7 Laser-Mediated Desorption on Pt(110)*

As mentioned in the introduction of the previous chapter, photochemical excitation is a method to influence a chemical reaction. The possibility of altering the pathway of a chemical reaction by selectively exciting a portion of the molecule, the so-called quantum control of chemical reactions [1], has been extensively investigated [2]. Experiments show how product pathways can be controlled by irradiation with laser beams by exciting reagent vibrational modes and by controlling the molecular collision geometry [3]. Quantum control of the yield of a chemical reaction has also been achieved [4].

For certain systems, like CO and oxygen coadsorbed on a metal surface, one can take advantage of the striking difference in the strength of the chemisorption to produce a selective desorption of the weakly adsorbed species by simply increasing the substrate temperature.

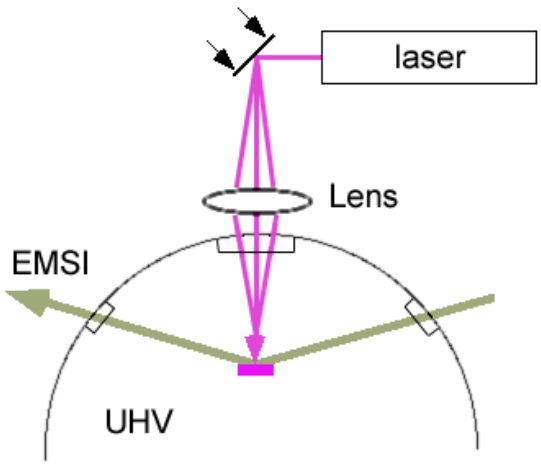

Fig. 7.1 The LITD-EMSI setup.

A more sophisticated method, called laser-induced thermal desorption (LITD), has been developed by Ertl and Neumann [5]. As schematically depicted in Fig. 7.1, a laser beam, with appropriate frequency and intensity, is focused onto the sample via a positioning stage and a lens. Pulsed-lasers have been used to investigate the kinetics of surface reactions [6], [7]. For instance, Seebauer and coworkers [8] studied the adsorption and desorption of NO, CO, and H_2 on Pt(111). Rotermund and coworkers [9] investigated the diffusion of CO on Pt(110) combining LITD with the imaging capabilities of PEEM.

* Reference at page 68

7.1 LITD and chemical waves

Fink and coworkers [10] succeeded in producing reaction fronts on a portion of the CO-poisoned surface where CO desorption had been induced by LITD. The fronts, propagating as chemical waves across the surface area, were detected by scanning-LEED and Kelvin-probe WF measurements. A combination of LITD and PEEM has been successfully adopted to investigate radiation-induced effects on chemical systems [9], [11]. Due to geometrical constraints of the PEEM, the incident laser light can hit the sample at rather unfavorable grazing angles. To circumvent this problem, mirrors were placed in the UHV chamber or a hole was drilled through the multichannel plate and the phosphor screen of the PEEM to let the radiation pass trough. In successive LITD investigations in our group the experimentally more convenient EMSI technique has been utilized.

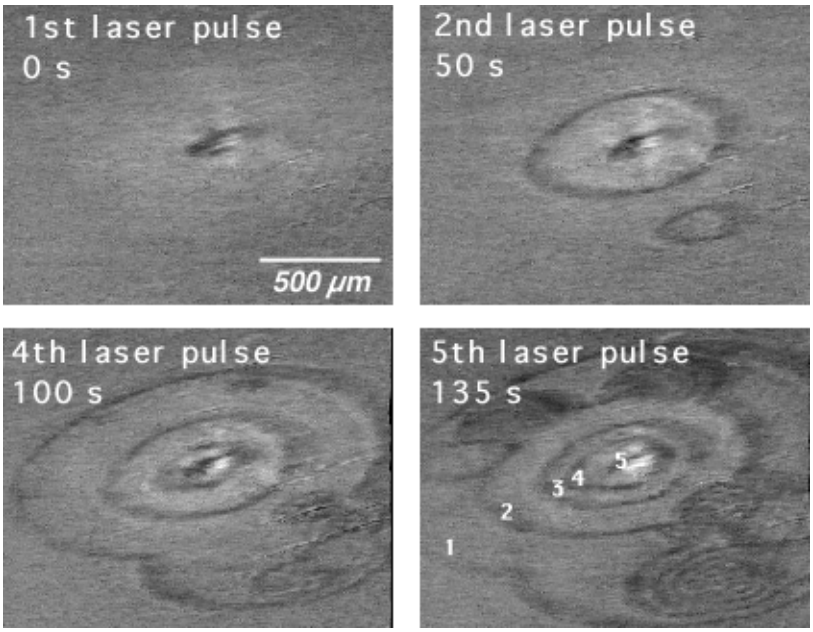

Fig. 7.2 Series of EMSI images of laser-induced oxygen fronts on a CO precovered Pt(110) surface.

In a LITD-EMSI experiment (schematically depicted in Fig. 7.1), Haas succeeded in producing the nucleation of oxygen pulses on a CO-covered Pt(110) surface [12]. Depending on the regime (bistable or excitable) he obtained expanding oxygen islands or ring-like oxygen fronts. By repeated pulses he was able to produce the target patterns shown in Fig. 7.2.

Bär and coworkers [13] performed extensive simulations on the effect of modifying the dynamics of a reaction–diffusion system by imposing modulations of the substrate properties that match the typical length scale of the spatio-temporal pattern. Fig. 7.3 illustrates a simulation of the *substrate wavelength* effect, the sinusoidal variation of the kinetic parameter of the substrate, which in turn produces periodical variations of the ratio of adsorbate concentrations. The original spiral (Fig. 7.3a) is increasingly perturbed, until it is almost fading out (Fig. 7.3d).

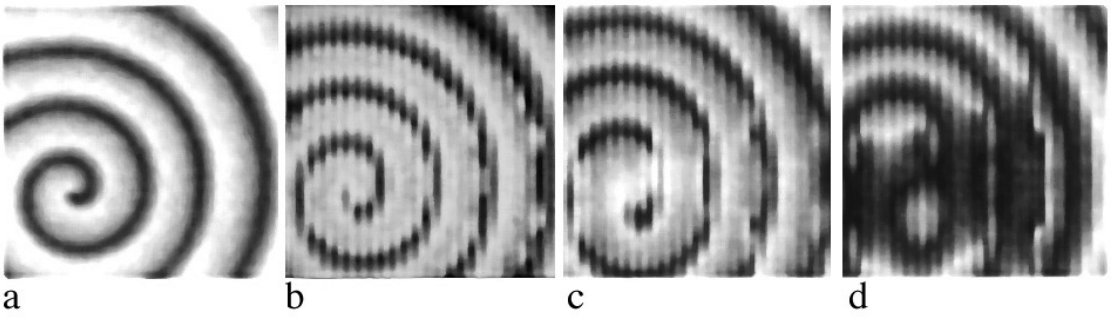

Fig. 7.3 Simulations of substrate wavelength effect on rotating spiral waves. The amplitude of the disturbance is increasing from b to d. After Ref. [13].

Our goal was to reproduce these simulations experimentally. The general approach is to perform a *distributed real-time feedback*. As schematically shown in Fig. 7.4, it can be achieved by acquiring the current spatio-temporal pattern with EMSI, comparing it with a predefined target image and, by steering the laser spot, creating the appropriate *disturbance* to drive the fronts towards the desired pattern.

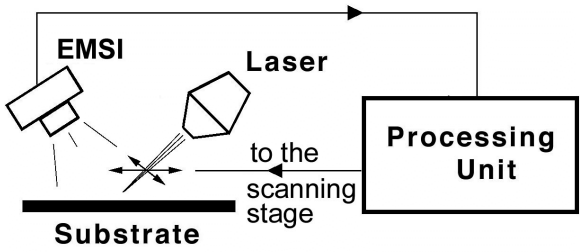

Fig 7.4 The scheme of a real-time distributed feedback.

By generating random patterns on this *addressable medium*, it could be even possible to exploit stochastic resonance phenomena [14] similar to the noise-supported traveling waves found by Kadar and coworkers [15] in the BZ reaction.

7.2 LITD–EMSI investigations

The Ar ion laser beam has been focused at the sample surface, down to about 50 µm, via a system of lenses and a scanning stage consisting of a pair of adjustable mirrors. To minimize the heat dissipation into the bulk an ultrathin (2000 Å) sample, described in section 6.1, has been employed. Moreover, since the reflectivity of an optically flat Pt surface for a 514 nm radiation can easily exceed 90%, powerful laser radiation is required to reach the CO desorption temperature.

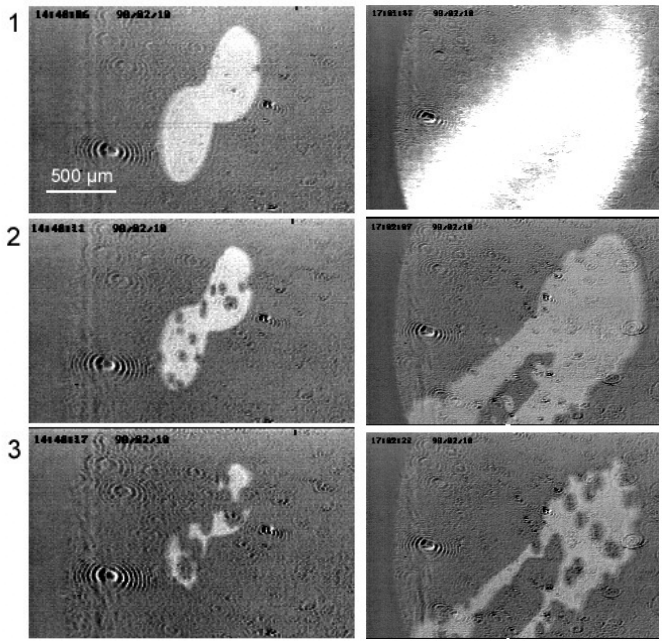

Fig. 7.5 Series of EMSI images (Δt = 5 s) on a 2000 Å thick, amorphous Pt sample; a) a line scan; b) a circle.T = 495 K; p(CO) = 1 · 10^{-5} mbar; p(O_2) = 1.4 · 10^{-4} mbar. Laser power: 1 W.

A CO-covered Pt surface was first prepared, as explained in section 1.5, by setting the CO partial pressure just above the threshold of the poisoning. When the portion of the sample surface irradiated with the laser (Fig. 7.5 b1) reaches the desorption temperature of CO, oxygen adsorption can take place, forming the bright oxygen-covered islands apparent in the EMSI images. In the first series of images, Fig. 7.5 a 1 trough 3, a line scan was used to “clean” the surface. The “8” shape of the resulting oxygen areas is due to the fact that the beam is spending most of the time at the end of the scanned region. After a couple of seconds the temperature falls again and CO islands start nucleating. Similar effects are observed in the second series of EMSI images, in Fig. 7.5 b 2 and 3, where a circular scan was employed.

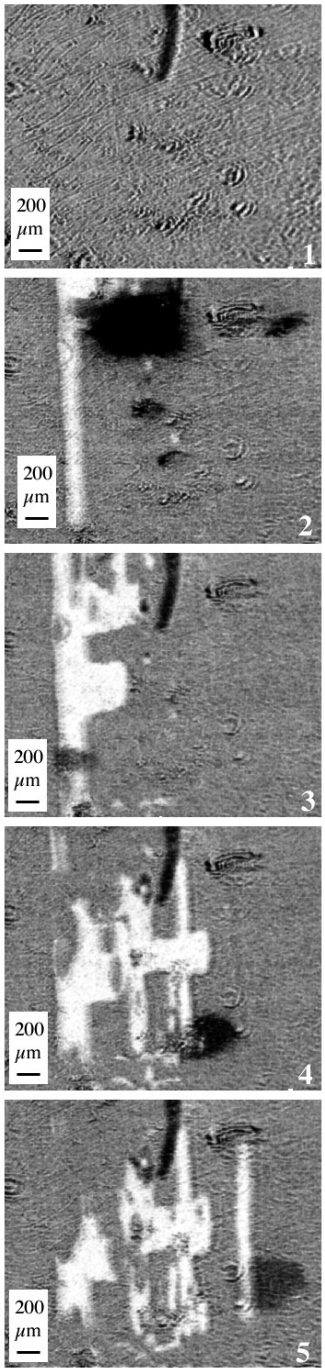

Fig. 7.6 Writing the institute's acronym by LITD – EMSI.

In the series of images shown in Fig. 7.6, it is presented the attempt to write the acronym of the institute by means of the laser-induced desorption. Two aspects are notable. First, it is manifest, e.g. in Fig. 7.5 a1, that the inherent distortion in the EMSI image is only partially corrected by tilting the camera, as already known [12]. Second, for a fixed spot size, the actual width of the oxygen channels can be tuned, by setting the laser power, or, alternatively, by tuning the speed of the scan. The right "leg" of the "H" has been written at a higher pace than the left one: as a result the former looks thinner than his colleague!

7.3 LITD-EMSI: outlook and perspectives

It is out of questions whether the present LITD-EMSI results fulfill the plans to replicate experimentally the substrate wavelength effect simulations. Nevertheless, they show that, provided some technical improvements, the CO+O/Pt system, studied with LITD-EMSI, will indeed offer the possibility to perform interesting *addressable media* experiments. More investigations, with improved focussing features, have been planned, and one can be confident that soon they will yield new examples of the use of new degrees of freedom to explore the phenomenology and to actively influence the spatiotemporal dynamics.

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