# Micromechanical sensor for studying heats of surface reactions, adsorption, and cluster deposition processes

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We present a newly designed highly sensitive micromechanical sensor devoted to thermodynamic studies involving supported clusters. The thermally sensitive element of the sensor consists of a micromachined silicon cantilever array, onto which a thin metal film is evaporated. Due to the difference between the thermal expansion coefficients of silicon and the metal employed, thermal bending is observed when heat is exchanged with the cantilever. The sensitivity and the response time of the cantilever are studied as a function of the film material (gold or aluminum) and the thickness of the metal film. With our routinely prepared cantilevers, a minimum power of 120 nW is measurable with a submillisecond response time, corresponding to a limit of detection in the femtojoule range. The high sensitivity of the sensor is demonstrated by measuring the heat exchange which occurs during the deposition of clusters on the cantilever. Experimentally, we illustrate the 1,3-butadiene hydrogenation reaction using a cluster model catalysts created by soft-landing palladium clusters onto the cantilever surface. © 2007 American Institute of Physics. [DOI: 10.1063/1.2740165]

### I. INTRODUCTION

Adsorption heats of reactants and products as well as reaction heats of catalytic processes are of critical importance for the identification of various mechanisms involved in catalytic reactions on real and model systems as well as for comparing experimental findings with numerical predictions.<sup>1,2</sup> Until the early 1990s, Clausius-Clapeyron analysis of adsorption isotherms and kinetic analysis of temperature programed desorption (TPD) experiments were the most widely employed tools in surface science to determine adsorption heats of molecules on surfaces.<sup>3</sup> These methods can only be used to investigate adsorption systems which are fully reversible. Consequently, important surface processes such as dissociative and reactive adsorptions cannot be studied. Moreover, none of the available techniques used in surface science is sensitive enough to obtain these thermodynamic quantities on highly dispersed species of low quantity, such as size-selected clusters supported on metal oxides. Consequently, new approaches are required.

Alternative techniques that may be used to measure heats of adsorption of gases on surfaces were developed in the 1930s and made use of concepts taken from calorimetry. Initially, metal wires or metal ribbons were employed both as substrate and as resistive thermometer.<sup>4–8</sup> Complementary techniques involving polycrystalline thin films grown *in situ* have been developed by Beeck.<sup>9</sup> This approach has been refined further by other research groups (see Ref. 10 for a review). These measurements suffer from problems associated with the polycrystalline nature of the films and from reliable preparation techniques. Comparison of the obtained data is therefore difficult. Through the development of a single-crystal adsorption calorimeter (SCAC), this problem was solved. Such experiments were pioneered by Kyser and co-workers for the Pt(111) system.<sup>11,12</sup> Even though the sensitivity of this particular experiment was still too low to allow extensive studies, it led to further developments of highly sensitive calorimeters for reactive studies on single crystals, especially by the groups of King and co-workers<sup>13-19</sup> and Ajo et al.<sup>20</sup> They established singlecrystal adsorption calorimetry as an analytical tool in surface science. The main property that provides the high sensitivity of SCAC is the low heat capacity of the thin crystal  $(\sim 1 \ \mu J \ K^{-1}).$ 

SCAC has been extensively employed to measure heats of adsorption of diatomic molecules and hydrocarbons on surfaces, to study the oxidation reaction of CO on platinum, to investigate coadsorption processes, and used to investigate the mechanisms of metal atom adsorptions on metallic surfaces (see Ref. 19 and references therein). In this context, it is worth mentioning that a pyroelectric polymer detector has also very recently been used to study the adsorption of Pd deposited onto "pristine" polymethyl methacrylate (PMMA) and electron-irradiated PMMA, which has been directly spin coated onto the detector.<sup>21</sup>

In parallel to standard single-crystal adsorption calorimeters, a thin film differential scanning calorimeter has been developed by Lai *et al.*<sup>22</sup> It consists of two thin metal strips,

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one of which is used to measure calorimetric information for a sample and the other employed as reference. This technique allows the calorimeter to function as both a heater and as a resistive thermometer. The latent heat of fusion, the heat capacity of nanoscaled tin particles,<sup>23,24</sup> as well as the melting points of aluminum clusters<sup>25</sup> have been measured by this particular technique.

The use of micromechanical cantilevers as the transducers of a calorimeter was first demonstrated by Gerber and co-workers.<sup>26–28</sup> The silicon cantilevers were coated with a thin metal film. Bending of the bilayered cantilever occurs due to the different thermal expansions of the silicon and the metal film. Consequently, bilayered cantilevers can be used to detect changes in temperature. The high sensitivity of the technique originates from the low heat capacity of a single cantilever (<1  $\mu$ J K<sup>-1</sup>) (Ref. 26) due to its reduced dimensions and from the ability to monitor the bending with high precision. A sensitivity in the femtojoule<sup>26-28</sup> range has been reported for the micromachined cantilevers, with a response time in the millisecond range.<sup>26–28</sup> This level of accuracy and sensitivity allows the study of phase transitions of n-alkanes,<sup>29</sup> for example. The micromechanical calorimeter approach has been compared to the pyroelectric calorimeter technique for the study of the formation energies of tin nanoclusters, thin films,<sup>30–32</sup> and silicon clusters.<sup>33</sup> It has been shown that the micromechanical calorimeter has the advantage of unique heat capacity in combination with a very short response time. In addition, it is possible to measure momentum transfer that may occur during cluster deposition<sup>31</sup> or exposure of the cantilever to a pulse of the reactant molecules.

In this article, we report on the development of a bimetallic sensor devoted to thermodynamic studies of small sizeselected clusters under ultrahigh vacuum (UHV) conditions. The calorimetric element of the sensor consists of a multilayered cantilever similar to that used by the group of Gerber. An extensive study of the sensitivity of the cantilever as a function of the properties of the metal film (composition and thickness) is performed. It is demonstrated that the detection limit of the bimetallic cantilevers is  $\sim 120$  nW, with a response time in the submillisecond range in vacuum. Consequently, a detection limit of  $\sim 60$  pJ is possible, making this detection method sensitive enough to measure adsorption and reaction heats (~200 kJ mol<sup>-1</sup>) on minute amounts  $(\sim 30 \times 10^{-12} \text{ g})$  of a Pd catalyst. The performance and sensitivity of the detector are illustrated by measuring the heat transfer during the deposition of clusters on the cantilever. The reliability of the sensor for catalytic studies involving supported clusters is demonstrated by studying the hydrogenation of 1,3-butadiene on Pd cluster catalysts.

Section II details the technique and provides an overview of the cluster deposition apparatus. The sensitivity of the detector is investigated in Sec. III. Finally, in Sec. IV the deposition of palladium clusters onto the cantilevers is investigated. The hydrogenation of 1,3-butadiene and the interaction of hydrogen with palladium clusters are also illustrated.



FIG. 1. Schematic view of the sensor. PSD, position sensitive detector; DL, detection laser; HL, heating laser; CA, cantilever array. In the inset, a micrograph of the cantilever array is shown.

### **II. EXPERIMENTAL DETAILS**

The experiment is composed of four parts: (a) the sensor, including the bimetallic cantilevers mounted onto a piezoelectrical slider; (b) the optical elements, including the position sensitive detector (PSD), a probe (diode) laser which is involved in the detection of the bending of the cantilever and a calibration (diode) laser; (c) the UHV chamber, the gas inlet system, and the cantilever exchanger; and (d) the cluster deposition apparatus. Since the cluster source has been described previously<sup>34</sup> only pertinent details will be discussed.

### A. Cantilever array

The sensor consists of eight micromachined cantilevers made from p-doped silicon (Concentris, models CLA-500-010-08 and CLA-750-010-08), on which a nanometer thick metal film is grown by evaporation. Two different cantilevers arrays are used, each cantilever having lengths of 500 and 750  $\mu$ m, respectively, with a width of 100  $\mu$ m and a thickness of  $\sim 1 \ \mu m$ . Each cantilever is separated by 150  $\mu m$ . The body of the cantilever array (Fig. 1) is attached to an aluminum holder, which has been anodized in order to reduce parasitic reflections from the two laser beams involved in the experiment. Prior to the preparation of the thin metal layer, impurities are removed from the surface of the cantilever with piranha solution  $(3:1 H_2SO_4)$  in concentrated  $H_2O_2$ ) and then rinsed with high purity methanol to remove moisture. The cantilever arrays are then introduced into a vacuum chamber. Once under vacuum, a high purity film of a given metal can be produced by evaporation, at a rate of  $\sim 0.4$  Å s<sup>-1</sup>. The evaporation rate is monitored continuously by a quartz microbalance. The final thickness of the metal film can be measured with a precision of 1 nm. During the evaporation procedure the cantilevers was held at constant temperature (320 K) to avoid any undesired bending of the cantilevers at room temperature (see also Sec. III). When evaporating gold, it is necessary to have a 1 nm thick chromium interlayer to increase the adhesion between gold and silicon.<sup>35</sup>

For the microcalorimetric measurements the clusters are deposited onto the uncoated side of the silicon cantilevers. It should be noted that the silicon cantilever surface is oxidized but this oxide layer has not been characterized in the following study.

### B. Piezoelectric inertial slider

In order that the cantilever can be positioned precisely with respect to the detection laser (see Sec. II C), a piezoelectric inertial slider is employed. The cantilever holder is attached to a trapezoidal copper support, which can be translated in two perpendicular directions, as shown in Fig. 1. The translation mechanism consists of three segmented piezoelectric tubes. Polished sapphire plates are placed in between the copper support and the piezoelectric tubes in order to ensure electrical insulation and decrease the mechanical resistance. A voltage ramp (rising time  $\sim 500 \ \mu s$ , peak amplitude  $\sim 400 \text{ V}$ ) is applied to deform the piezoelements and provide directional movement of the cantilever. Rapid movement of the piezoelements following the voltage ramp produces no further translation due to a lack of inertia. The piezoelements are driven at a frequency of 20 Hz resulting in a translation rate of  $\sim 1 \ \mu m \ s^{-1}$ .

### C. Optical detection device

The bending of the cantilever is induced by heating and is then detected with an optical device typically employed in atomic force microscopy. The output of a diode laser (Schäfter Kirchhoff, Model 57FCM, 670 nm, 1 mW full power) is coupled into the vacuum chamber via an UHV compatible optical fiber (Diamond GmbH). The tip of the fiber is positioned at a distance of ~5 mm from cantilever array at an angle of 45°. The reflected light is then monitored by the position sensitive detector (SiTek, Model 2L 45, 45 ×45 mm<sup>2</sup> active area, inherent resolution <1 ppm or 225 Å, respectively) located perpendicularly to the reflected beam at a distance of 15 cm. The PSD can be positioned to ensure optimum detection of the reflected laser beam.

Output currents from perpendicular edges of the PSD are converted into voltages  $U_1$  and  $U_2$  and amplified by electronics of in-house design. The sum of the two measured voltages  $U_1+U_2$  (proportional to the intensity of the light detected by the PSD) and the difference voltage  $U_1-U_2$ (proportional to the light intensity and to the geometric center of the laser spot) are calculated. The spot position can be evaluated by taking the quotient of the difference and sum of  $U_1$  and  $U_2$ . The output from the PSD can be digitized by an oscilloscope (LeCroy, WaveRunner 6030, 350 MHz) for measurements on the millisecond time scale. Alternatively, for measurements made on a longer time scale, an analog-todigital converter controlled by LABVIEW can be used for data collection.

### **D.** Calibration laser

Since every cantilever has a unique response (even when prepared in the same conditions), it is necessary to calibrate the cantilevers with the calibration diode laser (Lasiris PTM Serie, StockerYale Inc., 635 nm, 1 mW full power). The output power of the laser can be continuously varied between 0 and 800  $\mu$ W. Due to the divergence of the calibration laser (~10° of conical aperture) and the distance of laser (no closer than 5 mm), only a small part of the initial power can reach the cantilever. In order to determine the exact amount of power absorbed by the bimetallic cantilever, the photon flux is determined. The flux is then normalized to the surface area of the cantilever. Taking the reflectivity of the metal films into account (95% for gold, 71% for aluminum),<sup>36</sup> maximum powers of ~6 and ~30  $\mu$ W can be determined for gold and aluminum, respectively.

As the wavelengths of the calibration laser (635 nm) and the detection laser (670 nm) are different, scattered light from the calibration laser can be removed by placing a longpass filter (cutoff wavelength of 665 nm, transmission <1%at 635 nm) in front of the PSD to increase precision.

### E. UHV sensor chamber

The optical detection array is decoupled from the main UHV chamber by a bellow assembly. Additional vibration damping is provided by three overpressure air suspension devices. The cantilever is aligned with the axis of the molecular beam through the positioning of the bellow assembly. Sample gases can be introduced with a calibrated leak valve (Varian Inc.) to produce an isotropic gas environment. Alternatively, the UHV chamber is equipped with pulsed piezo-electric valves which have been purposely designed for catalytic studies.<sup>37</sup> The gas flux through the pulsed valves can be controlled by the driving voltage of the piezoelement and the opening time of the valve.

The sensor chamber is evacuated by a 1000 L s<sup>-1</sup> turbomolecular pump, backed with an oil-based rotary pump. The base pressure in the chamber reaches  $\sim 2 \times 10^{-9}$  Torr without baking. During cluster deposition the chamber pressure is elevated to  $\sim 3 \times 10^{-7}$  Torr as a consequence of the helium carrier gas used in the cluster source.

### F. In situ cantilever exchanger

For each experiment a new cantilever is used. A sample exchanger and transfer chamber has been designed to ensure that the cantilevers can be quickly exchanged, without affecting the quality of the vacuum. Up to 20 cantilevers can be stored in the transfer chamber. A used cantilever can be removed from the sensor with a wobble stick (Vacuum Generators, Model ZWS075) and replaced with a newly prepared cantilever from the storage chamber. The piezoelectric slider can then be used to realign the new cantilever with the laser beams.

### G. Cluster deposition source

The sensor chamber is coupled to cluster deposition facilities. The cluster source including ion optics has been described in detail previously.<sup>34,37</sup> Neutral and charged clusters are produced with a 100 Hz laser vaporization source, and guided along the optical axis of the vacuum chambers through the use of a combination of a radio-frequency octopole ion guide and electrostatic lenses. Cations are deflected through 90° by an electrostatic quadrupole bender of inhouse design. Mass selection of the cluster beam is achieved with a commercial radio-frequency quadrupole mass spectrometer (Extrel, rod diameter of 9.5 mm, maximum limit of 4000 amu). The typical diameter of the cluster beam following passage through the mass spectrometer is  $\sim 3$  mm. The cluster beam is finally focused onto a cantilever by a recently developed focusing octopole.<sup>38</sup> The focusing properties allow the cluster beam diameter to be reduced by a factor of 2–3. Since the area of a cantilever is  $7.5 \times 10^{-2}$  mm<sup>2</sup>, it is advantageous to focus the beam to direct the produced clusters onto the cantilever and dramatically reduce the deposition time. During the deposition, the focusing octopole is positioned at a distance of  $\sim 1$  mm from the cantilever array. Following the deposition, the sensor chamber and hence the cantilever are retracted from the octopole. The cluster current is measured by connecting the copper support to a picoampere meter. Size-selected Pd<sub>30</sub> clusters are deposited with a current of  $\sim 200$  pA, while currents as high as 5–10 nA are measured without mass selection.

# III. MODES OF OPERATION AND PROPERTIES OF BIMETALLIC CANTILEVERS

### A. Mode of operation

The detailed behavior of the multilayered cantilever depends on the temperature distribution along the length of the cantilever.<sup>27,28</sup> In a mechanical model,<sup>39</sup> two different scenarios can be envisaged to describe the bending of the cantilever under a thermal load. In the "thermometer mode," the body of the cantilever acts as a heat bath and is in thermal equilibrium with the cantilever (see Fig. 2 in Ref. 27). As a consequence, the temperature along the cantilever is constant. The bending  $\delta_N^T$  and the vertical deflection  $\Delta_N^T$  of the tip of the cantilever are given by

$$\delta_N^T = \Gamma_N (T - T_0) \ell, \quad \Delta_N^T = \frac{1}{2} \Gamma_N (T - T_0) \ell^2,$$
 (1)

where *T* is the temperature of the heat bath,  $T_0$  the reference temperature at which the cantilever is straight, and  $\ell$  is the length of the cantilever. The function,  $\Gamma_N$ , depends on (a) the number of layers *N* of a given material *i*, (b) the thermal expansion coefficient  $\alpha_I$ , (c) the thickness  $h_i$ , and (d) the Young modulus  $E_i$  of the layers. The expressions for  $\Gamma_N$  are given in Appendix for two- and three-layer systems (*i*=1,2 and *i*=1,2,3, respectively). The relevant physical properties of the different materials employed in this study are given in Table I.

If the cantilever is heated uniformly along its length with an external source of power, the cantilever operates in "calorimeter mode."<sup>27</sup> In this mode of operation, heat flows along the cantilever to the cantilever holder. The holder is assumed to behave as a heat sink which maintains a constant temperature,  $T_0$ .<sup>27</sup> For the calorimeter mode the bending  $\delta_N^C$  and the vertical deflection  $\Delta_N^C$  of the cantilever tip are given by

TABLE I. Density  $\rho$ , Young modulus *E*, thermal expansion coefficient  $\alpha$ , thermal conductivity coefficient *k*, and heat capacity per unit of mass *c* for gold, aluminum, chrome, and silicon (Ref. 56).

Element	$ ho 10^3 { m kg} { m m}^{-3}$	<i>Е</i> 10 <sup>11</sup> Ра	$\alpha$ 10 <sup>-6</sup> K <sup>-1</sup>	$\begin{array}{c} K \\ W \ m^{-1} \ K^{-1} \end{array}$	C 10 <sup>2</sup> J K <sup>-1</sup> kg <sup>-1</sup>
Gold	19.3	0.78	14.2	320	1.27
Aluminum	2.7	0.70	23.1	235	9.04
Chrome	7.1	2.79	4.9	94	4.48
Silicon	2.3	0.47	2.6	150	7.2

$$\delta_N^C = \Gamma_N \frac{2P}{3w\sum_i \kappa_i h_i} \ell^2, \quad \Delta_N^C = \Gamma_N \frac{P}{8w\sum_i \kappa_i h_i} \ell^3.$$
(2)

In Eq. (2), *P* is the total heating power, *w* is the width of the cantilever,  $\kappa_i$  is the coefficient of thermal diffusion for layer *i*, and  $h_i$  is the thickness of layer *i*. Both modes of the sensor have been investigated and are detailed in Sec. IV.

### B. Sensitivity of the cantilevers

In order to optimize the sensitivity, the multilayered cantilever has been studied experimentally and theoretically as a function of the metal coating, the film thickness, and the length of the cantilever.

In Fig. 2 the theoretical sensitivity of the cantilever in the calorimeter mode is illustrated as a function of the relative film thickness for three different films: gold, aluminum, and a gold film with a 1 nm chrome interlayer. The relative film thickness  $\Theta$  is defined as a function of the absolute thickness  $h_1$  of the metal layer and is given by

$$\Theta = \frac{h_1}{\sum_i h_i}.$$
(3)

In the case of a bimetallic cantilever, the sensitivity of the cantilever is proportional to the difference between the ex-



FIG. 2. Predicted sensitivity of the cantilever in the calorimeter mode as a function of the relative thickness  $\Theta$  of the metal film: gold film (thin line), aluminum film (thick line), and a gold film with a 10 nm chrome interface (dotted line). It follows from the thickness of the bare Si cantilever (1  $\mu$ m) that optimum film thicknesses for aluminum and gold are 240 and 200 nm, respectively.

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pansion coefficients  $\alpha_i$  of the two layers. Therefore, the sensitivity is predicted to be about two times higher for aluminum than for gold. The Young modulus  $E_i$  also influences the sensitivity, but is less important since the values of the Young modulus of different metals are similar. The sensitivity of the cantilever with respect to the film thickness is controlled by two opposite effects. As the metallic film thickness is increased, so is the bending moment of the cantilever. With a thin metal film coating, a linear dependency of the sensitivity with the film thickness is observed. In contrast, the thermal capacity of the cantilever increases with the amount of deposited metal. Additionally, the thermal diffusion to the body of the cantilever is enhanced for large surface areas. The latter two effects act to decrease the sensitivity of multilayered cantilevers as a function of thickness. This leads to an optimum film thickness of 240 and 200 nm for aluminum gold, respectively. It should be noted that according to the three-layer model, the presence of the chromium interlayer (1 nm) provides negligible influence to the overall sensitivity of the cantilever.

Experimentally, the sensitivity of our prepared cantilevers as a function of film thickness was determined by heating the cantilever with the calibration laser, as described in Ref. 26. The thermal bending of the cantilever is determined by the displacement of the reflected laser spot on the PSD as a function of the power absorbed by the cantilever. To obtain the absorbed power, the laser output power was corrected by the relative areas of the sensor and the laser spot as well as the reflectivity of the metal films. The sensitivity of each cantilever is calculated from the slope of the PSD signal as a function of the absorbed power. Consequently, the sensitivity can be quoted in units of  $(nW)^{-1}$ . Cantilevers, 500  $\mu$ m in length, have been prepared by atom evaporation to give film thicknesses between 60 and 150 nm for gold, and between 60 and 120 nm for aluminum. Thicker films could not be prepared because the heat from the evaporator caused the cantilevers to bend during deposition. In addition, several gold coated cantilevers with a length of 750  $\mu$ m were also prepared.

The experimental results are summarized in Fig. 3. As predicted by the mechanical model, the sensitivity of the cantilevers increases with the thickness of the metal film. As mentioned above, optimum film thicknesses (200 nm for gold and 240 nm for aluminum, Fig. 2) could not be obtained experimentally. Hence, the theoretical predictions illustrated by Fig. 2 could not be verified. Attempts to produce cantilevers prepared with high film thicknesses failed as the cantilevers started to bend at room temperature. The detection laser could not be focused on the tip of the cantilever under these conditions. The quadratic dependence of the sensitivity with cantilever length, predicted by the model of the calorimeter mode [Eq. (2)], can be observed in the experimental data recorded using two different cantilever lengths (500 and 750  $\mu$ m, constant gold thickness). In Fig. 3, a higher increase in sensitivity (approximately a factor of 4) is observed, in comparison with the quadratic dependence (a factor of 2.25). Comparing the aluminum and gold coated cantilevers, as predicted by the theoretical model, we observe the sensitivity of aluminum coated cantilevers to be almost



FIG. 3. Sensitivity of the cantilever as a function of the thickness of the metal film for 500  $\mu$ m (circles) and 750  $\mu$ m (triangles) cantilevers coated with gold (filled symbols) and aluminum (open symbols).

four times larger than that of the gold coated cantilevers (see Fig. 3). This increase reflects the higher thermal expansion coefficient of aluminum compared to gold (see Table I). Due to the higher temperature required to evaporate aluminum, reliable production of aluminum-coated cantilevers for a film thickness higher than 80 nm proves to be challenging. For this reason the cantilevers used in this study involve only the use of gold coatings. If the cantilevers are produced with 120 nm gold coatings approximately 90% are suitable for use. Previously used cantilevers are recycled by removing the metal films in an acid solution.

*Response time*. The response time of the cantilever to a thermal load was obtained by using the pulsed calibration laser. Typical temporal responses of the cantilever to a thermal load measured on an oscilloscope are shown in Fig. 4. It can be seen both in air and in vacuum that the heating time is only slightly higher than the cooling time. In order to obtain a response time, the signal of the cantilever bending was fitted with an exponential function. The response time of the



FIG. 4. Time-dependent response of the cantilever (750  $\mu$ m long, coated with a 120 nm gold film) to a laser pulse (a) in air and (b) in vacuum. It should be noted that there is a difference in the time scales between (a) and (b).



FIG. 5. Response time (heating) of the cantilever measured in air as a function of the thickness of the gold film for 500  $\mu$ m (circles) and 750  $\mu$ m (triangles) cantilevers.

cantilever operated under vacuum is significantly reduced in comparison with that measured in air.

The dependence of the (heating) response time in air, as a function of the gold film thickness, is depicted in Fig. 5 for both cantilever lengths. The response time is mainly dependent on the length of the cantilever, which defines the time scale of the heat exchange between the cantilever and the cantilever body. As discussed above, the cantilever body should ideally act as a heat sink in the calorimeter mode. The response time of the cantilever does not depend strongly on the thickness of the metal coating, as shown by Gerber and co-workers.<sup>27,28</sup> For a cantilever with a length of 750  $\mu$ m, the response time is predicted to be ~1.2 ms. The longer response time obtained experimentally (~2 ms) is attributed to the additional heat dissipation through the air.<sup>40</sup>

Obtained detection limit. The detection limit of a typical cantilever (gold coating thickness of 120 nm, 750  $\mu$ m in length) is  $8.5 \times 10^{-6}$  nW<sup>-1</sup>. This value was achieved by averaging 120 calibration laser pulses. With a typical PSD resolution of 0.001 unit (1 unit is defined as 22.5 mm, signal-tonoise ratio of 2), the minimum detectable power is 118 nW. Normalizing the minimum detection limit to the area of a cantilever  $(7.5 \times 10^{-8} \text{ m}^2)$ , a value of 1.6 W m<sup>-2</sup> is obtained. In air (vacuum) a response time of  $\sim 2 \text{ ms}$  ( $\sim 0.5 \text{ ms}$ ) allows a minimum detectable energy value of 236 pJ (59 pJ) to be achieved. If this value is not reached by averaging up to 2500 laser pulses, the quality of the cantilever was considered to be insufficient. Through the optimization of film deposition techniques, film thickness and the choice of metal can be improved. This could then lead to an even higher detection limit. Nonetheless, for the studies considered here the current detection limit is more than sufficient.

Mechanical and thermal responses. Although the main function of the bimetallic cantilevers is thermal sensing, they can also be used to detect very small mechanical forces. Both mechanical and thermal contributions can therefore be detected when a cantilever is used in a pulsed molecular beam



FIG. 6. Response of the cantilever (750  $\mu$ m long, coated with a 120 nm thick gold film) to pulses of neon for increasing pulse duration. The signal is typically averaged over 200–300 pulses.

experiment. To deconvolve the thermal signature from the mechanical contribution, the latter was determined through calibration using pulses of inert gases. Figure 6 shows the response of the cantilever to pulses of neon, for increasing flux. A single peak is observed with a response time approximately five times faster than expected for a thermal response time. Therefore, we ascribe the measured cantilever response to the momentum transfer from the gas phase atoms. This is consistent with the fact that Ne does not adsorb onto the surface of the cantilever at room temperature. Additionally, a small counteraction is observed. From this result, it may be seen that the cantilever deflection is efficiently damped.<sup>41</sup> The weak superimposed oscillation at a frequency of 47 kHz is the signature of the third eigenmode of the lateral oscillations of the cantilever. This oscillation is theoretically predicted to have a frequency of 43 kHz.<sup>42</sup> The first and second lateral eigenmodes, with frequencies of 3 and 15 kHz, are not observed.

It is important to note that the momentum transfer between the gas pulse and the cantilever is mass independent as observed for helium, argon, or neon. Firstly, the mean velocity of the pulsed gas atom particles is proportional to the inverse of the square root of the mass, and thus the momentum is proportional to the square root of the mass. Secondly, the flux of the gas through the pulsed valve is proportional to the inverse of the square root of the mass. As both of these factors coexist any dependency of mass is removed.<sup>43</sup>

In order to extract the thermal contribution of the cantilever response, the signal obtained for inert gas pulses can be subtracted from the total response. We therefore obtain the cantilever response due solely to the heat transfer from the reaction (see below).

### IV. CALORIMETRIC APPLICATIONS: CLUSTER BINDING ENERGIES, REACTION RATES, HEATS OF ADSORPTION, AND REACTION HEATS

In the following, possible applications of the sensor utilizing supported  $Pd_N$  clusters are described. Transition metals from group 10 are highly interesting systems for heteroge-



FIG. 7. Dependence of the bending rate of the cantilever on the cluster current for unselected palladium clusters with a mean size distribution of 25 atoms. The cantilever is 750  $\mu$ m long and coated with a 120 nm thick gold film. The values of the heat rate have been corrected to take into account the heating due to the presence of the focusing octopole. In the inset, the heat rates as a function of the octopole power are depicted. Note that the power corresponds to the value set on the radio-frequency transceiver, and not to the power actually transferred to the octopole.

neous catalysis. In particular, platinum and palladium are most widely used catalysts for the hydrogenation of unsaturated hydrocarbons such as butadiene, a key process in industrial reactors. Thus, theoretical and experimental studies have been devoted to such systems, including Pt and Pd surfaces,<sup>44–47</sup> nanocrystals supported on oxides,<sup>48,49</sup> and mixed Pd–Co catalysts.<sup>50</sup> These efforts lead to a better understanding of the influence of the support and the binding modes of hydrogen and 1,3-butadiene to the catalysts on their efficiency and selectivity. Furthermore, the binding energies of the clusters themselves to the substrate are of great interest. In this respect, calorimetric measurements on model systems can be of great use to better understand the role of binding mechanisms in such catalytic reactions.

Firstly, the cantilever response during the cluster deposition process is introduced and then the results concerning the hydrogenation reaction of 1,3-butadiene on  $Pd_N$ , supported on the naturally grown silicon-oxide film, are discussed. For these studies, cantilevers with a length of 750  $\mu$ m, coated with a 120 nm thick gold film, were used.

### A. Heat exchange during cluster deposition: Estimation of binding energies

In Fig. 7, the response of the bimetallic sensor during cluster deposition ( $Pd_N, N > 25$ ) onto the silicon-oxide surface of the cantilever is shown. The cantilever bending is not constant, but increases with time. At a first glance, this observation was surprising. The total power released during the cluster deposition is the sum of the kinetic energy of the clusters, the plastic deformation of the cluster upon deposition, the binding energy between the cluster and the support, and from the neutralization of the cluster cations. According to the model discussed in Sec. 3, the released power should lead to a thermal bending which is constant in time.

As stated above the cantilever can also function as a thermometer (if the temperature T along the cantilever is uniform). In this mode of operation the thermal bending is proportional to the variation of the temperature  $(T-T_0)$ , where  $T_0$  is the temperature at which the cantilever is straight ( $\delta_N^C$ ) =0). In fact, upon cluster deposition within a few milliseconds (corresponding to the response time of the cantilever), the nonuniform temperature distribution along the cantilever reaches a steady-state condition. If the cantilever is subjected to a continuous source of external heat power, the cantilever body no longer acts as a perfect heat sink (low heat capacity, imperfect thermal contact between the cantilever body and the cantilever holder) and the temperature of the cantilever body increases. Under these conditions, the observed thermal bending of the cantilever is related to the temperature increase according to Eq. (1). It is noteworthy to recognize that the sensitivity of the cantilever in the thermometer mode can be derived from the sensitivity in the calorimeter mode, using Eqs. (1) and (2). In the present case, if a detection limit of  $\sim 120$  nW is assumed in the calorimeter mode, the cantilever is able to detect temperature changes of approximately 1 mK. As the heat capacity of the whole body of the cantilever can be defined (7 mJ  $K^{-1}$ ), a temperature difference of this magnitude can be detected after a few seconds with a continuous heating power of 1  $\mu$ W. Therefore, the timedependent bending of the cantilever observed during the cluster deposition is due to the uniform change of the cantilever temperature.

In the present experiment, the change in temperature during cluster deposition partly originates from the focusing octopole. This heating has been studied as a function of the radio-frequency power, with the cluster source turned off (see inset of Fig. 7). The cantilever bending is observed even though cluster deposition is not being carried out. This observation can be explained by considering the radiated heat from the focusing octopole which are slightly heated by the radio-frequency generator. When the radio-frequency power is turned off, the cantilever is continually heated for several minutes due to the thermal inertia of the rods. The cantilever finally starts to cool after approximately 6 min. If the octopole is turned off and moved away from the cantilever, then the cooling starts immediately, a result consistent with the interpretation of the octopole as the heating source.

In order to study the cluster deposition accurately, it is necessary to subtract the heating effect of the octopole from the signal recorded during deposition, as shown in Fig. 7. The corrected cantilever bending is described in terms of the bending rate as a function of the cluster current. The temperature of the cantilever still exhibits a noticeable increase with time. From a fit to the data, the slope of the bending rate is obtained and has a value of  $2.68 \times 10^{-5}$  s<sup>-1</sup> pA<sup>-1</sup>. From the use of the calibration laser  $(5.52 \times 10^{-7} \text{ J unit}^{-1})$ , a value of  $1.48 \times 10^{-11}$  W pA<sup>-1</sup> is obtained as the total power released upon clusters deposition, which corresponds to a total heat release of 14.8±3.6 eV per deposited cluster. This is an important result, as it allows the interpretation of the energetics of cluster deposition and, in particular, the evaluation of the approximate binding energies of the clusters with the support. Given a mean kinetic energy of the clusters  $(Pd_N; N)$  >25) of ~2 eV and an energy release of the cluster cations due to neutralization of ~5 eV,<sup>51</sup> the adhesion energy (the energy balance between the energetic cost of the deformation of the cluster once in contact with the substrate and the binding energy of the cluster to the substrate) is estimated to be 7–8 eV. This estimation compares favorably with existing data.<sup>52,53</sup> Medium-sized Pd<sub>N</sub> clusters favor compact structures and the adhesion energy per cluster atom at the interface is about 0.3–0.5 eV.<sup>52,53</sup>. Assuming that 10–12 atoms are at the interface, the binding energy can be estimated to lie between 3 and 6 eV per cluster.

These experimental results indicate that this new bimetallic sensor is indeed capable of approximating cluster binding energies. The accuracy of the measurements will be improved in the future by using size-selected clusters, for which the kinetic energies and electron affinities are known more precisely. In addition, it may be feasible to decelerate and neutralize the clusters prior to deposition, in order to diminish the contribution of heat transfer by these processes.

## B. Hydrogenation of 1,3-butadiene: Reaction rates, binding energies, and reaction heats

As discussed, the binding of hydrogen and 1,3-butadiene to Pd catalysts is of great interest. The new experimental heat sensor can be used to determine the reaction rate of the hydrogenation of 1,3-butadiene. Furthermore, the possibility to determine binding energies of molecules on size-selected clusters supported on the cantilever sensor will be illustrated.

For this purpose, model catalysts were prepared by depositing palladium clusters (Pd<sub>N</sub>; N > 25) at room temperature onto the natural oxide layer of the Si cantilever (uncoated side). The mean cluster current during deposition measured at a single cantilever was 0.1 nA. Integrating the cluster current during deposition results in a cluster density of 1% ML (monolayer) [with respect to the surface density of Pd(111)]. This corresponds to the deposition of 1.5  $\times 10^{10}$  clusters onto the cantilever.

After depositing the  $Pd_N$  clusters onto the cantilever, an isotropic pressure of 1,3-butadiene was introduced into the UHV chamber using a leak valve. The partial pressure of 1,3-butadiene was varied between  $3 \times 10^{-8}$  and 3  $\times 10^{-6}$  Torr. The hydrogenation of 1,3-butadiene adsorbed onto the  $Pd_N$  cluster was induced by exposing the model catalyst to hydrogen pulses. The piezodriven pulsed valve was operated at 1 Hz with a pulse width of  $\sim$ 150 ms. Under these conditions, no net increase in temperature of the cantilever is observed, indicating that the sensor is operating in the calorimetric mode. A typical response (average of 200 pulses) of the cantilever to the hydrogen pulse is displayed in Fig. 8. As discussed above, the signal exhibits two contributions, the fast mechanical response (positive contribution) and slower thermal response of the cantilever (negative contribution). The opposite deflection direction of the two contributions indicate that the silicon-oxide layer of the cantilever is facing the incoming gas pulses, in agreement with our geometric configuration. To extract the heat released to the cantilever, it was additionally subjected to an inert gas pulse under the same experimental conditions; the difference signal of the reactive and the inert gas pulse was calculated (see



FIG. 8. Thick curve: averaged response of the cantilever (750  $\mu$ m long, coated with a 120 nm thick gold film), onto which 1% ML of palladium clusters has been deposited, and with an isotropic partial pressure of 1,3-butadiene of  $3.9 \times 10^{-7}$  Torr, to pulses of hydrogen (A typical flux of hydrogen under our operation conditions is  $10^{15}$  molecules per pulse). Dotted curve: averaged response of the cantilever to pulse of Ne under the same valve conditions. Hatched area: difference between the two signals. The area under the curve is proportional to the total heat released to the cantilever. For obtaining the signals 200 pulses have been averaged.

Fig. 8). The area under the curve can be interpreted as the total heat exchanged with the cantilever due to the reaction.<sup>54</sup>

In Fig. 9 the reaction heats of the hydrogenation as a function of the 1,3-butadiene partial pressure at constant  $H_2$  pulses are summarized. Based on these results, a maximum reaction rate under typical experimental conditions can be obtained at a 1,3-butadiene partial pressure of  $5 \times 10^{-7}$  Torr. At this partial pressure, the heat transferred to the cantilever is  $\sim 1.66 \times 10^{-19}$  J per cluster, per pulse. At low 1,3-



FIG. 9. Heat of reaction per cluster and hydrogen pulse detected with the cantilever sensor as a function of the isotropic pressure of 1,3-butadiene during the hydrogenation of 1,3-butadiene on size-distributed, supported palladium clusters.



FIG. 10. Reaction rate of the hydrogenation of 1,3-butadiene on sizedistributed palladium clusters supported on  $SiO_2$  measured in a separate p-MBRS setup as a function of the isotropic pressure of 1,3-butadiene; cluster coverage 1% ML.

butadiene partial pressures, no heat formation is detected, although the adsorption for  $H_2$  can be detected under the same conditions, but without 1,3-butadiene introduced as background gas (see below). This indicates that the  $H_2$  adsorption is hindered by the presence of small amounts of 1,3-butadiene. By comparison, at high 1,3-butadiene partial pressures, the reaction rate is diminished indicating that the clusters are saturated (poisoned) by 1,3-butadiene.

For the analysis and a qualitative comparison with the 1,3-butadiene partial pressure dependent result, additional measurements utilizing pulsed molecular beam reactive scattering (p-MBRS) coupled with an absolutely calibrated mass spectrometer<sup>37</sup> were performed under the same experimental conditions (1% ML Pd<sub>N</sub>, room temperature). The hydrogenation of 1,3-butadiene  $(C_4H_6)$  can result either in the formation of butene  $(C_4H_8)$  or butane  $(C_4H_{10})$ . The mass spectrometer indicated two main peaks from the reaction product, with masses of 43 and 41 amu and a ratio of 2:1. In order to assign these masses, these results were compared to the mass signals obtained from dosing defined amounts of butene and butane into the UHV chamber (see Ref. 57). The main masses detected using butane are 43 and 41 amu, in a ratio of 2:1, whereas butane results in a main peak at 41 amu (no signal at 43 amu). Under the experimental conditions (high hydrogen partial pressure during the pulse), the hydrogenation of 1,3-butadiene is therefore complete and only butane  $(C_4H_{10})$  is formed. The obtained reaction rates measured by p-MBRS as a function of the 1,3-butadiene back pressure are shown in Fig. 10. Size-distributed cluster samples do not allow direct comparison between the p-MRBS and the calorimetric studies. The important result of this qualitative comparison is that the number of produced butane molecules exhibits a similar behavior to that observed by the sensor, i.e., the highest reaction rate is observed at the same 1,3butadiene pressure  $(5 \times 10^{-7} \text{ Torr})$ , as in the calorimetric measurements.

With the knowledge of the reaction product, the bimetallic sensor can be used to determine the released heat of the investigated process (normalized in kJ mol<sup>-1</sup>). For the present process, if the released heat is already known [i.e., 235 kJ mol<sup>-1</sup> (Ref. 55)] the number of produced (or adsorbed) molecules per cluster and per pulse can be calculated from the measured total released heat and the number of deposited clusters. From the heat of reaction 235 kJ mol<sup>-1</sup> together with the Avogadro constant (6.02) $\times 10^{23}$  molecules mol<sup>-1</sup>), a heat of reaction of 3.9  $\times 10^{-19}$  J molecule<sup>-1</sup> is calculated. Comparing this value to the measured maximum released heat on the cantilever of  ${\sim}1.66{\times}10^{-19}~J$  per cluster, per pulse (at  $5{\times}10^{-7}$  Torr 1,3butadiene partial pressure, see Fig. 9), we can estimate the average number of produced butane molecules on the cantilever sensor. A total of 0.43 butane molecules per  $Pd_N$  cluster and hydrogen pulse can be deduced. It is important to note that from deposition to deposition, the effective surface area of the catalyst varies for size-distributed clusters. Consequently, the results from the two different methods cannot be directly compared.

There are two basic methods to determine normalized heats of adsorption on size-selected clusters supported on the cantilever sensor. One possible and precise way is the use of two pulsed molecular beams. This procedure is most favorable when investigating surface reactions involving two different reactants. In the first step, a pulsed molecular beam of one reactant, e.g., 1,3-butadiene, is pulsed onto the cantilever. The total heat of adsorption during this process is recorded by the cantilever bending. In the second step, the other reactant is pulsed onto the supported clusters inducing the complete surface reaction. The total heat of reaction during this process is also obtained from the response of the cantilever, since the heat of reaction is independent of the catalyst material (in contrast to the heat of adsorption), by comparing the measured heat of reaction with the literature value of this process. The total heat of reaction can be normalized and thus be used as an internal calibration of the released heat. In order to determine the normalized values of the heat of adsorption, measured in the first step, the number of adsorbed molecules per cluster needs to be determined. This can be simply done by a TPD experiment. An alternative method of determining normalized values is by the calculation of reaction rate in addition to the number of adsorbed molecules in separate p-MBRS and TPD experiments.

### C. Hydrogen interaction with Pd<sub>N</sub> clusters

In addition to the hydrogenation of 1,3-butadiene, the interaction of hydrogen with supported  $Pd_N$  clusters was studied. In these measurements, the clusters were exposed to pulses of hydrogen at 1 Hz (pulse width ~150 ms) without introducing 1,3-butadiene as background gas. As in the experiments described above, under these conditions the sensor acts in the calorimeter mode. The response of the cantilever was recorded with the oscilloscope and the signal is averaged over typically 300 pulses (see Fig. 11). With each hydrogen



FIG. 11. Cantilever response of size-distributed  $Pd_N$  clusters subjected to hydrogen pulses without 1,3-butadiene introduced as background gas; 2% ML cluster coverage, 200 pulses averaged.

pulse, there is repeated heat exchange with the cantilever sensor and no saturation effect is observed during the continuous pulsing. By extracting the thermal contribution, a total heat release of  $\sim 1.2$  nJ pulse<sup>-1</sup> is obtained for a cluster density of 2% ML. This allows an average exchanged heat of  $4 \times 10^{-20}$  J per pulse, per cluster to be elucidated. Currently, the exact mechanism of hydrogen interaction with the supported  $Pd_N$  clusters is unknown. Since no saturation effect under continuous pulsing is observed, the following explanation for the observed net energy transfer is suggested. The net energy detected could be associated with a transfer of kinetic or vibrational energy of the hydrogen molecules (adsorption and desorption processes). Alternatively, the hydrogen molecules could be adsorbed (and dissociated) on the Pd<sub>N</sub> clusters and diffused onto the cantilever substrate/holder. This would indicate a spill-over process.

### V. SUMMARY

A new experiment designed to investigate the energetics of the cluster deposition process, binding energies of small molecules to clusters, and reaction heats of chemical processes on clusters is presented herein. The thermal bending of a multilayered micromachined cantilever is successfully employed in these studies. The sensitivity of the sensor is studied as a function of the length of the cantilever, the elemental metal coating, and the thickness of this metal film. An ultimate heat power of ~120 nW can be routinely detected with a response time of ~0.5 ms in vacuum. This leads to a sensitivity of ~60 pJ.

Two modes of operation of the device are possible: thermometer and calorimeter modes. In the thermometer mode, information on the heat release during cluster deposition has been extracted and approximate binding energies of the clusters to the substrate are obtained. In the calorimetric mode, the response of the cantilever to the adsorption of  $H_2$  on palladium clusters and to the hydrogenation reaction of 1,3butadiene on palladium catalysts has been studied leading to integral values of the interaction energy and heat of reaction, respectively. Moreover, the experimental data reveal the possibility to measure normalized heats of adsorption on model catalysts consisting of small size-selected metal clusters supported on a naturally grown  $SiO_2$  layer of a micromachined silicon cantilever.

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### APPENDIX: THERMAL BEHAVIOR OF MULTILAYERED CANTILEVERS

The expressions of the functions  $\Gamma_N$  in Eqs. (1) and (2) for a cantilever with N layers (N=2;3) are given by

$$\Gamma_2 = \frac{6(\alpha_1 - \alpha_2)E_1E_2h_1h_2(h_1 + h_2)}{E_1h_1^4 + E_2h_2^4 + 2E_1E_2h_1h_2(2h_1^2 + 3h_1h_2 + 2h_2^2)}, \quad (A1)$$

and

$$\Gamma_{3} = \frac{6}{K(h_{1},h_{2},h_{3})} \{ (\alpha_{2} - \alpha_{3}) E_{2} E_{3} h_{2} h_{3} (h_{2} + h_{3}) + (\alpha_{1} - \alpha_{2}) E_{1} E_{2} h_{1} h_{2} (h_{1} + h_{2}) + (\alpha_{1} - \alpha_{2}) E_{1} E_{3} h_{1} h_{3} (h_{1} + h_{3}) \},$$
(A2)

with

$$\begin{split} K(h_1,h_2,h_3) &= E_1^2 h_1^4 + E_2^2 h_2^4 + E_3^2 h_3^4 + 2 E_1 E_2 h_1 h_2 (2 h_1^2 \\ &\quad + 3 h_1 h_2 + 2 h_2^2) + 2 E_2 E_3 h_2 h_3 (2 h_2^2 + 3 h_2 h_3 \\ &\quad + 2 h_3^2) + 2 E_1 E_3 h_1 h_3 [2 h_1^2 + 3 h_1 h_3 + 2 h_3^2 \\ &\quad + 6 h_2 (h_1 + h_2 + h_3)] \end{split}$$
(A3)

The intermediate layer in the last case is labeled 2.

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