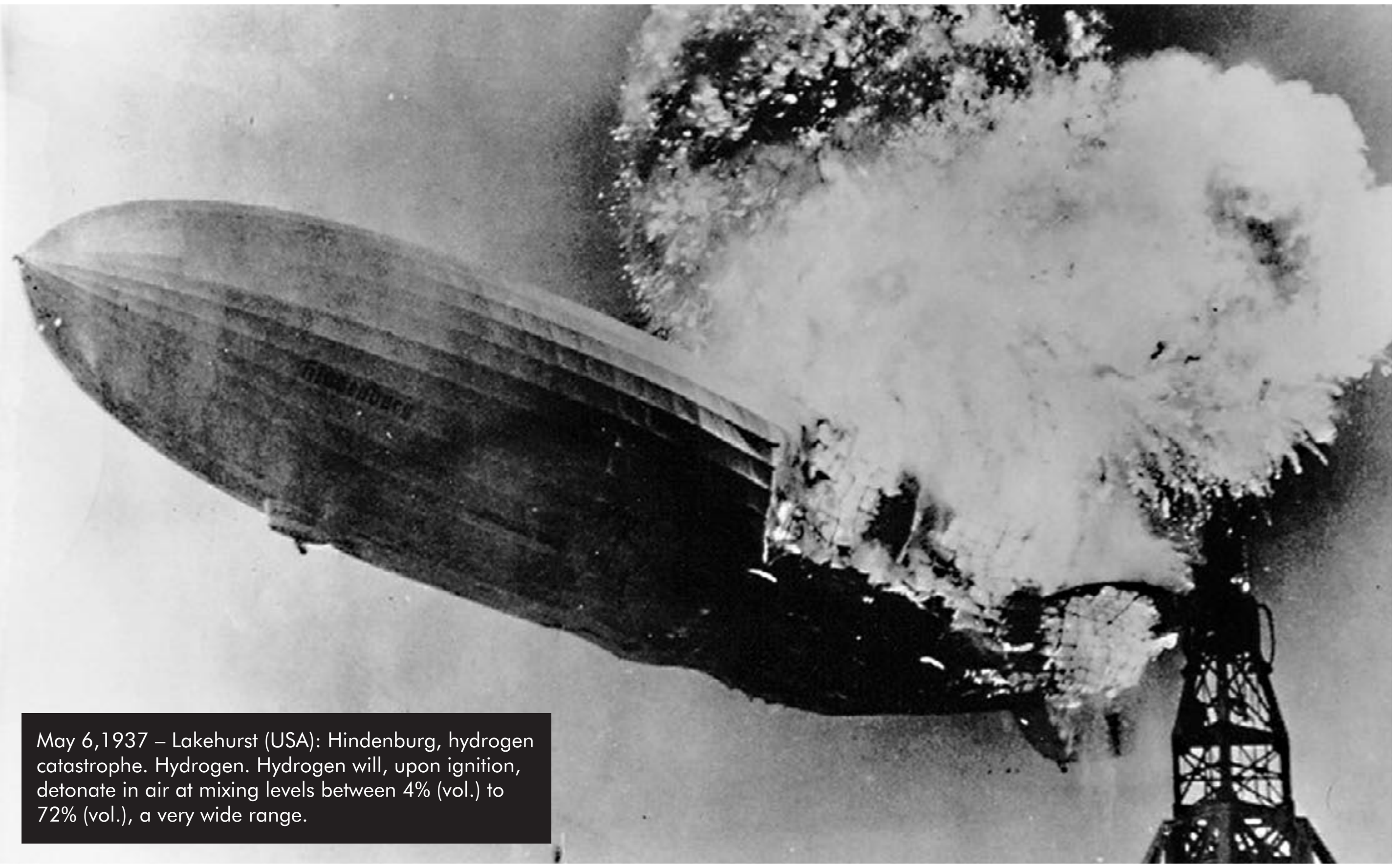
Metallic Photonic Crystal Hydrogen Sensor

A Sensitive, Small and Cost Effective Option

Cornelius Grossmann, Todd Meyrath and Harald Giessen



May 6,1937 – Lakehurst (USA): Hindenburg, hydrogen catastrophe. Hydrogen. Hydrogen will, upon ignition, detonate in air at mixing levels between 4% (vol.) to 72% (vol.), a very wide range.

Hydrogen has gained a substantial amount of interest in recent years, and it is considered to be an important future carrier of energy. Hydrogen has been well-known since the 18th century and was used as the first lifting gas for balloons and airships in history. The current use of hydrogen is quite diverse.

In the chemical industry hydrogen is used as hydrogenating agent, e.g., to increase the saturation level of unsaturated fats and oils or as reducing agent of metallic ores. The petroleum industry makes use of hydrogen for the production and processing of petrochemical fuels. There are some side-show branches where hydrogen is used for example as a shielding gas for welding methods or as a power fuel in submarines. The underlying idea of the future use of hydrogen is to use a renewable or nuclear energy source to dissolve water – via electrolysis – into hydrogen and oxygen. The hydrogen would then be stored in one way or another and function as an energy carrier that can be turned back into energy either by burning it with oxygen or by using it in a fuel cell to directly generate electrical power. In particular fuels cells have received a lot of attention in the past ten years because of their very high efficiencies.

Why is Sensing of Hydrogen so Important?

Hydrogen will, upon ignition, detonate in air at mixing levels between 4 % (vol.) to 72 % (vol.), a very wide range. It burns with an invisible flame, making burning hydrogen leaks hard to detect by the human eye. To make things worse, it is tasteless, odourless, and colourless, making detection for a human without aids almost impossible. Wherever hydrogen is used, and wherever it can mix with air and ignite, monitoring for leaks is necessary to avoid catastrophes. For industrial, research and military applications, the sensors are part of the inevitable initial investment and the costs are not a major issue. However, if consumer products are to be powered with hydrogen, there can be no doubt that the most stringent measures will be required to prevent a hydrogen leak and to detect it once it has occurred. Currently, sensors capable of registering a hydrogen leak at explosive levels and reporting it quickly cost on the order of a thousand US dollars. Research is urgently required into hydrogen sensors that are small, light, reliable, fast, reusable and above all – cost effective.

Applications for Photonic Crystals

Here, we are going to present a metallic photonic crystal sensor for gas applications. In general, plasmonics has the potential to touch many different fields as diverse as physics, nanooptics, spectroscopy, biology and sensing. Micro- and nanostructering of the material allows us to tailor the optical properties in a wide spectral range. Many revolutionary concepts seem to be feasible with this kind of tailored materials in the future, e.g., cloaking or the "perfect lens". However, up to today there are few real-world applications for photonic crystals even though the optical plasmon resonance has been a promising candidate for sensing applications for a number of years. In the structure we present here, the optical properties of our device are sensitive to hydrogen, providing a distinct effect that can be measured optically. The structure in this work is a multilayer sample, consisting of a WO_3 waveguide and an additional nanostructure of gold on top. The structure is depicted in Figure 1a, Figure 1b shows a height profile of the sample. The cross-section in Figure 2 gives detailed information about the dimensions.

In order to obtain some more information about the whole sample, the different layers can be resolved with scanning electron microscopy (Fig. 3a). In higher magnification, the gold wires are nicely visible (Fig. 3b).

The effect that we aim to measure is shown qualitativly here. It is called the gasochromic effect. Hydrogen incorporation into the WO_3 causes a colour change to this layer. Hydrogen diffuses into the porous WO_3 crystal, which causes a change of the optical properties of the photonic crystal (Fig. 4). This effect has been well known for several years and has been established in the construction industry as part of so-called "smart windows".

Nanostructured Surface

Why use a nanostructured surface? Figure 4 demonstrates that the response of bare WO_3 to hydrogen is rather qualitative, making it difficult to predict the exact amount of hydrogen In our configuration, the WO_3 acts as a waveguide, and in combination with the gold wire array on top, its resonance frequency depends on the amount of hydrogen around. Choosing the right dimensions, coupling of the waveguide mode and the plasmonic mode of Au to a new quasiparticle called waveguide-plasmon-polariton takes place. Its spectral behaviour is strongly depending on the hydrogen concentration due to the hydrogen sensitivity of WO_3.

Figure 5 shows a typical simulated extinction spectrum and the shift of the resonance due to H_2 incorporation. The presence of the waveguide resonance and its steepness increase the sensitivity substantially.

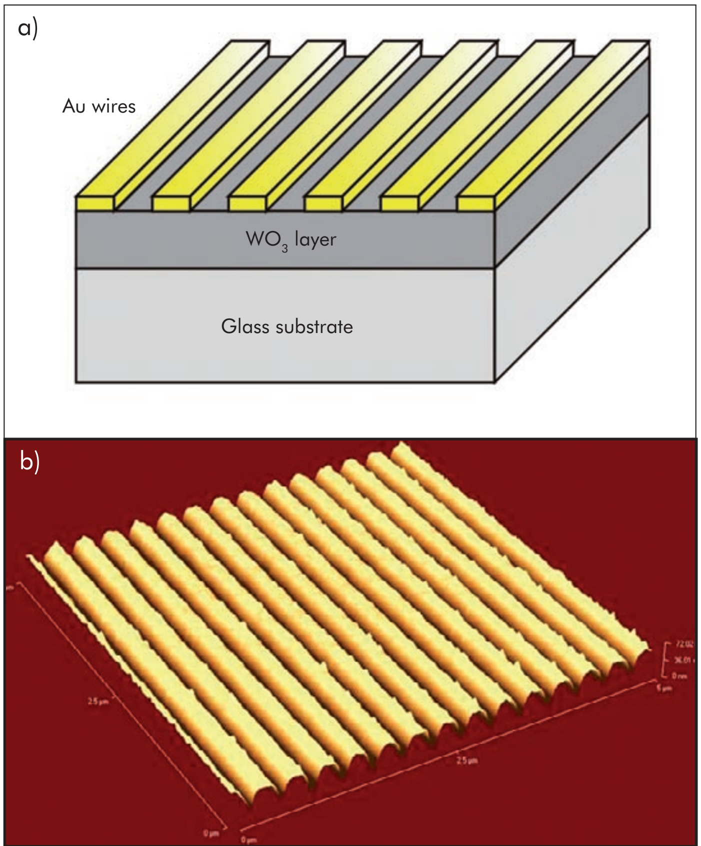


Figure 1: The structure in this work is a multilayer sample, consisting of a WO_3 waveguide and an additional nanostructure of gold on top: (a) Schematic structure; (b) Atomic force miscroscope (AFM) picture:Tilted view of the surface modulation.

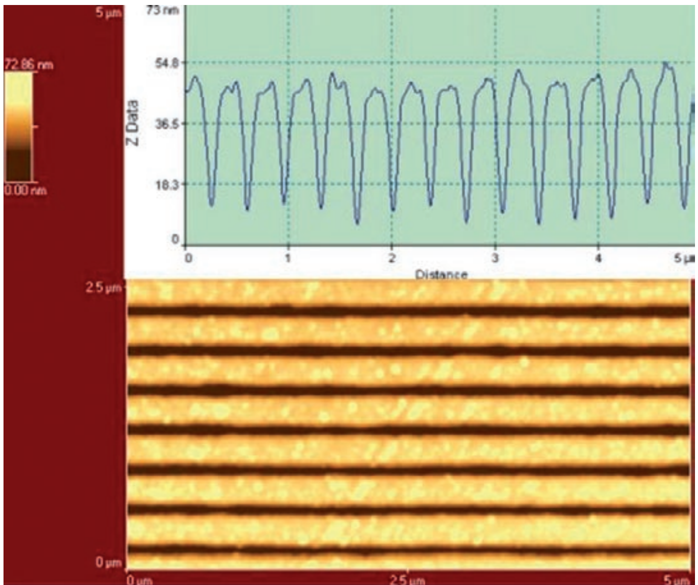


Figure 2: AFM picture: top view of the sample surface and cross-section. The cross-section gives detailed information about the dimensions.

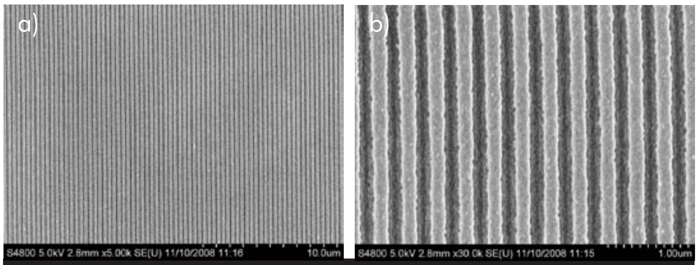


Figure 3: Scanning electron microscope (SEM) pictures of WO_3/Au layers (bright areas are Au). In higher magnification, the gold wires are nicely visible (b).

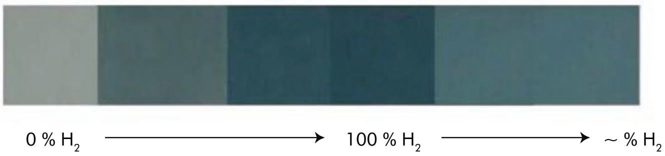


Figure 4: The gasochromic effect: Colour change of WO_3 with in- and decreasing H_2-concentration.

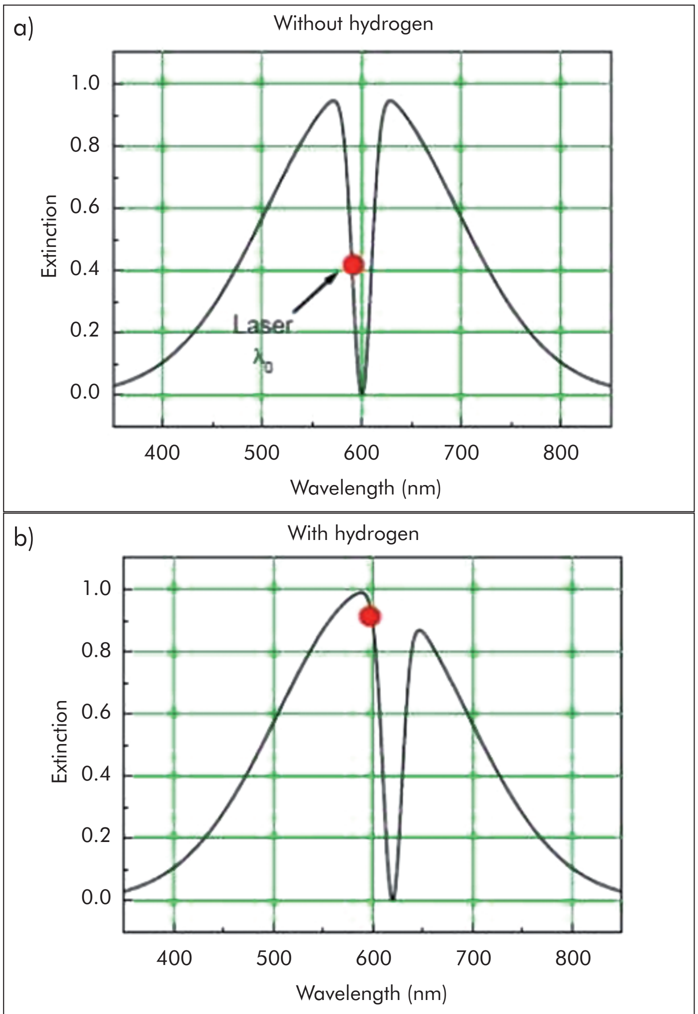


Figure 5: Simulation of the resonance shift due to hydrogen incorporation. The presence of the waveguide resonance and its steepness increase the sensitivity substantially.

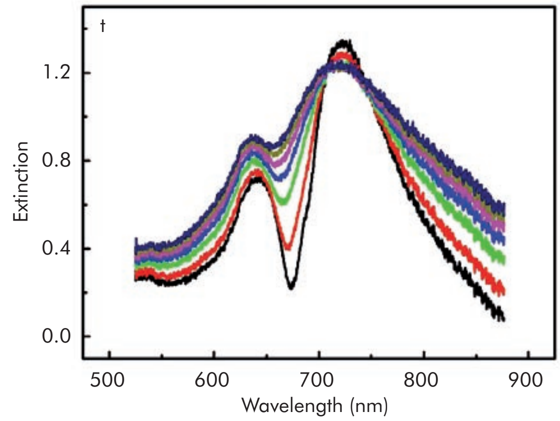


Figure 6: Measurement of the extinction in dependence of the wavelength as a function of time. The sequence of colours is from black to dark blue. The polarization of the light is TM (perpendicular to the wires).

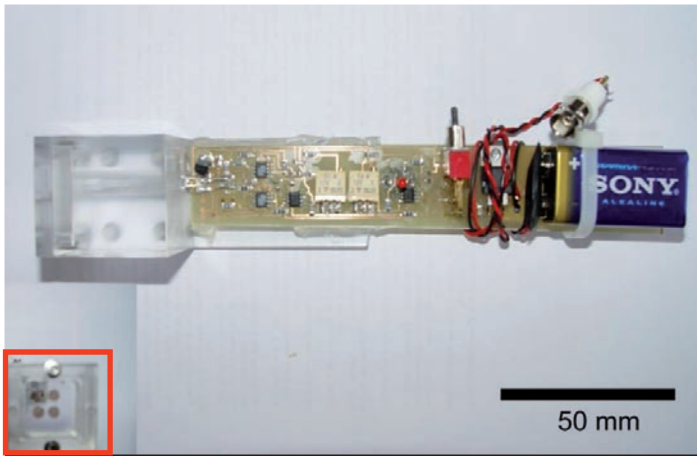


Figure 7: Hand-held prototype H_2-sensor. The laser diode (LD) operates at 640 nm and a photodiode measures (PD) in reflection the change in the signal due to hydrogen incorporation in the metallic photonic crystal. The inset shows a front view of the sensor head to visualize the reflective alignment of LD and PD.

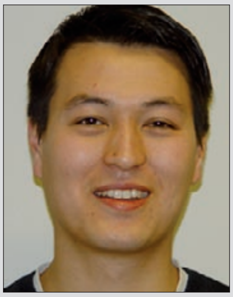
The change of the extinction spectra in presence of 5 % Vol. H_2-gas is shown in Figure 6. The spectra show the extinction of the metallic photonic crystal as a function of time, demonstrating the increased diffusion of hydrogen into the structure. We plot the extinction (negative logarithm of transmission) over wavelength. A typical increase in extinction of 0.5 corresponds to a transmission change of 500 %. The advantage stems from the combination the sensitivity of WO_3 and the accuracy of photonic resonances which are combined in this new sensor design.

Most conventional hydrogen sensors available on the market are based on electrochemical changes of certain properties of a semiconducter in presence of hydrogen, e.g., the ohmic resistance. They are longlife stable and very precise but expensive and dangerous in explosive environments such as refineries or in the process industry. An optical sensing does not require electric contacts in the potentially explosive environment. In mass-production fabrication, this could be a very sensitive, secure, small, and cost effective option in comparison to the conventional ones.

In Figure 7, we show a hand-held prototype of our sensor, suitable for threshold surveillance of the lower-explosion-limit of hydrogen at 4 %(Vol.). The laser diode operates at 640 nm and a photodiode measures in reflection the change in the signal due to hydrogen incorporation in the metallic photonic crystal. The sensor head with the sample and the whole electronics for the sensor are placed on a circuit board. Future designs will be further miniaturized to fulfill the industrial requirements concerning supply voltage and output current. This makes the whole device a plug-and-play sensor that can be used by many of our partners in the "hydrogen economy".

Outlook

The concept can be extended towards an "all-optical hydrogen sensor". This will give the opportunity to spatially separate the detection and analysis of the measurement, which adds to the level of safety.



Cornelius Grossmann studied Physics at University of Stuttgart and receives his Diploma in 2009. At the 4.Physics Institute, he works on nano-structuring of metals and dielectrics for photonic crystals as well as metamaterials and their applications.

Dr. Todd P. Meyrath received his Ph.D in Physics in 2005 from the University of Texas at Austin for Bose-Einstein condensation experiments, and his masters in Electrical Engineering in 2001 from the California Institute of Technology. He is currently an Alexander-von-Humboldt fellow in Stuttgart, Germany.

Prof. Dr. Harald Giessen, director of the 4th Physics Institute, University of Stuttgart, was awarded his Ph.D in 1995 from University of Arizona-Tucson for investigation of ultrafast dynamics in quantum dots. After that, he moved to the Max-Planck Institute for Solid-State Research in Stuttgart and worked with Dr. Kuhl in ultrafast spectroscopy. In 1997, he moved to University of Marburg as "Habilitand" in the group of Prof. W.W Rühle. In 2001, he became an associate professor at University of Bonn before he received the call as full professor at the 4. Physics Institute at University of Stuttgart in 2005

Cornelius Grossmann, Dr. Todd Meyrath and Prof. Dr. Harald Giessen, 4th Physics Institute, University of Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany, phone: (49) 711 6856 5111, fax: (49) 711 6856 5097, e-mail: giessen@physik.uni-stuttgart.de, web: www.pi4.uni-stuttgart.de