanning probe microscopy can be used;
- To support applications in biology or catalysis, measurements in liquids and at elevated temperatures should be possible;
- The best possible spatial resolution should be available;
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- The method should be robust and easy to use;
- Measurement time should be controlled within reasonable limits.

### 1.3 Thesis contents

Spectroscopy at the nanometer scale means obtaining spectroscopic information at extremely high spatial resolution, which in this thesis means below 100 nm. There are many ways to extract nanoscale spectroscopic information. However, most methods are complicated, only suitable for a specific application, and often require a highly trained operator. The goal of this project is to develop an easy-to-use versatile tool that can be used to obtain high-resolution morphological data and spectroscopic information simultaneously, and can work in extreme conditions.

Chapter 2 starts with an introduction to methods that can be used to acquire morphological information and chemical information. A brief literature overview and theoretical background of relevant areas such as atomic force microscopy (AFM), scanning near-field optical microscopy (SNOM) and vibrational spectroscopy is provided to make the reader familiar with these subjects. Furthermore, the current status and opportunities for further developments and improvements in these technologies are discussed.

Integration is not easy for these physical and chemical characterization methods, but would certainly expand the applicability of an analysis tool. Fiber-based technologies, such as fiber-top or ferrule-top sensors, are ideal to realize this goal [10–13]. Optical fibers are robust, designed to transmit light and easily available. Chapter 3 is a technical chapter that explains the mechanical details of fiber-top and ferrule-top probes including their advantages and disadvantages. Section 3.4, which describes the fabrication procedure of ferrule-top probes with optical access, is particularly important since this set of probes enables optical imaging beyond the diffraction limit.

The first demonstration of AFM+SNOM probes is presented in chapter 4. A ferrule-top sensor, as described in section 3.4, is used to obtain a near-field optical transmission and topography image of a test grating simultaneously. An evanescent field on top of a prism, of which the intensity decays exponentially within one wavelength distance from the surface, functions as the light source. As demonstrated in this chapter, the design of these probes allows for measurements in liquids without the requirement for special precautions and with a similar performance as in air.

The design of these probes is one of the key assets that allows measurements in harsh conditions and in difficult-to-access areas. Chapter 5 shows two applications of
fiber-based devices in which measurements in such difficult environments are required. A ferrule-top AFM+SNOM probe is used to follow transmission and topography changes in the loading and unloading of H$_2$ switchable mirrors. Secondly, to design a fiber-top probe that can be used in small, difficult to reach areas, a cantilever is fabricated on top of an etched fiber with a diameter of about 20 µm. This probe is used to measure the topography of an AFM test grating inside a 100 µm wide and 1 mm deep hole. In addition, the same probe is used for nanoindentation experiments, potentially to characterize an object inside a small hole (for example a cell inside a porous material [14]).

The development of semiconductor lasers is another field where topography and optical measurements at the nanometer scale can provide valuable information for product improvement, and where heat generation hampers the applicability of conventional instruments. In **chapter 6** an AFM+SNOM probe is utilized to measure the mode structure of vertical cavity surface emitting lasers (VCSELs). It is known that the mode structure changes upon device degradation before any other sign of damage can be observed using other techniques. In an accelerated lifetime experiment a VCSEL is exposed to high current overload, while consecutive AFM+SNOM measurements are carried out to monitor VCSEL degradation. In these kind of experiments, heat generation is often problematic and makes conventional SNOM experiments prone to failure.

Combining two techniques in one instrument is, however, not always the best approach. Scanning methods are often slow and designed for imaging very small areas. Furthermore, a limiting factor for using a powerful spectroscopic method such as Raman spectroscopy is the low light throughput of SNOM fibers. Using two different instruments allows one to utilize the strong assets of both techniques most efficiently. **Chapter 7** shows such an approach, combining atomic force microscopy and Raman microscopy to study a photo-catalytic reaction at the nanometer scale. Through the preparation of a special sample and data analysis, high-resolution morphology information obtained by the AFM and the chemical information from the Raman spectrometer is correlated. This way kinetic information is obtained from hundreds of nanometer-sized catalytic sites at a large 100 x 100 µm$^2$ sample area.

Finally, **chapter 8** provides a discussion of the results presented in this thesis and looks ahead to explore possible future developments.
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